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Rheological and structural characterization of tomato paste and its influence on the quality of ketchup

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Abstract

Three hot break tomato pastes were investigated to determine the effect of their characteristics on the properties of tomato ketchup, processed in an industrial-scale facility (i.e. diluted, heated, homogenized and cooled). Pastes and ketchups were characterized by particle size distribution, volume fraction, and rheological behavior in steady and dynamic shear. The ketchups were also subjected to sensory assessment. The processing of pastes into ketchups induced large structural changes, which were reflected in all parameters studied. The volume fraction of solids (ϕ) accurately reflected the changes that the paste suspensions underwent during processing and it appeared to be a good predictor of the flow behavior of both the pastes and the ketchups. The corresponding flow curves were found to be well described by the Carreau model in a large range of shear rates and concentrations. However, the rheological characteristics of the commercial pastes studied did not directly correlate to those of the corresponding ketchups. Instead, our results suggest that the change in structure induced by processing might be governed by other properties of the paste, such as the fraction of small and large particles and their sensitivity to breakage, together with the viscosity of the aqueous phase.

Keywords: Rheology; Structure; Tomato paste; Quality; Ketchup

1. Introduction

The viscosity of tomato ketchup is a major quality component for consumer acceptance. Several parameters contribute to the flow behavior of tomato ketchup, including the quality of the raw material (i.e. tomato paste) and the processing conditions. A high quality paste and continuous control and adjustment of the variables for processing it are thus required to achieve a constant and desirable quality in the final product (i.e. ketchup).

Several researchers have shown that difficulties in quality control arise from the great variation in flow behavior in commercial tomato paste caused by different agronomical and processing conditions (Sánchez, Valencia, Gallegos, Ciruelos, & Latorre, 2002; Thybo, Bechmann, & Brandt, 2005). A number of studies have been conducted on the rheological behavior of tomato products at low concentrations, resulting in evidence that many factors play a role in determining the viscosity of tomato products, including the degree of maturity, particle size and particle interactions, content of solids as well as temperature of processing (Beresovsky, Kopelman, & Mizrahi, 1995; Haley & Smith, 2003; Harper & El Sahrigi, 1965; Rao, Bourne, & Cooley, 1981; Sharma, LeMaguer, Liptay, & Poysa, 1996; Yoo & Rao, 1994). However, for concentrated tomato products such as tomato paste, few studies are available (Lorenzo, Gerhards, & Peleg, 1997; Sánchez et al., 2002), probably due to a number of measurement problems that occur because of the high concentration of large particles, which constitute the main structural component in the tomato paste. Moreover, tomato paste exhibits complex rheological behavior, i.e. it is a non-Newtonian, shear-thinning and time-dependent fluid that shows an apparent yield stress (Abu-Jdayil, Banat, Jumah, Al-Asheh, & Hammad, 2004; Rao et al., 1981).

Traditional devices used for quality control of tomato products are the Bostwick consistometer and the

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Brookfield viscometer. The former allows for an empirical measurement of the distance that a specific volume of fluid can flow under its own weight in a known interval of time. This device provides a single point measurement and is thus not suitable for concentrated products (Hayes, Smith, & Morris, 1998; Marsh, Buhlert, & Leonard, 1980). The Brookfield viscometer requires a discrete number of measurements at different velocities to determine the complete apparent flow curve. The measurements involve a non-well-defined shear rate profile throughout the fluid tested (Cullen, Duffy, & O'Donnell, 2001), which makes it difficult to measure non-Newtonian fluids. However, despite these problems, both methods are extensively used by the food industry.

Although Bostwick and Brookfield readings successfully predicted tube viscometry data according to Cullen et al. (2001), it has been difficult to draw clear conclusions in order to correlate consumer quality perception with data obtained with these devices (Apaiah, Goodman, & Barringer, 2001; Barret, Garcia, & Wayne, 1998). This discrepancy has led to the use of a semi-empirical control of tomato production that relies to a great extent upon the experience of the operators.

An objective and well-defined method of quality control would thus be highly useful in determining processing parameters. For example, the extent of dilution can be determined more accurately by having a better knowledge of the effect of the flow behavior of the concentrated tomato paste on the properties of the ketchup.

The goal of this study was hence to optimize tomato paste processing into ketchup by improving the quality control of both the raw material and the final product. In this investigation the processing of tomato paste into ketchup has been performed on an industrial-scale, which makes the results immediately relevant for actual industrial applications without any need for additional scaling-up.

Because the commercial tomato pastes used were similar to and fulfilled the industrial specifications for the raw material we were able to study the differences in the quality of ketchups produced from slightly different raw materials. This paper thus presents the results of a structural and rheological study of tomato pastes and their processed ketchups and of how these properties influence the sensorial perception of the tomato ketchup.

2. Material and methods

2.1. Tomato paste

Three commercial hot-break tomato pastes purchased from three Mediterranean producers were used in this study. The commonly evaluated properties of the tomato pastes are summarized in Table 1. All pastes fulfill the specifications of quality for processed commercial ketchup.

The effect of the concentration on the rheological properties of the pastes was studied in paste suspensions of different concentrations, i.e. 1000, 400 and 332 g/kg. The diluted suspensions were prepared by manually mixing certain amount of paste in distilled water.

2.2. Processing of tomato paste into ketchup

The tomato paste was processed into ketchup in an industrial-scale facility, with the paste content fixed to 332 g/kg suspension. The processing steps were (a) dilution in water to the desired content of tomato paste, (b) mixing with spices, vinegar, salt and sugar, (c) pasteurization, (d) homogenization, (e) warm-filling into 1 kg-bottles and (f) cooling to room temperature. The properties of the tomato ketchups are also summarized in Table 1.

In order to study the effect of small variations in concentration on the rheological properties of the ketchup, the ketchups were further suspended in distilled water to obtain a paste content of 300 and 265 g/kg suspension.

2.3. Dry-matter and water insoluble solids

Total solids (TS) were determined using a vacuum oven at 70 °C (8 h). In order to determine the water-insoluble solids (WIS), 20 g of product were added to boiling water for the extraction of the soluble solids. The mixture was centrifuged, and the supernatant filtered repeatedly until it

Table 1
The properties of the tomato pastes and ketchups, i.e. pH, soluble solids, Bostwick and Brookfield data, analyzed by the producers

	pH (–)	Soluble solids (°Brix)	Bostwick[a] (cm)	Brookfield[b] (cP)	Total solids (g/kg wb[c])	Water insoluble solids (g/kg wb[c])
Paste 1	4.2	22.8±0.3	4.5±0.1	–	245.0±4.5	55.8±0.8
Paste 2	4.3	23.2±0.8	3.4±0.2	–	257.0±1.5	62.6±3.1
Paste 3	4.2	22.5±0.9	4.1±0.2	–	237.0±8.1	65.5±4.2
Ketchup 1	3.8	26.2±0.1	3.1±0.1	23700±141.0	271.6±2.2	18.3±0.2
Ketchup 2	3.8	26.5±0.6	2.8±0.1	24100±141.0	274.3±0.5	18.1±0.7
Ketchup 3	3.8	27.1±0.4	2.8±0.2	24800±1697	272.6±1.3	17.2±0.4

The total solids and water insoluble solids are also included.

[a] Pastes were diluted to 8.3°Brix, and the length of the measurement was 10 s; ketchups were non-diluted and measured for 30 s.

[b] Brookfield viscometer, spindle no. 5, speed 10 rpm.

[c] wb: wet basis.

had reached a refractive index of about zero (Ouden, 1995). The residue (WIS) was dried in an oven at 100 °C for 16 h.

2.4. Particle size distribution

The particle size distribution (PSD) was measured using a laser diffraction analyser (Coulter LS 130, England), applying the Fraunhofer optical model. Each sample was run in duplicate. The area based diameter (d_{32}) was defined as

$$d_{32} = \sum_i n_i d_i^3 \Big/ \sum_i n_i d_i^2, \tag{1}$$

where n_i is the percentage of particles with a diameter d_i. The percentage of small ($<10\,\mu$m) and large ($>100\,\mu$m) particles was obtained by integrating the particle size distribution curve between the abovementioned limits. Cell wall material distribution and form were studied using light microscopy (Olympus BX50, Japan) with a magnification of about 50, in at least six pictures for each sample.

2.5. Volume fraction

The samples were centrifuged at ~110 000*g* for 20 min at 20 °C in an ultracentrifuge (Optima LE-80K, Beckman, California) equipped with an SW41Ti rotor (tube diameter $d = 2r = 14$ mm). The volume fraction of solids was calculated as

$$\phi = \frac{V_s}{V_t}, \tag{2}$$

where $V_s = \pi r^2(2/3r + L_s)$ is the volume of solids and $V_t = \pi r^2(2/3r + L_t)$ is the total volume of the suspension. The corresponding lengths (L_s and L_t, solids and total length, respectively) were measured on the centrifuge tubes using a vernier caliper.

The supernatant achieved was kept for further viscosity measurements.

2.6. Steady-shear viscosity measurements

The viscosity of the supernatant was measured at 20 °C in a controlled-stress rheometer (StressTech®, Reologica, Sweden) equipped with a bob and cup concentric cylinder ($R_0/R_i = 27/25$ mm).

The viscosity of the tomato pastes and ketchups was measured at 20 °C in a controlled-stress rheometer (StressTech®, Reologica, Sweden) equipped with a four-blade vane in order to eliminate the slip phenomenon. The vane was 21 mm in diameter and 45 mm in height, and was placed in a cup 27 mm in diameter. The vane was carefully loaded at stresses below 0.8 Pa. Special care was taken to minimize air inclusions in the sample.

All rheological measurements were carried out at least in duplicate. The maximum relative standard error (RSE) allowed between replicates was 5%, but in most of the cases RSE ≈ 1%:

$$\mathrm{RSE}(\dot\gamma_i) = \left| \frac{\log \eta_{1,\dot\gamma_i} - \log \eta_{2,\dot\gamma_i}}{(\log \eta_{1,\dot\gamma_i} + \log \eta_{2,\dot\gamma_i})/2} \right|, \tag{3}$$

where η is the viscosity and $\dot\gamma$ is the shear rate of replicate $i = 1,2$.

To study the stress dependence of the viscosity, the tomato suspensions were subjected to an increasing shear stress in 100 intervals from 0.07 to 465 Pa. Each stress was applied to the sample for 10 s to allow it to stabilize, and then measurements were averaged during the following 10 s of shearing. The flow curve measured in this way was extrapolated to obtain the apparent yield stress. The apparent yield stress was calculated using the mathematical tool developed by Mendes and Dutra (2004), who defined the apparent yield stress as the stress where the function $\mathrm{d}\ln\sigma/\mathrm{d}\ln\dot\gamma$ reaches a minimum. Moreover, the apparent viscosity (η_a) of the suspension was described using the Carreau model:

$$\eta_a = \frac{\eta_0}{[1 + (\lambda_c \dot\gamma)^2]^N}, \tag{4}$$

where η_0 is the apparent zero-shear viscosity, λ_c is a time constant and N is a dimensionless exponent. The parameters of the model were determined using the Matlab function *fminsearch*, which performs a multidimensional unconstrained nonlinear minimization (Nelder–Mead) of the error (SSL), i.e. of the sum of squares of the logarithm of the experimental and predicted values

$$\mathrm{SSL} = \sum_{i=1}^{n} (\log \eta_i - \log \eta_p)^2. \tag{5}$$

2.7. Dynamic rheological measurements

Dynamic rheological measurement of tomato samples was carried out in a controlled-stress rheometer (StressTech®, Reologica, Sweden) using the above-described vane. The stress sweep tests at a frequency of 1 Hz were carried out in order to determine the range of linear viscoelastic response under oscillatory shear conditions.

The frequency sweep measurements under conditions of linear viscoelasticity were performed at constant stress amplitude (0.5 Pa in pastes and 0.1 Pa in ketchups) in the range of frequencies 0.01–100 Hz. The measurements were performed at least in duplicate.

2.8. Sensory analysis

The sensory analysis was performed by a non-trained panel consisting of five females and three males. Each tomato ketchup was subjected to evaluation of its textural and sensorial (flavor and taste) properties. The descriptors used in the evaluation, which are adapted from Tornberg, Carlier, Willers and Muhrbeck (2005), are summarized in

Table 2
Textural and sensorial parameters evaluated and descriptors used

Perception type	Attribute	Description
Texture before consumption	Spreadability	The dish is bended to evaluate if the ketchup spreads quickly or slowly
	Elasticity	Stickiness of the ketchup to a spoon when it is lifted from the plate
	Grainy	The product is spread in a thin layer to evaluate if dots occur
	Adherence	Adherence of the ketchup to the spoon when it is filled with product
Visual appearance	Color	Scale varying from yellow to red-brown
	Smoothness	Surface smooth or rough
Texture after consumption	Thickness	Thick or liquid texture based on pressing the ketchup on the palate
	Tomato taste	Scale varying from natural tomato taste to burned tomato taste
Overall acceptance	Acceptance	Evaluate if the ketchup is liked or not

Table 2. All sensory attributes were evaluated in a scale from 1 to 9 (low and high, respectively) on four samples, consisting of three ketchups and one repetition. For comparison, all four samples were served simultaneously at room temperature.

2.9. Statistical analysis

An analysis of the variance (ANOVA) was performed to evaluate the effects of processing and concentration on the volume fraction and the rheological parameters (Minitab v.14, 2003). The level of significance was set at $p<0.05$. Another ANOVA was carried out to assess the effect of origin on the characteristics of pastes and ketchups. All significant parameters were then analyzed by Pearson correlation matrix to determine the independent variables, which were further classified using principal components analysis (PCA, Minitab v.14, 2003). The sensory data were also analyzed using PCA (Minitab v.14, 2003).

3. Results and discussion

3.1. Changes in the structure, PSD and volume fraction after processing tomato paste into ketchup

In Fig. 1, microscopic pictures show the structure of the original paste and of the ketchup suspension after processing. Fig. 1A reveals that the paste structure consists mostly of whole cells with apparently intact cell walls, along with some broken cells and cell wall material suspended in an aqueous media. Fig. 1B shows that processing the paste into ketchup induced significant changes in the structure: few entire cells remained after processing and those that did remain were generally small. The ketchup suspensions mainly contain cell wall fragments and randomly distributed cellular material, and the particles tend to aggregate becoming difficult to observe them individually.

The PSD of both pastes and ketchups is shown in Fig. 2 as area-based diameter (d_{32}). All samples of pastes and ketchups exhibit at least a bimodal size distribution. In tomato paste suspensions two main peaks are observed, one at about 250 μm and the other at about 2 μm. However, paste 1 appears to be differently structured regarding the small particle fraction, with three peaks at 4, 8 and 27 μm, respectively. Concerning the ketchup suspensions, the PSD also shows two peaks, at about 75 μm and at about 1 μm. While the PSD of the large particle region is almost identical for the three ketchups, the small particle region shows large differences between them, ketchup 3 being the one with the largest particles.

The percentage of large particles is shown to be drastically reduced by homogenization. In the original tomato pastes, the number of particles greater than 100 μm was around 50% (determined as the area under the PSD curve in Fig. 2), whereas in the ketchups this number was reduced to about 20% by processing. In addition, the percentage of small particles (<10 μm) was almost doubled (Table 3). These changes appeared to be related to the origin of the pastes (ANOVA, $p<0.03$) in both pastes and ketchups. For example, paste 2 has the highest number of large particles, but its corresponding ketchup 2 shows few remaining large particles than the other ketchups. These findings indicate that the different fractions (i.e. large and small particles) of the pastes have different susceptibility to breakage during processing depending on the paste origin. It has been reported in the literature (Sánchez et al., 2002; Valencia, Sánchez, Ciruelos, & Gallegos, 2004) that the size of the particles in ketchup did not depend on the screen size used during the manufacture of tomato paste. As our findings indicated, the size of the paste particles does not necessarily determine that of the ketchup particles.

The volume fraction (ϕ), determined by ultracentrifugation, is also reported in Table 3. Earlier results showed that in paste suspensions the volume fraction was proportional to the amount of paste (results not shown). However, in the ketchups in the present study, ϕ is higher than expected according to the amount of paste, indicating that the homogenization process has a large impact on the volume occupied by the particles. Moreover, in pastes and ketchups, the change in ϕ was significantly different for each origin (ANOVA, $p<0.03$): i.e. while paste 2 showed the larger ϕ as a paste, its corresponding ketchup 2 resulted in the lowest ϕ. These findings thus indicate that processing induces the particles to swell and also that the components

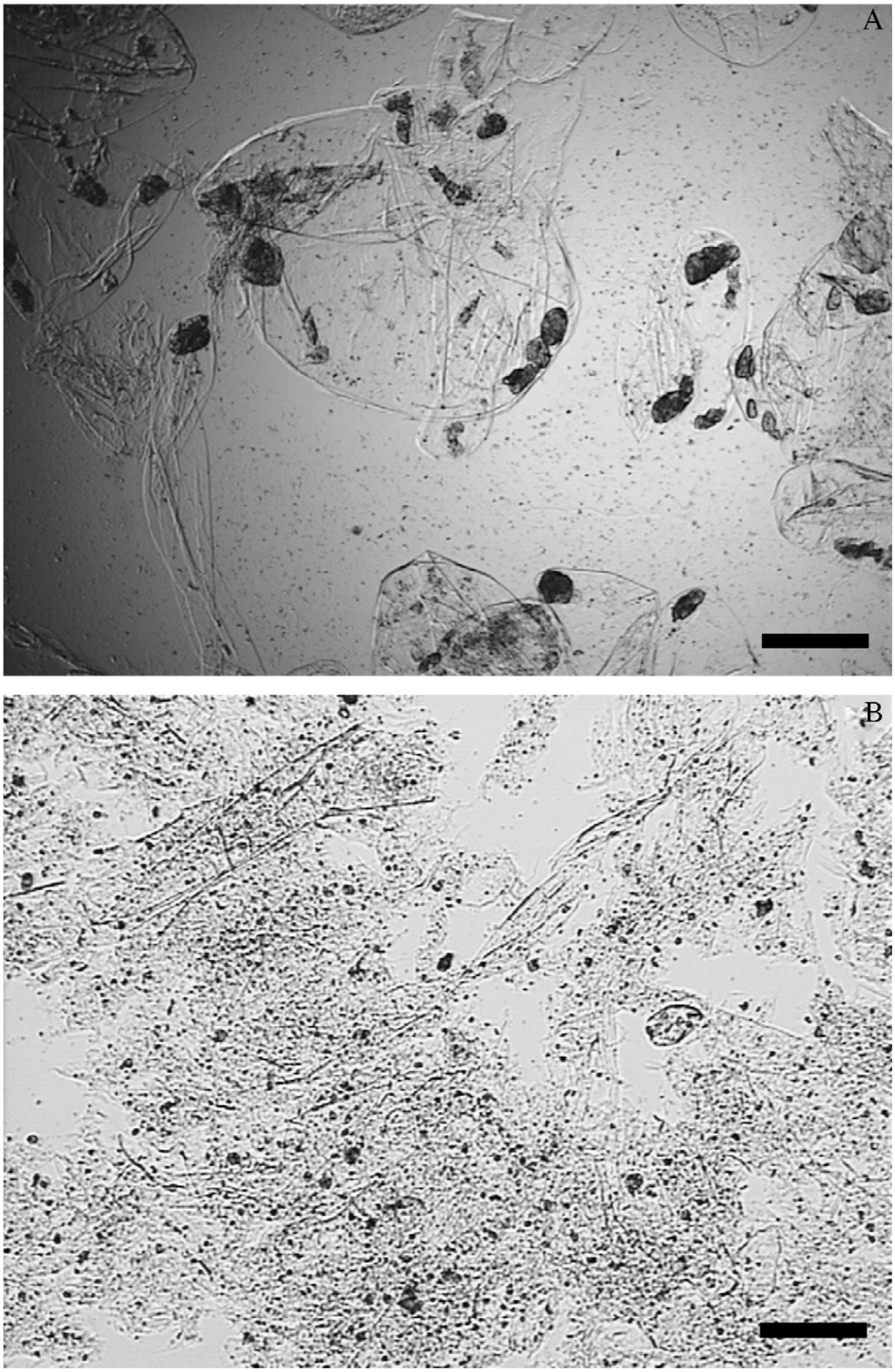

Fig. 1. Microscopic pictures of typical suspensions of tomato paste (A) and tomato ketchup after homogenization (B). The bar is 150 μm.

of each paste have slightly different swelling properties. The concentration of the suspensions was also calculated as WIS (i.e. expressed as weight), but because the WIS value resulted merely in a factor of dilution (Table 1) and did not reflect the changes in structure after processing, we have chosen to express concentration as ϕ in the rest of this study.

3.2. Changes in the rheological properties after processing

3.2.1. Viscosity of the supernatant

The supernatant of the pastes was non-Newtonian, and thus their viscosity was calculated at $100\,s^{-1}$, being in the range of 1.8–2.3 Pa s (Table 3). The continuous phase of the ketchups was a Newtonian fluid, the viscosity of which

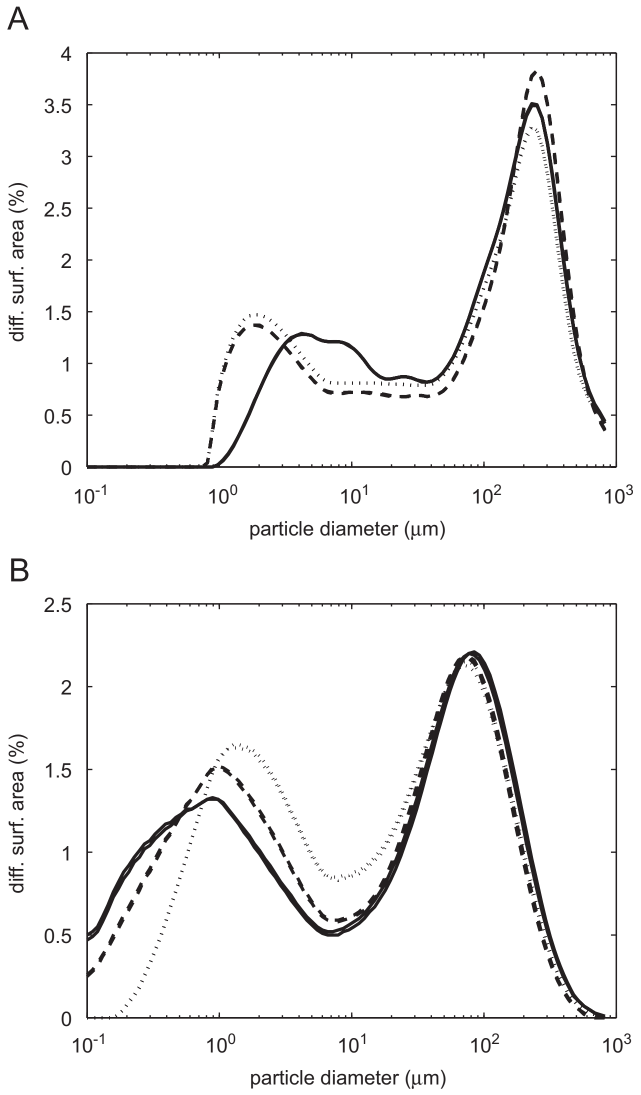

Fig. 2. Particle size distribution of the original tomato paste (A) and the corresponding ketchup after homogenization (B), for the three origins studied: 1 (___), 2 (_ _) and 3 (……). Two repetitions are shown.

Table 3
Volume fraction (ϕ), percentage of small ($<10\,\mu$m) and large particles ($>100\,\mu$m) and viscosity of the supernatant (η_s, RSE < 1%) in both the pastes and their corresponding ketchups

	ϕ (–)	Particles < 10 μm (%)	Particles > 100 μm (%)	η_s (Pa s)
Paste 1	0.54 ± 0.012	24.19 ± 0.08	51.44 ± 0.04	2.317
Paste 2	0.59 ± 0.003	27.93 ± 0.03	52.73 ± 0.08	1.926
Paste 3	0.52 ± 0.010	30.53 ± 0.04	47.02 ± 0.04	1.831
Ketchup 1	0.37 ± 0.017	46.45 ± 1.12	19.40 ± 0.39	0.015
Ketchup 2	0.32 ± 0.003	48.98 ± 0.06	16.41 ± 0.42	0.012
Ketchup 3	0.34 ± 0.002	46.29 ± 0.22	17.03 ± 0.74	0.012

ranged between 12 and 15 mPa s (Table 3). Since a sugar solution of similar °Brix would have ~2.8 mPa s, the increased viscosity must be due to other soluble components such as pectins. The origin of the paste does significantly influence the value of the supernatant viscosity ($p < 0.04$) in both pastes and ketchups.

3.2.2. The apparent shear-viscosity in pastes and ketchups at different concentrations

The flow behavior of the suspensions is shown in Fig. 3 as the apparent shear viscosity as a function of the shear rate. An initial Newtonian plateau is followed by a shear-thinning region, which seems to change slope at shear rates around 0.1–1 s^{-1}. According to Fig. 3 the apparent viscosity (η_a) of the suspension can be described using the Carreau model (Eq. (3)). The parameters of the model are summarized in Table 4. The viscosity data for both pastes and ketchups could be acceptably predicted by the Carreau model for various concentrations and a large range of shear rates (Fig. 4), as shown in Table 4 the SSL being low. Similar values for the Carreau parameters of tomato pastes were reported by Valencia et al. (2003). It has to be noted, however, that the Carreau model does not take into consideration the second change of slope in the shear-thinning region. This discontinuity of the flow curve, that seems to be characteristic of concentrated suspensions, has been discussed elsewhere (Tiziani & Vodovotz, 2005).

The apparent zero-shear viscosity η_0 is shown to be a function of the concentration of the suspensions (ϕ), having a relationship of the type $\eta_0 \propto \phi^{3.75}$ ($R^2 = 0.92$, Fig. 4). The time constant λ shows a weaker relationship with the concentration ($\lambda \propto \phi^{1.49}$, $R^2 = 0.68$). The N value, which is related to the slope of the shear-thinning region, is, however, independent of the concentration and is significantly lower for pastes ($N = 0.39$) than ketchups ($N = 0.41$). No influence of the origin was reflected in any of the Carreau parameters.

The results reported above are not consistent with either Brookfield or Bostwick data (Table 1). For example, both paste and ketchup 2 flow the shortest distance during the Bostwick measurement, which only agrees with the η_0 determined in this study for paste 2 (being the highest), but not for its corresponding ketchup (being the lowest). Moreover, ketchup 1 has the lowest Brookfield viscosity, which is the opposite of that observed by our rheological measurements. As it has been discussed in the Introduction, these devices are not precise enough to notice small differences of quality and should therefore only be used as a gross test.

3.2.3. Effect of the concentration and processing on the apparent yield stress

The yield stress is defined as the minimum stress required by a material to initiate flow. The critical stress for the onset of the shear thinning region (see arrows in Fig. 3) is commonly used to characterize an apparent yield stress. This parameter is related to the structure of the suspensions, and in gels it is an indicator of the strength of the network. The apparent yield stress was plotted as a function of the volume fraction in Fig. 4, showing a relationship of the type $\sigma_y \propto \phi^{2.06}$ ($R^2 = 0.92$). The yield

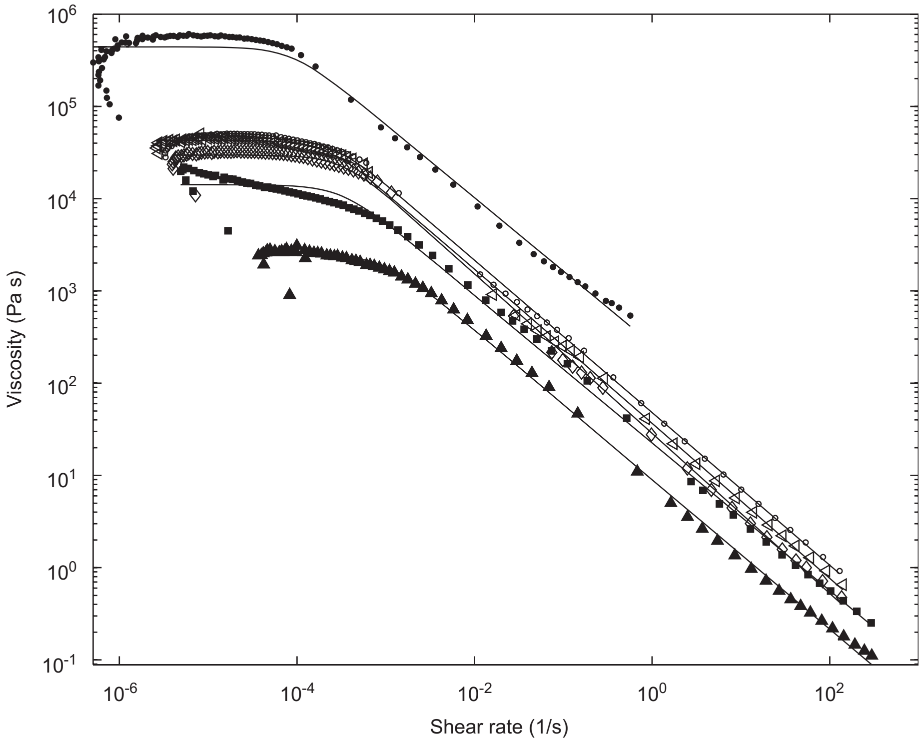

Fig. 3. Apparent steady-shear viscosity η_a (Pa s) as a function of the shear rate $\dot{\gamma}$ (s^{-1}) for a typical paste (filled symbols) and its corresponding ketchup (empty symbols), at different concentrations (ϕ): 0.54 ●, 0.21, ■, 0.18 ▲, 0.37 ○, 0.33 ▷, and 0.26 ◇. The Carreau model (—) fitting is also shown.

Table 4
Carreau model parameters (apparent zero-shear viscosity η_0, time constant λ_c, and exponent N) for pastes and ketchups at different concentration, and estimation of the error of the fitting (SSL) based on Eq. (5)

	ϕ (–)	η_0 (10^3 Pa s)	λ_c (10^3 s)	N (–)	SSL (–)
Paste 1	0.54	486	11.5	0.41	1.6
	0.21	11	2.7	0.40	0.6
	0.18	3	1.6	0.40	0.4
Paste 2	0.59	742	26.8	0.37	0.7
	0.23	23	4.5	0.41	0.7
	0.19	11	4.9	0.40	0.6
Paste 3	0.52	662	18.4	0.38	0.2
	0.21	21	4.8	0.40	0.3
	0.17	9	4.2	0.40	0.1
Ketchup 1	0.37	50	4.4	0.41	0.3
	0.33	40	4.5	0.42	0.3
	0.26	28	3.1	0.43	0.4
Ketchup 2	0.32	43	4.4	0.41	0.3
	0.29	29	4.3	0.42	0.3
	0.23	26	3.6	0.43	0.2
Ketchup 3	0.34	43	4.7	0.41	0.2
	0.31	42	5.3	0.41	0.2
	0.24	30	3.4	0.43	0.3

The mean value of two replicates is given (RSE < 5%).

value was significantly affected by processing and concentration (ANOVA, $p < 0.05$), i.e. it decreased by dilution and, at the same paste content, increased by homogenization. Regarding the origin, no differences were observed in the case of pastes, but in the ketchups the yield value was significantly different for each origin (ANOVA, $p < 0.05$), being the higher value for ketchup 1 and the lowest for ketchup 2.

3.2.4. Dynamic viscoelastic properties in the original pastes and their corresponding ketchups

The linear viscoelastic region of the suspensions, i.e. when G' is independent of the stress, occurs in a range of stresses between 0.01 and ~20 Pa for pastes and 0.01 and ~4 Pa for ketchups (Table 5). Under linear viscoelastic conditions, the elastic modulus G' is higher than the loss modulus G'' for all the samples, indicating that the pastes and ketchups behaved as gels. However, the pastes and ketchups do not show the same trends with respect to their origin (ANOVA, $p < 0.05$), i.e. paste 2 shows the highest values for both moduli, but its corresponding ketchup 2 shows the lowest values. On the contrary, paste 1 shows the lowest values as a paste, but its corresponding ketchup 1 results in the highest moduli. These facts might indicate that different components in the paste behave slightly differently under processing, giving rise to different networks. In addition, the phase angle shows no differences between pastes and ketchups (ANOVA, $p < 0.05$) and the average value was $11.8 \pm 1.3°$ for all concentrations, which is low and indicates a strong network structure.

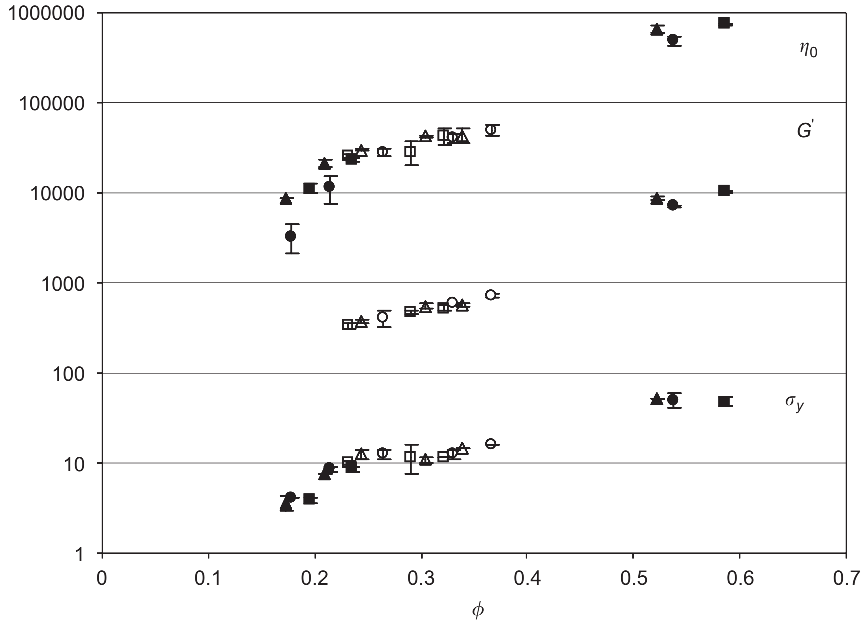

Fig. 4. Apparent zero-shear viscosity (η_0, Pa s), elastic modulus (G', Pa) and apparent yield stress (σ_y, Pa) as a function of the volume fraction (ϕ) for pastes (filled symbols) and ketchups (empty symbols) from different origins 1, 2 and 3 (○, □, △, respectively).

Table 5
Storage and loss moduli (G'_0 and G''_0), complex viscosity (η^*_0) and phase angle (δ), for both pastes and ketchups in the linear viscoelastic region, determined during the stress sweep measurement (1 Hz)

	ϕ (–)	G'_0 (Pa)	G''_0 (Pa)	η^*_0 (Pa s)	δ (°)
Paste 1	0.54	7124.2	1503.2	1160.1	12.0
Paste 2	0.59	10411.0	2363.9	1699.2	12.8
Paste 3	0.52	8817.7	2110.1	1475.3	12.5
Ketchup 1	0.37	732.9	184.9	120.3	14.2
Ketchup 2	0.32	526.7	118.7	86.1	12.7
Ketchup 3	0.34	565.7	130.7	92.4	12.6

Both elastic (G') and loss moduli (G'') as a function of the frequency ω (Fig. 5) indicate the same trends in pastes and ketchups: G' increased slightly with increasing frequencies, whereas G'' remained constant or decreased slightly at low frequencies (ω), and then increased with ω.

The mechanical spectra of model dilute solutions are predicted by the general linear model to exhibit $G' \propto \omega^{2.0}$ and $G'' \propto \omega^{1.0}$, with $G'' > G'$ and $\omega \to 0$. The mechanical spectra of a gel, instead, are expected to be independent of the ω (Ferry, 1980; Ross-Murphy, 1988). Recently, it has also been shown experimentally that during the sol–gel transition, $G' \propto \omega^{0.5}$ (Liu, Qian, Shu, & Tong, 2003). The dependency of the moduli to the frequency seems to be explained by a power-law relationship (Eqs. (6) and (7)). However, in the systems studied here, at $\omega < 0.1$ Hz, the loss modulus G'' was almost independent of ω and seemed to show a minimum at low frequencies, in both pastes and ketchups, which is typical of highly structured materials. The power-law relationship is hence only valid at higher frequencies, $\omega > 0.1$ Hz, and the parameters obtained from Eqs. (6) and (7) are summarized in Table 6. At higher ω, the values of G' and G'' were proportional to $\omega^{0.1}$and $\omega^{0.2}$, in pastes and to $\omega^{0.1}$ and $\omega^{0.3}$ in ketchups. The behavior observed in these suspensions seems to correspond to that of "physical gels" or "weak gels", which falls between the true gels characterized by covalent cross-linked materials, and the concentrated suspensions, characterized by entanglement networks. Moreover, the ratio $G''/G' = \tan\delta$ is in the order of 10^{-1} for both pastes and ketchups, whereas that of true gels is in the order of 10^{-2} (Lizarraga, Vicin, González, Rubiolo, & Santiago, 2006). The slope of log G' vs. ω hence indicates that the suspensions are strongly aggregated gels ($0.1 < n' < 0.2$).

$$G' = k'(\omega)^{n'}, \tag{6}$$

$$G'' = k''(\omega)^{n''}. \tag{7}$$

It can be seen, from Fig. 5, that the behavior of pastes is different to that of the ketchups regarding the origin: once again, paste 2 shows the highest G' and G'', whereas ketchup 2 shows the lowest values of G' and G''. The value of the power-law parameters in pastes (Table 6) are in agreement with those reported by Rao and Cooley (1992).

3.3. A general description of pastes and ketchups by their structural and rheological properties

In the previous sections we have described a number of characteristics of the pastes and ketchups, such as the particle size, volume fraction, and the rheological behavior in steady and dynamic shear, and how these properties are affected by concentration, processing and origin. Several of these variables were significantly dependent on the origin of the paste (ANOVA $p < 0.05$).

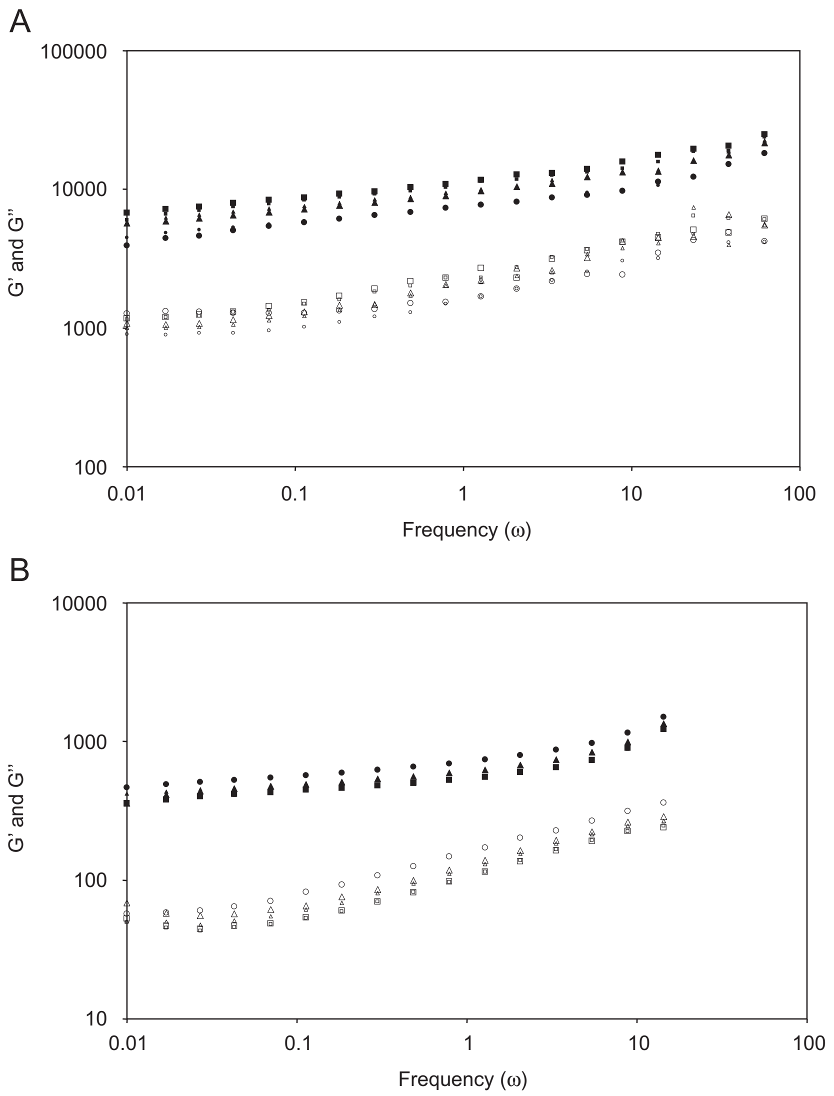

Fig. 5. Elastic G' (Pa) (filled symbols) and loss modulus G'' (Pa) (empty symbols) as a function of the frequency ω (Hz) in three tomato pastes (A) and its correspondent ketchups (B), from different origins 1, 2 and 3 (○, □, △, respectively). Two repetitions are shown. Note that the scales are different.

Table 6
Power-law parameters for the correlation between the storage and loss moduli (G' and G'') and the frequency (ω), according to Eqs. (6) and (7)

	ϕ (–)	K' (Pa s$^{n'}$)	n' (–)	K'' (Pa s$^{n''}$)	n'' (–)
Paste 1	0.54	7556.4	0.1226	1659.9	0.2546
Paste 2	0.59	11607.5	0.1399	2539.0	0.2077
Paste 3	0.52	9763.3	0.1212	2156.5	0.2484
Ketchup 1	0.37	735.5	0.1084	159.5	0.3032
Ketchup 2	0.32	560.0	0.1023	106.6	0.3313
Ketchup 3	0.34	633.8	0.1064	125.1	0.3164

A Pearson correlation matrix was performed in order to obtain those independent variables that could describe the samples by their origin. The corresponding PCA of those variables grouped the samples clearly by origin (Fig. 6), where factors 1 and 2 explained 57.3% and 40.0%, respectively, of the variation in pastes, and 65.5% and 33.3%, of the variation in ketchups.

The PCA describes, in a general picture (Fig. 6), pastes and ketchups. Paste 1 is mostly characterized by the high viscosity of the supernatant η_s and a low content of small particles; paste 2 shows the largest ϕ, which corresponds to the highest amount of large particles and therefore, gives the largest η_0. Paste 3 is characterized by a large content of small particles and a low content of large particles. The corresponding ketchup 1 shows higher η_s, a large increase in small particles and the highest ϕ. Ketchup 2 has the larger decrease in large particles and the lowest ϕ. Ketchup 3, finally, is characterized by the biggest size of the small particles. Different variables were therefore chosen to describe the pastes and the ketchups, for example the apparent zero-shear viscosity is useful to describe the pastes, whereas another variable such as the change in the size of the particles is better in describing the ketchup characteristics.

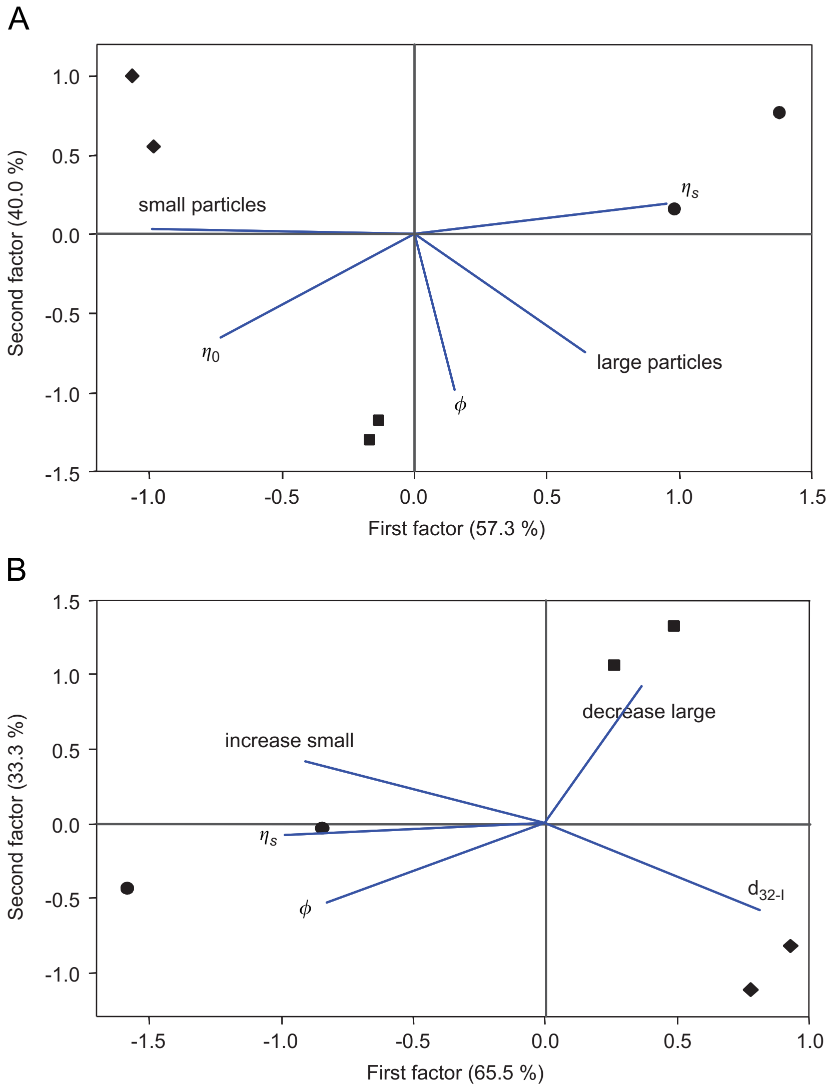

Fig. 6. Principal components analysis (PCA) plots for the instrumental variables describing (A) pastes and (B) ketchups from different origins 1, 2 and 3 (●, ■, ♦, respectively).

3.4. Sensory assessment on ketchups based on different pastes

The ketchups were also subjected to sensory assessment. The sensory characteristics of the three ketchups are summarized in Table 7. No significant differences between the ketchups were noticed ($p > 0.05$), probably because the assessors were not especially trained for tomato products and the differences between the ketchups were small.

Table 7
Sensory attributes of ketchups evaluated in an arbitrary scale 1 to 9 (mean values and standard deviation of the assessors, $n = 8$)

Perception type	Attribute	Ketchup 1	Ketchup 2	Ketchup 3
Texture before consumption	Spreadability	4.6±2.0	6.0±1.6	6.0±0.9
	Elasticity	5.3±2.3	5.0±1.8	3.6±1.6
	Grainy	2.9±1.6	3.8±1.7	4.6±1.8
	Adherence	4.0±1.8	3.8±1.8	4.6±1.8
Visual appearance	Color	4.8±0.9	5.5±0.9	5.5±1.1
	Smoothness	5.7±1.2	5.6±1.3	5.8±1.3
Texture after consumption	Thick	6.1±1.8	5.6±1.1	4.8±1.3
	Tomato taste	5.5±1.2	5.4±0.9	5.3±0.5
Overall acceptance	Acceptance	6.5±1.7	6.9±1.1	7.0±0.8

3.5. Does characterization of the pastes allow a prediction of the quality of the ketchup?

In the previous sections we have shown that each paste and ketchup is well-described by the particle size, volume fraction, and the rheological behavior in steady and dynamic shear. It has also been shown that the processing of pastes into ketchups induces structural changes in the suspensions. Moreover, the variations in the behavior of the suspensions after processing are observed to depend on the starting material, i.e. the paste origin. Considering that pastes and ketchups, separately, are well-described by their steady and dynamic rheological properties, and that those properties are closely related to ϕ of the suspensions, it seems plausible that knowing ϕ the characteristics of the ketchups can be predicted. However, it is noted that the highest volume fraction in a paste does not imply the highest volume fraction in its corresponding ketchup. The origin of the paste seems thus to be responsible of the differences from the expected behavior after processing. Our study indicates that the volume fraction depends on several factors such as WIS, fraction of small particles, fraction of large particles, shape and aspect ratio of the particles and viscosity of the supernatant, among others; which is in agreement with a previous theoretical review by Servais, Jones and Roberts (2002).

The changes in the fractions of small and large particles are apparently related to the origin of the paste, i.e. the components of that paste and their susceptibility to breakage during processing. It is noted that the higher the content of large particles, the higher the ϕ of the paste suspensions. In addition, it appears that the higher the viscosity of the supernatant and the larger the increase in small particles after homogenization, the higher the ϕ in the processed ketchups. Further research is hence needed in order to discern between the effects of these parameters and of processing on the structure of the suspensions and their ϕ.

4. Conclusions

The rheological characterization of each paste and ketchup individually gives a good description of their flow properties. However, the knowledge of the properties of one paste is not sufficient to predict the properties of its corresponding ketchup. The changes that each paste undergoes during processing depend on a number of parameters including the rheological properties but also the particle properties such as their volume, size and shape, and their susceptibility to breakage. The measurements performed in the industry give only a "gross" estimation of the viscosity under specific conditions. A better prediction of the ketchup characteristics from the paste data is industrially very interesting because it allows to control and optimize the processing parameters, for example the amount of paste added or the degree of homogenization needed. Our results may then contribute to improve the quality control performed during processing. Further work is needed in order to define those properties that are able to reflect the variation in the expected flow behavior after processing.

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