Components of Vane Yield Stress of Structured Food Dispersions

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ABSTRACT: The vane technique was used to determine the static (σ_{os}) and dynamic (σ_{od}) yield stresses of 6 commercial foods: mayonnaise, mustard, ketchup, applesauce, and 2 brands of tomato puree (samples TD and TR). The samples, other than TR, exhibited shear-thinning behavior. For those samples, based on a model proposed earlier, the contributions of bonding (σ_b) , network (σ_n) , and viscous (σ_v) to yield stress of the products were determined. For the homogenized products, $\sigma_b > \sigma_n$, whereas for those processed in a finisher, $\sigma_n > \sigma_b$. Because sample TR exhibited shear-thickening behavior, the model to estimate yield stress components was not applicable. The structural conditions necessary for the validity of the proposed model are established. Equilibrium stress (σ_a) values obtained by extrapolation of vane torque data to infinite time were comparable to σ_{od} values.

Keywords: yield stress, vane method, static yield stress, dynamic yield stress, bonding, network, viscous

Introduction

Pluid foods that contain much dissolved high-molecular-weight compounds and/or suspended solids exhibit non-Newtonian and viscoelastic behavior (Rao 1992). Yield stress is the minimum stress required to initiate flow, and is 1 measure of the strength of a network of interacting particles. Genovese and Rao (2003) discussed indirect methods and the vane method of determination of yield stress of structured food products and listed related studies. Briefly, extrapolation of shear flow data to zero shear rate is a popular, relatively fast, indirect means of estimation of yield stress, in which shear stress (σ) shear rate ($\dot{\gamma}$) data is fitted to a constitutive equation, such as the Herschel-Bulkley (Eq. 1) or the Casson (Eq. 2) model:

$$\sigma = \sigma_{0-HB} + k\dot{\gamma}^n \tag{1}$$

$$\sqrt{\sigma} = \sqrt{\sigma_{0-C}} + \sqrt{\eta_{\infty}\dot{\gamma}} \tag{2}$$

where, *k* is the consistency index, *n* is the flow behavior index, η_{∞} is the infinite shear rate viscosity, and σ_{0-HB} and σ_{0-C} are the Herschel-Bulkley and Casson yield stresses, respectively. The value of yield stress so obtained is largely dependent on the quality and quantity of data at low shear rates, the fitting model selected, and the range of shear rates where it is applied.

Because of minimum disruption of structure and wall-slip effects, the vane test is a reliable and a direct method of measurement of yield stress. A vane with at least 4 blades is fully immersed in the sample and rotated slowly at a constant speed until the torque reaches a maximum value (T_m) and the sample fails (Dzuy and Boger 1983). The yield stress (σ_0) is then calculated from Eq. 3 and 4:

$$\sigma_0 = K^{-1} Tm \tag{3}$$

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where, K is the vane parameter that depends on the diameter (D) and height (H) of the vane:

0.
$$K = \frac{\pi D^3}{2} \left(\frac{H}{D} + \frac{1}{3} \right)$$
 (4)

Michaels and Bolger (1962) and Metz and others (1979) discussed a structural model for dispersions of particle flocs that associate randomly to form weakly bonded aggregates and tenuous networks, giving rise to plastic properties. Genovese and Rao (2003) showed that by applying an energy balance at the point of maximum deformation (yield point) in the vane test, the contributions of different structural components to the total yield stress can be estimated as follows:

$$\sigma_0 = \sigma_b + \sigma_v + \sigma_n \tag{5}$$

$$\sigma_0 = \sigma_{0s} \tag{6}$$

$$\sigma_b = \sigma_{0s} - \sigma_{0d} \tag{7}$$

$$\sigma_{v} = \eta_{\infty} \dot{\gamma} \tag{8}$$

where, σ_b is the stress required to break the bonds between the flocs, σ_v is the stress dissipated due to purely viscous drag, and σ_n is the stress required to break the aggregate network; σ_{0s} and σ_{0d} are the static and dynamic yield stresses of the samples with undisrupted and disrupted structure, respectively. Similar concepts have been used in recent studies on dispersions: including flocs or clusters (Zhou and others 1999; Maranzano and Wagner 2002); the stress decay following yield stress was associated with the breaking of bonds (James and others 1987; Truong and Daubert 2000), and σ_n was associated with forces required to push aggregated particles away from each other and breaking their network (Zhou and others 1999).

The main objectives of this work were to determine the contribution of the structural components: bonding, network, and viscous to the yield stress of different commercial food products, and if structure-inducing processes affected those components. Other

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objectives were to determine the equilibrium value after stress decay and its relationship with the dynamic yield stress, and the conditions required for Eq. 7 to be applicable.

Materials and Methods

Samples

The food products selected for study were: mayonnaise MT (Tops Markets, Buffalo, N.Y.), ketchup KH (Heinz, Pittsburgh, Pa.), mustard MF (French's, Springfiled, Mo.), applesauce AM (Mott's, Rye brook, N.Y.), and tomato purees from two manufacturers, TD (De Cecco, Northumberland, Pa.) and TR (Redpack, Elwood, In.). For each product, several large containers (3 to 4 kg) from the same batch were purchased at a local supermarket. Dry solids content of the ketchup, applesauce, and tomato purees was determined by vacuum drying overnight at 97 °C to 98 °C and 3.1 to 6.5 KPa (absolute pressure), and soluble solids content with a refractometer (ABBE, American Optical Corp., Buffalo, N.Y., U.S.A.).

Mayonnaise is an oil-in-water (O/W) emulsion prepared from vegetable oil, egg yolk, and other ingredients; its viscoelastic behavior is due to the network formed between lipoproteins adsorbed around neighboring oil droplets (Ma and Barbosa-Cánovas 1995). Mustard is a network of particle aggregates obtained by milling mustard seeds in water and mixing the slurry with other ingredients (Aguilar and others 1991). Applesauce and tomato concentrates are dispersions of insoluble plant matter in aqueous media (Qiu and Rao 1988). To obtain the former, apples whose skin and core are removed are sliced, cooked with steam, and finished in a pulper (Wiley and Binkley 1989). Tomato puree is concentrated tomato pulp after the removal of skins and seeds and contains 8% to 24% natural tomato soluble solids. Ketchup is obtained by milling tomato puree to increase consistency (Hayes and others 1998).

The structure of these food dispersions is influenced strongly by specific unit operations during manufacture: homogenization for mayonnaise, ketchup, and mustard (Aguilar and others 1991; Ma and Barbosa-Cánovas 1995), finishing for applesauce, and finishing and evaporation for tomato puree (Qiu and Rao 1988).

Rheological measurements

Vane yield stress and flow measurements were conducted at 25 ± 0.1 °C using a 6-blade vane attached to a controlled shear rate viscometer (Haake Rotovisco RV30, Karlsruhe, Germany) as described in Genovese and Rao (2003). Briefly, each sample was gently poured into a jacketed stainless-steel (JSS) vessel, 7.2-cm dia, 11.7-cm height, and allowed to rest for 30 min for structure recovery and temperature equilibration. The vane impeller, D = 4.0 cm, H = 6.0 cm, was immersed entirely in the sample and rotated at the lowest speed, $N_1 = 0.05$ rpm, during 20 min. Magnitudes of torque (T) were recorded on a computer using the viscometer software, Rotation RV30, and converted to T/K versus time curves. The static yield stress (σ_{0s}) of the undisrupted sample was calculated from the peak value of torque.

As a 2nd step, a flow test was performed by applying continuous rotation from 0 to 258.6 rpm and back to 0 rpm. The shearing time was 10 min each for the ascending and descending shear cycles. Following the flow test, the yield stress of the disrupted sample was measured at the same $N_1 = 0.05$ rpm, and this value was considered to be the dynamic yield stress (σ_{0d}) (Genovese and Rao 2003). To evaluate the effect of rotational speed on σ_{0s} and σ_{0d} , they were determined at another 5 different values of N up to 2.07 rpm, using a new sample for each N. For mayonnaise, the maximum possible value of N was 0.52 rpm due to torque-overload at higher rotational speeds. Each measurement was done at least in triplicate, and averaged for further analysis.

Vane-shear rate values were calculated assuming that the average shear rate ($\dot{\gamma}$) around the paddle is directly proportional to N (Eq. 9) (Rao and Cooley 1984). The shear stress for the flow curves was determined with Eq. 10.

$$\dot{\gamma} = k_s \frac{N}{60} \tag{9}$$

$$r = A T$$
 (10)

where, k_s and A are constants determined for each vane. For the paddle used in this work, $k_s = 11.6$ /rev (Qiu and Rao 1988), and A = $4563/m^3$ (Genovese and Rao 2003). The angular deformation (θ , rad) at the point of failure was calculated as follows:

$$\theta = \frac{2\pi}{60} N t_m \tag{11}$$

where, t_m (s) was the time required to reach the maximum torque.

Results and Discussion

data he vane yield stress (*T/K*) at different shear rates of the undisrupted (*u*) and disrupted (*d*) samples of mayonnaise MT and tomato puree TD, over the 1st 1000 s are shown in Figure 1 and 2. Because similar overall behavior was seen with samples of ketchup KH, mustard MF, and applesauce AM, their response curves are not shown here. Results obtained with tomato puree sample TR are discussed in a separate section. Torquetime curves of the 5 dispersions exhibited the 3 typical regions: (1) an increase in stress, representing the elastic response due to stretching of network bonds, (2) a peak stress, taken as the collapse of the microstructure or yield point, and (3) a stress decay associated with the gradual breaking of bonds or structure breakdown.





Figure 1-Time-torque/vane parameter (T/K) curves at different shear rates and 25 °C for the undisrupted (filled symbols) and disrupted (open symbols) of Mayonnaise MT. Symbols: \bullet , \blacksquare , \diamond , \blacktriangle , and \lor denote shear rates 0.01/s, 0.03/s, 0.05/s, 0.07/s, and 0.10/s, respectively. Filled symbols = structure undisrupted; open symbols = structure disrupted.

From the peak of each curve, the yield stress value was determined, named static (σ_{0s}) in the case of the *u*-samples, and dynamic (σ_{0d}) for the *d*-samples; the corresponding static and dynamic angular deformations at the yield point, θ_s and θ_d , were calculated with Eq. 11 (Table 1). Values of θ_s and θ_d increased with vane shear rate only for sample KH, but did not follow a defined trend for the other products. On the other hand, values of both σ_{0s} and σ_{0d} showed a clear increase with shear rate for all the 5 products. As illustrated in Genovese and Rao (2003), the values of yield stress: σ_{0s} and σ_{0d} can be plotted against the corresponding angular deformations at the yield point, θ_s and θ_d to obtain texture maps of each product (not shown here).

The shear rate dependency of both the static or total yield stress (σ_0) and the bonding stress (σ_b) can be also visualized in terms of energy rate per unit volume of displaced fluid (Genovese and Rao 2003):

$$E_0 = \sigma_0 \dot{\gamma} \tag{12}$$

$$E_b = \sigma_b \dot{\gamma} \tag{13}$$

where, E_0 and E_b [W/m³] are analogous to σ_0 and σ_b , respectively. In Eq. 12, $\dot{\gamma}$ is the shear rate at which the static yield stress was measured ($\dot{\gamma}_s$). In theory, the shear rate at which the dynamic yield stress was measured ($\dot{\gamma}_d$), and that associated with the breaking of bonds ($\dot{\gamma}_b$) in Eq. 13 should be the same. However, the value of shear rate at the yield point was always slightly smaller than the preset value. This difference ranged from 0.001/s at low shear rates to 0.005/s at high shear rates. Therefore, a weighted average value of $\dot{\gamma}_b$ was calculated. By analyzing values of stress instead of energy, one can avoid altogether the errors due to the aforementioned discrepancies in shear rates. The calculated values of E_0 and E_b for the 5 dispersions followed power law relationships with shear rate ($R^2 \ge 0.997$):

$$E_0 = a\dot{\gamma}^c \tag{14}$$

$$E_{h} = g \dot{\gamma}^{j} \tag{15}$$

where, *a*, *c*, *g*, and *j* are constants, whose values were determined for each product (Table 2). Combining Eq. 12 and 13 with Eq. 14 and 15, expressions for the shear rate dependency of σ_0 and σ_b were obtained:

$$\sigma_0 = a\dot{\gamma}^{c-1} \tag{16}$$

$$\sigma_b = g \dot{\gamma}^{j-1} \tag{17}$$

Flow curves of mayonnaise, ketchup, mustard, applesauce, and tomato puree TD showed typical shear thinning with yield stress (plastic) behavior combined with thixotropy, as previously reported (Tiu and Boger 1974; Barbosa Cánovas and Peleg 1983). Here, for illustration, the data on mayonnaise and tomato puree TD are shown in Figure 3. To estimate the contribution of the viscous drag (σ_v) using Eq. 8, the viscosity at infinite shear rate (η_{∞}) was needed; it was determined by fitting the shear stress-shear rate data of each product with the Casson model (Eq. 2, Table 3). Because the Casson yield stress (σ_{0-C}) was determined from the down curve of the cycle after extensive shearing and structure breakdown of the sample, its values were comparable to those of the dynamic yield stress (Table 1); they were either slightly lower (MT, MF, and AM) or slightly higher (KH and TD) than σ_{0d} .

Contribution of the network breakdown (σ_n) was calculated by difference using Eq. 5, in combination with Eq. 8, 16, and 17:

$$\sigma_n(\dot{\gamma}) = a\dot{\gamma}^{c-1} - g\dot{\gamma}^{j-1} - \eta_\infty \dot{\gamma}$$
(18)

Figure 4 and 5 show experimental values of σ_0 and σ_b , values



Figure 2-Time-torque/vane parameter (T/K) curves at different shear rates and 25 °C for the undisrupted (filled symbols) and disrupted (open symbols) of Tomato Puree TD. Symbols: \bullet , \blacksquare , \blacklozenge , \blacktriangle , and \blacktriangle denote shear rates: 0.01/s, 0.03/s, 0.05/s, 0.10/s, 0.20/s, and 0.40/s-, respectively. Filled symbols = structure undisrupted; open symbols = structure disrupted.



Figure 3–Ascending (filled symbols) and descending (open symbols) flow curves of Mayonnaise (MT) and Tomato Puree (TD) at 25 $^\circ\text{C}$

| | | Shear rate (/s) | | | | | | | |
|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--|--|
| Sample | 0.01 | 0.03 | 0.05 | 0.07 | 0.10 | 0.20 | 0.40 | | |
| MT θ _s | 0.42 ± 0.03 | 0.41 ± 0.03 | 0.44 ± 0.05 | 0.42 ± 0.03 | 0.47 ± 0.04 | _ | _ | | |
| σ_{0} | 164 ± 13 | 187 ± 26 | 214 ± 24 | 235 ± 40 | 253 ± 9 | _ | | | |
| θ_d | 0.32 ± 0.12 | 0.22 ± 0.03 | 0.21 ± 0.05 | 0.26 ± 0.09 | 0.21 ± 0.04 | — | — | | |
| σ_{0c} | , 58.1 ± 9.9 | 58.9 ± 7.8 | 66.6 ± 4.0 | 72.9 ± 11.7 | 72.3 ± 3.1 | — | — | | |
| KH θ _s | 0.26 ± 0.02 | 0.27 ± 0.02 | 0.32 ± 0.00 | — | 0.32 ± 0.00 | 0.37 ± 0.00 | 0.51 ± 0.01 | | |
| σ_{0s} | 49.9 ± 2.2 | 51.3 ± 4.6 | 56.3 ± 5.7 | — | 60.9 ± 0.8 | 62.6 ± 2.3 | 70.5 ± 6.4 | | |
| θ_d | 0.27 ± 0.03 | 0.28 ± 0.05 | 0.28 ± 0.02 | — | 0.40 ± 0.10 | 0.51 ± 0.13 | 0.75 ± 0.00 | | |
| σ_{0c} | , 23.1 ± 1.4 | 25.7 ± 0.3 | 25.9 ± 0.9 | — | 28.6 ± 0.9 | 29.9 ± 0.9 | 32.4 ± 0.1 | | |
| MF θ | 0.39 ± 0.11 | 0.36 ± 0.07 | 0.29 ± 0.02 | — | 0.32 ± 0.00 | 0.38 ± 0.00 | 0.48 ± 0.03 | | |
| σ_{0} | 50.5 ± 3.0 | 54.8 ± 5.9 | 55.3 ± 6.0 | _ | 60.6 ± 5.9 | 66.1 ± 0.9 | 72.3 ± 2.0 | | |
| θ_{d} | 0.37 ± 0.03 | 0.37 ± 0.05 | 0.37 ± 0.04 | _ | 0.36 ± 0.04 | 0.37 ± 0.02 | 0.49 ± 0.02 | | |
| σ_{0c} | 22.6 ± 0.8 | 23.5 ± 2.2 | 23.3 ± 1.1 | _ | 23.5 ± 1.6 | 25.2 ± 0.4 | 27.5 ± 1.5 | | |
| AM θ | 0.88 ± 0.02 | 0.76 ± 0.03 | 0.65 ± 0.07 | _ | 0.59 ± 0.03 | 0.58 ± 0.07 | 0.69 ± 0.15 | | |
| σ_{0} | 61.9 ± 7.0 | 64.2 ± 9.1 | 64.3 ± 7.2 | _ | 66.8 ± 11.5 | 69.0 ± 12.6 | 72.5 ± 8.3 | | |
| θ_{d} | 0.52 ± 0.03 | 0.54 ± 0.05 | 0.52 ± 0.08 | _ | 0.50 ± 0.11 | 0.55 ± 0.07 | 0.66 ± 0.13 | | |
| σ_{0c} | 48.8 ± 6.0 | 49.2 ± 7.3 | 47.0 ± 5.9 | _ | 50.5 ± 10.3 | 49.2 ± 7.1 | 51.7 ± 7.1 | | |
| TD θ | 0.61 ± 0.12 | 0.45 ± 0.01 | 0.45 ± 0.03 | _ | 0.43 ± 0.04 | 0.52 ± 0.01 | 0.75 ± 0.02 | | |
| σ_{0} | 25.2 ± 0.5 | 26.0 ± 0.8 | 26.9 ± 0.6 | _ | 28.5 ± 2.1 | 30.9 ± 1.9 | 30.8 ± 1.4 | | |
| θ_{d} | 0.47 ± 0.06 | 0.38 ± 0.09 | 0.39 ± 0.00 | _ | 0.43 ± 0.08 | 0.42 ± 0.07 | 0.75 ± 0.02 | | |
| σ_{00} | 20.6 ± 0.5 | 20.8 ± 0.6 | 22.1 ± 0.7 | | 23.6 ± 1.1 | 24.4 ± 1.9 | 24.5 ± 1.8 | | |

Table 1-Static and dynamic yield stress (σ_{os} and σ_{od}) and angular deformation (θ_s and θ_d) at different shear rates of the vane and 25 °C, for Mayonnaise MT, Ketchup KH, Mustard MF, Applesauce AM, and Tomato Puree TD

Table 2—Power law model (Eq. 14 and 15) parameters for total, $E_o \dot{\gamma}$, and bonding, $E_b \dot{\gamma}$, energy data on Mayonnaise (MT), Ketchup (KH), Mustard (MF), Applesauce (AM), and Tomato Puree (TD)

| | <i>E₀</i> [W/m ³] | | | E | <i>E_b</i> [W/m³] | | | |
|--------|--|------|----------------|------|-----------------------------|----------------|--|--|
| Sample | а | с | R ² | g | j | R ² | | |
| MT | 376 | 1.18 | 1.000 | 290 | 1.22 | 0.999 | | |
| KH | 74.7 | 1.09 | 0.999 | 39.9 | 1.10 | 0.998 | | |
| MF | 76.9 | 1.10 | 1.000 | 50.0 | 1.13 | 1.000 | | |
| AM | 74.1 | 1.04 | 1.000 | 23.4 | 1.12 | 0.999 | | |
| TD | 32.9 | 1.06 | 1.000 | 6.77 | 1.09 | 0.997 | | |

| Table 3-Casson model (Eq. | 2) parameters | for down flow |
|----------------------------|---------------|---------------|
| curves of Mayonnaise (MT), | Ketchup (KH), | Mustard (MF), |
| Applesauce (AM), and Toma | to Puree (TD) | |

| Sample | <i>σ</i> _{0-C} (Pa) | η_{∞} (Pa s) | R ² |
|--------|------------------------------|------------------------|----------------|
| МТ | 46.9 | 0.398 | 0.993 |
| KH | 33.0 | 0.157 | 0.979 |
| MF | 17.5 | 0.213 | 0.999 |
| AM | 33.7 | 0.342 | 0.990 |
| TD | 27.2 | 0.072 | 0.886 |
| | | | |

predicted by Eq. 16 and 17, as well as contributions of viscous and network stresses predicted by Eq. 8 and 18, for mayonnaise and tomato puree TD, respectively. Over the low shear rates used, it was found that $\sigma_v \approx 0$, and consequently $\sigma_n \approx \sigma_{0d}$. Interestingly, differences in the manufacturing processes were reflected in the values of σ_b and σ_n of the products. The products homogenized in a colloid mill: mayonnaise, ketchup, and mustard, showed $\sigma_b > \sigma_n$, whereas those that have been finished or pulped: applesauce and tomato puree, showed $\sigma_n > \sigma_b$. Because the magnitude of σ_n depends on the number and nature of the particles (Metz and others1979), it appears that disintegration of particles during homogenization decreases the contribution of the aggregate network, but increases that of interparticle bonding to the overall structure of the material.

The relative contribution of each structural component: bonding, network, and viscous stresses (denoted as: $\Im \sigma_b, \Im \sigma_n$, and $\Im \sigma_v$, respectively) to the total yield stress (Table 4) also reflected differences among products of the same group (viz homogenized or finished). For homogenized products, $\Im \sigma_b$ decreased in the order MT > MF > KH, whereas for finished products, $\Im \sigma_n$ decreased in the order TD > AM. For all the 5 products, $\Im \sigma_b$ and $\Im \sigma_v$ increased with shear rate (although $\Im \sigma_v$ values were negligible), whereas $\Im \sigma_n$ showed the opposite trend.

Equilibrium shear stress

Analogous to vane torque-time curves, stress-overshoot curves also exhibit an initial increase, a peak, and a decay whose asymptotic value is called equilibrium stress (σ_{∞}) (Elliot and Ganz 1977; Rao 1999). Truong and Daubert (2000) found that vane curves of tofu and gellan gels exhibited both σ_0 and σ_{∞} , and suggested that ($\sigma_0 - \sigma_{\infty}$) values were indicative of structure breakdown, possibly associated with the strength of internal bonds making up the body (cohesiveness and/or adhesiveness). The solid-like samples of Truong and Daubert (2000) reached σ_{∞} in a few seconds. However, in this work and our earlier study (Genovese and Rao 2003), the semisolid-like dispersions did not reach σ_{∞} even after several min; this is 1 reason that the value of σ_{0d} was proposed for calculation of σ_b (Eq. 7).

Values of σ_{∞} of the 5 dispersions were estimated by extrapolation of the torque-time curves to infinite time. The experimental data from the stress decay region of the undisrupted samples were well-described by the model of Peleg (1980) ($R^2 \ge 0.984$), Eq. 19 through 21:

$$Y(t) = [\sigma_0 - \sigma(t)]/\sigma_0 \tag{19}$$

$$t/Y(t) = k_1 + k_2 t$$
 (20)

$$\sigma_{\infty} = \sigma_0 \left(1 - 1/k_2 \right) \tag{21}$$

where, *t* is the time after the point of failure ($t_m = 0$), and k_1 and k_2 are constants that were determined for each product at each shear rate (values not shown). The reciprocal of k_1 represents the initial

decay rate, and the reciprocal of k_2 is the asymptotic limit of Y(t) when $t \rightarrow \infty$.

The effect of increasing shear rate on values of σ_{∞} depended on the product (Figure 6): an increase for mayonnaise, ketchup, and tomato puree TD; a decrease for mustard, and no significant variation for applesauce. Values of σ_{∞} and σ_{0d} were in good agreement for ketchup and, except for mayonnaise, were relatively close for the other products; for mayonnaise, values of σ_{∞} were higher than those of σ_{0d} . These discrepancies between σ_{∞} and σ_{0d} may be attributed to either that values of σ_{∞} obtained by extrapolation of data over 20 min are not truly representative of the equilibrium stresses of the material, or that they do not reflect identical product structures.

A shear-thickening dispersion

Unlike the other 5 food products studied, including the tomato puree TD and the 3 starch dispersions studied earlier (Genovese and Rao 2003), the tomato puree TR exhibited time-dependent shear-thickening (anti-thixotropic) behavior in the vane yield tests at 0.1/s, 0.2/s, and 0.4/s (Figure 7), and in the flow tests at shear rates <25/s (Figure 8). Generally, tomato puree has been considered to be a thixotropic material (Barrett and others 1998), as exhibited to a very slight degree by sample TD (Figure 3). However, Hayes and others (1998) noted that no conclusive measurements have been reported on thixotropic behavior of tomato concentrates.

Values of static and dynamic yield stress showed the expected increase with shear rate and, in addition, values of σ_{0d} were higher than of σ_{0s} (Figure 7). In other words, the yield stress of the sample increased after application of high shear in the flow test. These observations can not be attributed only to the anti-thixotropic behavior of TR because the cross-linked waxy maize starch dispersion studied by Genovese and Rao (2003) was also anti-thixotropic but did not show $\sigma_{0d} > \sigma_{0s}$.

The sample TR had higher content of dry solids: $12.5\% \pm 0.1\%$ and soluble solids: 14.6 ± 0.1 °Brix than sample TD: $9.6\% \pm 0.1\%$ and 10.3 ± 0.2 °Brix, respectively. Mewis and Vermant (2000) noted that at sufficiently high particle volume fractions and shear rates, shear thickening will happen in most suspensions. While we do not know



Figure 4—For mayonnaise MT: experimental values of static (\bullet) and bonding (static-dynamic) yield stress (\blacktriangle), and empirical fits with Eq. 16 and 17; contributions of viscous and network components calculated with Eq. 8 and 18, respectively.

| | | % Contribution to total yield stress | | | | | |
|-----------------------------|-------------|--------------------------------------|----------------|----------------|----------------|------------|------------|
| Shear rates Sample (1/s) | | Bon | ding | Netw | vork | Visc | ous |
| MT | 0.01 & 0.10 | 65.1 (0.01) | 70.9 | 34.9 (0.01) | 29.1 (0.10) | 0.0 | 0.0 |
| KH | 0.01 & 0.40 | 52.6 (0.01) | 53.2 (0.40) | 47.4 | 46.7 | 0.0 | 0.1 |
| MF | 0.01 & 0.40 | 55.5 (0.01) | 63.0 (0.40) | 44.5 | 36.9 | 0.0 | 0.1 |
| AM | 0.01 & 0.40 | 21.8 | 29.3 | 78.2 | 70.5 | 0.0 | 0.2 |
| TD | 0.01 & 0.40 | 18.2 (0.01) | 20.1 (0.40) | 81.8 (0.01) | 79.8 (0.40) | 0.0 (0.01) | 0.1 (0.40) |

^aThe applied shear rate (1/s) is shown in parentheses.

the reasons for the anomalous behavior of sample TR, it is of interest to establish the conditions required for Eq. 7 ($\sigma_b = \sigma_{0s} - \sigma_{0d}$) to be valid. To do that, Eq. 5 was applied to the same sample with undisrupted (Eq. 22) and disrupted (Eq. 23) structure:

$$\sigma_{0s} = \sigma_{bs} + \sigma_{vs} + \sigma_{ns} \tag{22}$$

$$\sigma_{0d} = \sigma_{bd} + \sigma_{vd} + \sigma_{nd} \tag{23}$$

where, the subscripts "*s*" and "*d*" stand for static and dynamic, respectively. The contribution of viscous drag in both equations is expected to be independent of the degree of structure of the sample, so that:

$$\sigma_{vs} = \sigma_{vd} \tag{24}$$

Subtracting Eq. 23 from Eq. 22 results in:

$$\sigma_{0s} - \sigma_{0d} = (\sigma_{bs} - \sigma_{bd}) + (\sigma_{ns} - \sigma_{nd}) \tag{25}$$



Figure 5-For Tomato Puree D: experimental values of static (\bullet) and bonding (static-dynamic) yield stress (\blacktriangle), and empirical fits with Eq. 16 and 17; contributions of viscous and network stresses calculated with Eq. 8 and 18, respectively.

In Eq. 7, σ_b is the bonding stress of the undisrupted sample, σ_{bs} :

$$\sigma_{0s} - \sigma_{0d} = \sigma_{bs} \tag{26}$$

Combining Eq. 25 and 26, the following expression is obtained:

$$\sigma_{bd} = \sigma_{ns} - \sigma_{nd} \tag{27}$$

The conditions required for Eq. 7 to be valid are in Eq. 24 and 27. Better insight can be obtained assuming that all the interparticle bonds are broken during the flow test, but the number and nature



Figure 6—Equilibrium stress of Mayonnaise (MT), Ketchup (KH), Mustard (MF), Applesauce (AM), and Tomato Puree D (TD) as a function of shear rate. Values of sample MT are on the right ordinate.



Figure 7 – Time-torque/vane parameter (T/K) curves at different shear rates and 25 °C for the undisrupted (filled symbols) and disrupted (open symbols) samples of Tomato Puree TR. Symbols: \bullet , \blacksquare , \blacklozenge , \blacktriangle , \lor , and \blacktriangle denote shear rates: 0.01/s, 0.03/s, 0.05/s, 0.10/s, 0.20/s, and 0.40/s, respectively. Filled symbols = structure undisrupted; open symbols = structure disrupted.

of the particles remain unaltered. Then the terms on both sides of Eq. 27 are approximately zero:

$$\sigma_{bd} \approx 0 \tag{28}$$

$$\sigma_{ns} \approx \sigma_{nd}$$
 (29)

It seems that the conditions in Eq. 28 and 29 were fulfilled by the 3 starch dispersions studied in Genovese and Rao (2003), and by the samples MT, KH, MF, AM, and TD analyzed in this work. However, it is obvious that for sample TR, Eq. 28 and/or 29 were not satisfied, and consequently Eq. 7 was not applicable. There is no easy method to determine whether interparticle bonds of tomato puree TR were destroyed or generated during shearing. On the other hand, the hydrocluster mechanism proposes that shear-thickening is a consequence of shear-induced self-organization of the particles into stress-bearing clusters (Maranzano and Wagner 2002). The selforganization is assumed to be due to the dominance of short-range hydrodynamic lubrication forces, whereby the flow generates transient packed clusters of particles separated from one another only by a thin aqueous layer. Thus, it is likely that the network stress component increased ($\sigma_{nd} > \sigma_{ns}$) due to such shear-induced clusters of particles.

Conclusions

The model developed by Genovese and Rao (2003) to determine the contribution of bonding, network, and viscous components to the yield stress, was applicable to mayonnaise, mustard, ketchup, applesauce, and 1 brand of tomato puree that exhibited shearthinning behavior. The model could not be applied to another brand of tomato puree, probably because of shear-induced self-organization of the particles into stress-bearing clusters. This observation led to establishing the conditions required for the model to be applicable. For the shear-thinning products, differences in manufacturing processing were reflected in the relative contribution of the structural components. Finally, the calculated equilibrium shear stress was slightly higher or lower than the dynamic



Figure 8–Flow behavior curves of Tomato Purees TR; ascending (filled symbols) and descending (open symbols) at 25 °C.

yield stress depending on the product, or even showed a different shear rate dependency.

Nomenclature

Important symbols are defined here; a few others are defined immediately after use.

- a, c, g, j Constants
- AM Applesauce
- E_b Energy dissipation rate to break the bonds, W/m³
- E_n Energy dissipation rate to break the aggregate network, W/ m^3
- E_T Total energy dissipation rate to produce deformation, W/
- m³
- E_v Energy dissipation rate due to purely viscous drag, W/m³ k Consistency coefficient, Pa sⁿ
- k_s Proportionality constant between rotational speed and shear rate
- KH Ketchup H
- MF Mustard F
- MT Mayonnaise T
- n Flow behavior index, dimensionless
- N Rotational speed, rpm
 - time, s

t

A

- TD Tomato puree D
- TR Tomato puree R
- T_m Maximum value of torque, N m

Greek Letters

- η_∞ Viscosity at infinite shear rate, Pa s
- $\dot{\gamma}$ Shear rate, per second
- σ_b Stress required to break the internal bonds, Pa
- σ_{0s} Static yield stress, Pa
- σ_{0d} Dynamic yield stress, Pa
- σ_0 Total yield stress, Pa
- σ_{0-HB} Herschel-Bulkley yield stress, Pa
- σ_{0-C} Casson yield stress, Pa
- σ_n Stress to break the aggregate network, Pa
- σ_v Stress due to purely viscous drag, Pa
 - Angular deformation, rad

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References

- Aguilar C, Rizvi SSH, Ramirez JF, Inda A. 1991. Rheological behavior of processed mustard. I: Effect of milling treatment. J Texture Stud 22:59–84.
- Barbosa-Cánovas GV, Peleg M. 1983. Flow parameters of selected commercial semi-liquid food products. J Texture Stud 14:213-34.
- Barrett DM, García E, Wayne JE. 1998. Textural modification of processing tomatoes. Crit Rev Food Sci Nutr 38:173–258.
- Dzuy NQ, Boger DV. 1983. Yield stress measurement for concentrated suspensions. J Rheol 27:321–49.
- Elliott JH, Ganz AJ. 1977. Salad dressings—preliminary rheological characterization. J Texture Stud 8:359–71
- Genovese DB, Rao MA. 2003. Vane yield stress of starch dispersions. J Food Sci 68:2295-301.
- Hayes WA, Smith PG, Morris EJ. 1998. The production and quality of tomato concentrates. Crit Rev Food Sci Nutr 38:537–64.
- Ma L, Barbosa-Cánovas GV. 1995. Rheological characterization of mayonnaise. Part II: Flow and viscoelastic properties at different oil and xanthan gum concentrations. J Food Eng 25:409–25.
- Maranzano BJ, Wagner NJ. 2002. Flow-small angle neutron scattering measurements of colloidal dispersion microstructure evolution through the shear-thickening transition. J. Chem Phys 117:10291–302.
- Metz B, Kossen NWF, van Suijdam JC. 1979. The rheology of mould suspensions. In: Ghose TK, Fiechter A, Blakebrough N, editors. Advances in biochemical engineering. Vol. 2. New York: Springer Verlag. p 103–56.
- Mewis J, Vermant J. 2000. Rheology of sterically stabilized dispersions and lattices. Prog Organic Coatings 40:111–7.
- Michaels AŠ, Bolger JC. 1962. The plastic flow behavior of flocculated kaolin suspensions. Ind Eng Chem Fund 1:153-62.
- Peleg M. 1980. Linearization of relaxation and creep curves of solid biological materials. J Rheol 24:451-63
- Qiu C-G, Rao MA. 1988. Role of pulp content and particle size in yield stress of apple sauce. J Food Sci 53:1165–70.
- Rao MA. 1992. Measurement of viscoelastic properties of fluid and semisolid foods. In: Rao MA, Steffe JF, editors. Viscoelastic properties of foods. London: Elsevier Applied Science. p 207–31 Rao MA. 1999. Rheology of fluid and semisolid foods: principles and applica-
- Rao MA. 1999. Rheology of fluid and semisolid foods: principles and applications. Gaithersburg, Md.: Aspen Publishers. 433 p.Rao MA, Cooley HJ. 1984. Determination of effective shear rates in rotational
- Rao MA, Cooley HJ. 1984. Determination of effective shear rates in rotational viscometers with complex geometries. J Texture Stud 15:327–35.
- Tiu C, Boger DV. 1974. Complete rheological characterization of time-dependent food products. J Texture Stud 5:329–38
- Truong VD, Daubert CR. 2000. Comparative study of large strain methods for assessing failure characteristics of selected food gels. J Texture Stud 31:335–53. Wiley RC, Binkley CR. 1989. Applesauce and other canned apple products. In:
- Wiley RC, Binkley CR. 1989. Applesauce and other canned apple products. In: Downing DL, editor. Processed apple products. New York: Van Nostrand Reinhold. p 215–38.
- Zhou Z, Solomon MJ, Scales PJ, Boger DV. 1999. The yield stress of concentrated flocculated suspensions of size distributed particles. J Rheol 43:651–71.