

RHEOLOGY OF FOOD DISPERSIONS

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ABSTRACT

We review the viscous and viscoelastic behaviours of concentrated food emulsions and plant food suspensions. Special attention has been given to the influence that food processing exerts on the rheological characteristics of the above-mentioned foodstuffs.

KEYWORDS: Viscosity; Viscoelasticity; Food; Dispersions; Processing.

1. INTRODUCTION

Traditionally, foods have been classified as hard solids, soft solids and liquids. Some examples of these general physical categories are shown in Table 1.

GENERAL CATEGORY	FOOD EXAMPLES
Hard solids	Chocolate, biscuits, hard cheese
Soft solids	Butter, ice-cream, tomato paste
Liquids	Water, honey, ketchup, mayonnaise

Table 1. General categories of foods

Many foods of commercial importance, such as baby foods, mayonnaise, salad dressings and plant food concentrates (orange, tomato, apple, etc) are concentrated dispersions of solid (suspensions) or fluid (emulsions) matter in fluid media, which may behave as soft solids or highly non-Newtonian liquids.

Rheology plays an important role in food manufacture and marketing [1], i.e. design of handling systems, quality control and evaluation of sensory stimuli associated with oral and non-oral evaluation of viscosity [2]. Starting with processing, it is notorious that process variables determine the microstructure formed for a given formulation, and hence its rheology. Often, processing is itself affected by the rheology of the product, especially if it is very viscoelastic or very shear-thinning. When the final product is formed its rheology should be measured in a precise manner,

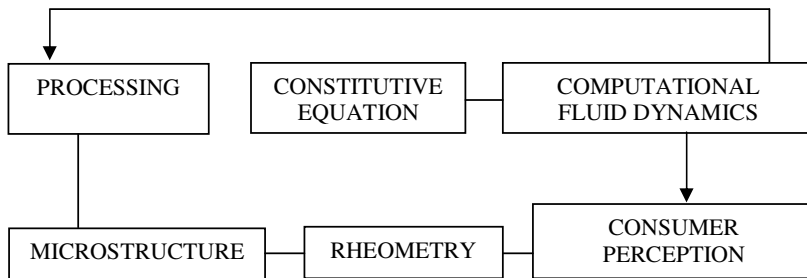


Figure 1. Important areas in the study of Food Rheology (reproduced from [1]).

accounting for any wall effects and selecting, for instance, the appropriate range of deformation rate for the particular application.

A suitable constitutive equation should be selected, then, to fit the rheometry results. This step is still quite challenging for semisolids food products, taking into account their dramatic shear-thinning response and the probable appearance of instabilities in a significant range of shear rates [3]. This suitable constitutive equation can be used to calculate flows in other geometries, i.e. process equipments, using Computational Fluids Dynamics. Finally, the measured product rheology should also be compared with the subjective consumer perception.

The aim of this paper is to review the state-of-the-art of the rheology of selected semisolid foodstuffs (concentrated emulsions and suspensions), mainly focused on their linear and non-linear viscoelastic characteristics.

2. RHEOLOGY OF FOOD EMULSIONS

An emulsion may be defined as a thermodynamically unstable heterogeneous system formed by at least two liquids, that are at best only slightly soluble, in which the internal phase is dispersed in the other in the form of small droplets, with diameters higher than $0.1 \mu\text{m}$ [4, 5]. Food emulsions are governed by the same principles than other emulsion systems. The only specific requirements for these emulsions are that they must possess long-term stability (several months or years) and they must contain only ingredients that are acceptable for human consumption [6]. A great number of food products are presented in the form of oil-in-water (o/w) emulsions, e.g. mayonnaise, salad dressing, coffee cream, cream liqueurs, soft drinks, ice creams, etc, or water-in-oil (w/o) emulsions, such as butter, margarine or spreads [7]. In some cases, it is possible to find multiple food emulsions, for instance water-in-

oil-in-water (w/o/w), which usually are presented as reduced-calorie products since this particular microstructure yields a drastic reduction of fat and energy content [8].

From a technological point of view, the rheology of food emulsions is fundamental mainly due to its relationship with emulsion stability, the most important factor to be considered in emulsion technology. Thus, a large number of structural parameters that influence emulsion stability also affect rheology, a fact that makes difficult a systematic understanding of the complex rheological response of concentrated emulsions. In general, emulsion stability depends on droplet size distribution, rheology of the continuous phase and inter-particle interactions [9], and all of them affect the bulk rheology of the emulsion. In addition to this, all of them are decisively influenced by processing conditions [10], such as energy input during emulsification, residence time, application of thermal treatments, mixing efficiency, etc.

During the last decade, a wide range of topics, related to emulsion rheology, have been studied. Among them it can be mentioned viscosity and viscoelasticity modelling, influence of composition, processing, thermal and high-pressure treatments and its relation to stability and microstructure. The research developed on these topics will be reviewed below.

2.1 Viscosity and viscoelasticity modelling.

Traditionally, most predictions of viscosity have been developed as a function of the disperse phase volume fraction, ϕ . For dilute, monodisperse emulsions, steady shear viscosity can be reasonably described by simulations of hard spheres (HS) dispersions at small capillary numbers, when the droplets are not greatly deformed [11]. However, as inter-droplet interactions depend on droplet size distribution, an increasing polydispersity yields high deviations from monodisperse HS predictions. Yaron and Gal-Or [12] and Choi and Schowalter [13] applied an equation that takes into account inter-droplet interactions derived from a cell model approach. More recently, Pal [14] showed that those models fail to describe emulsions containing milk fat. A modified form of the Phan-Thien and Pham [15] equation for relatively concentrated emulsions was satisfactorily applied to describe the viscosity of these food emulsions (sets 8A-8D in figure 2):

$$\eta_r \left(\frac{2\eta_r + 5K}{2 + 5K} \right)^{3/2} = (1 - K_o\phi)^{-5/2}, \quad \dots\dots\dots(1)$$

η_r being the relative viscosity and K the viscosity ratio (ratio of the dispersed-phase viscosity to continuous-phase viscosity). In this model, it is assumed that emulsion is unflocculated and the effective volume, V_{eff} , of a single droplet is proportional to the true volume of a single droplet in a factor, which takes into account the presence of the surfactant on the interface ($V_{eff} = K_oV_o$). The influence of the interfacial viscosity and surface and bulk diffusion of surfactant was discussed in some detail by Danov [16]. However, most of food emulsions are usually highly concentrated, showing a marked non-Newtonian behaviour. This behaviour has been related to droplet deformation, flocculation or the non-Newtonian behaviour of the dispersed phase [17, 18].

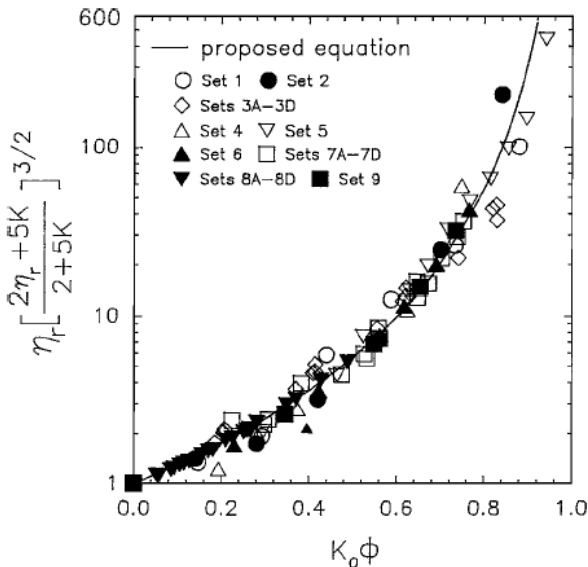


Figure 2. Comparison between experimental data and Pal’s equation (reproduced from reference [14]).

The general evolution of viscosity with shear rate (or shear stress) shows three different regions, a constant viscosity, η_o , at low shear rates (or shear stress), a power-law decrease in viscosity, and finally a constant viscosity, η_∞ , at high shear rates, characteristic of an unflocculated system. As Barnes [19] pointed out, each region of shear rate (or shear stress) is associated to different applications (physical stability, levelling, pouring, rubbing...) and also to important unit operations related to the manufacture of an emulsion such as mixing [20] or pumping [21]. Wilkinson, Cross, or Carreau models have been widely used to describe this behaviour [10, 18, 22, 23].

As shown in figure 3, the combined influence of both shear rate and disperse fraction (also emulsifier concentration) on viscosity was modelled by applying a superposition method which leads to a master flow curve in which the shift factor affecting shear rate is a function of the oil weight fraction [24]. This master flow curve may be fitted to any of the above-mentioned models, by including the influence of ϕ in the different parameters.

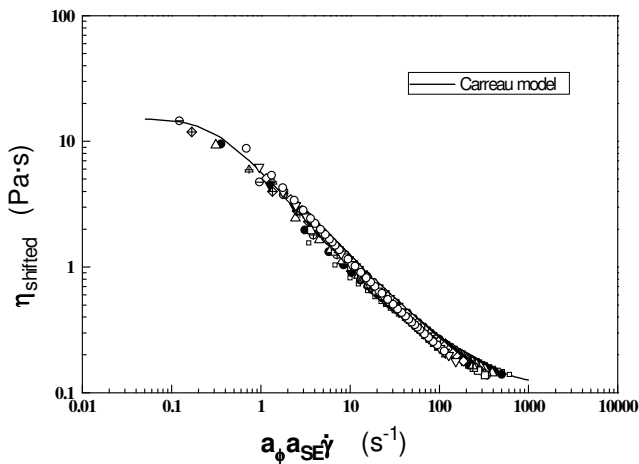


Figure 3. Master flow curve for emulsions containing 1-10% wt. sucrose ester and 55-85% wt. oil (reproduced from reference [24]).

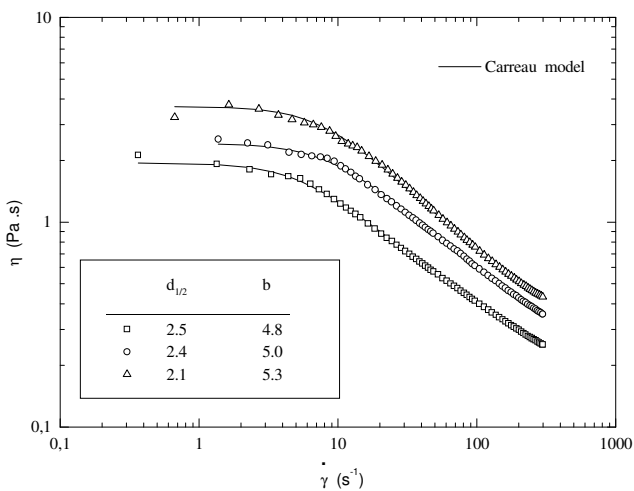


Figure 4. Viscous flow curves obtained from salad dressing-type emulsions with identical composition but manufactured using different processing conditions (adapted from reference [10]).

However, if the influence of ϕ on emulsion viscosity is considered, it is also necessary to take into account the effect of droplet size distribution, DSD. Thus, for instance, figure 4 shows three different flow curves obtained from salad dressing-type emulsions with identical composition but different mean droplet size and polydispersity, achieved by modifying processing variables. In this figure, $d_{1/2}$ is the median of DSD and b is a parameter that changes inversely to the polydispersity. As can be seen, the lower mean droplet size and polydispersity, the higher viscosity is. This is usually attributed to the fact that narrower droplet size distribution and lower mean diameter yield stronger inter-particle interactions. On the other hand, Partal et al. [24] have found a linear correlation between some rheological parameters (high-shear-rate-limiting viscosity and flow index) and polydispersity.

Traditionally, the linear viscoelastic response of food emulsions was studied through creep and recovery experiments [25-27]. Thus, for instance, Gladwell et al., [28] proposed a Kelvin-Voigt model with two characteristics retardation times to describe the creep compliance of mayonnaise-type emulsions. However, the use of small-amplitude, oscillatory shear (SAOS) experiments has been focusing special interest. The mechanical spectrum may vary from the typical liquid-like behaviour for unflocculated or weakly flocculated emulsions, either with $G'' > G'$ in a wide range of frequencies or showing a crossover between both dynamic functions, to the classical gel-like behaviour for highly flocculated emulsions [19]. The frequency dependence is mainly affected by inter-droplet interactions, disperse volume fraction and continuous medium. Thus, for instance, as shown in figure 5, G' and G'' curves intersect for salad dressing-type emulsions stabilized with 1% wt guar gum but show a well developed plateau region when the thickener consists of 0.5% wt guar gum and 0.5% wt xanthan gum [23]. If some of the structural parameters previously mentioned (i.e. disperse volume fraction, viscosity of the continuous phase or emulsifier concentration) do not affect qualitatively the mechanical spectrum, normalized dynamic functions can be obtained by using the plateau modulus as normalization factor [29, 30].

In most cases, the linear viscoelastic behaviour can be phenomenologically described according to the Maxwell generalized model [23, 31]. However, the Oldroyd [32] and Palierne [33] models have been also applied on food emulsions [34, 35] if the disperse phase volume fraction, the mechanical spectrum of each phase and the equilibrium interfacial tension between phases are known. More recently, Pal [36] has developed a set of equations for describing the shear modulus of concentrated emulsions of two immiscible elastic liquids using a differential scheme. The models were tested with food emulsions containing polysaccharides as thickening agents, considering the continuous media as purely elastic liquids. However, as the same author pointed out [37], the equations developed in this work could be also used to describe the linear viscoelastic behaviour of emulsions subjected to sinusoidal stress or strain, being the shear modulus now a complex quantity.

On the other hand, the linear relaxation spectrum, $H(\lambda)$, has been occasionally used to model the linear viscoelastic response of food emulsions. As well known, the loss, G'' , and storage, G' , moduli and the linear relaxation modulus, $G(t)$, are related to the linear relaxation spectrum by means of the following equations:

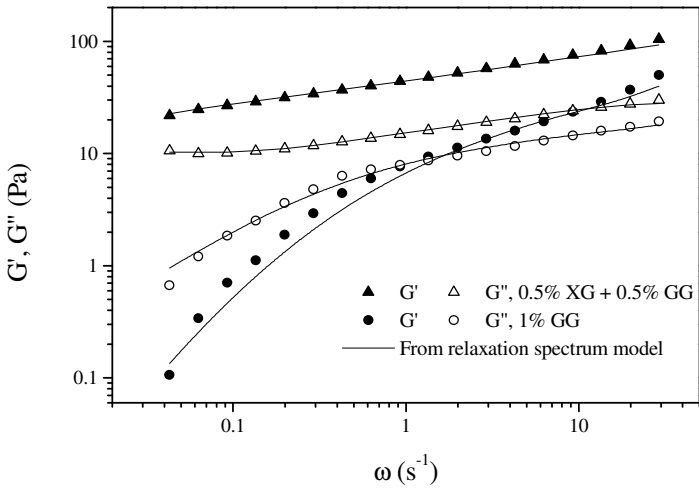


Figure 5. Storage (G') and loss (G'') moduli as a function of frequency (ω) for 40 % w/w oil-in-water emulsions stabilized with 1% Tween 60 and different thickeners (reproduced from reference [23]).

$$G'(\omega) = G_e + \int_{-\infty}^{\infty} H(\lambda) \frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} d(\ln \lambda) \quad \dots\dots\dots(2)$$

$$G''(\omega) = \int_{-\infty}^{\infty} H(\lambda) \frac{\omega \lambda}{1 + \omega^2 \lambda^2} d(\ln \lambda) \quad \dots\dots\dots(3)$$

$$G(t-t') = G_e + \int_{-\infty}^{\infty} H(\lambda) \exp\left[-(t-t')/\lambda\right] d(\ln \lambda) \quad \dots\dots\dots(4)$$

The calculation of the linear relaxation spectrum, $H(\lambda)$, implies inverting any of the Fredholm integral equations which relate it to the values of a given linear viscoelasticity function. Such inversion is an ‘ill-posed’ problem, as small changes in the rheological functions give rise to strong oscillations in the spectra [38-40], so that unstable and even solutions without physical sense may be obtained. For that reason, approximation methods [39] have been applied to perform such calculations by simplifying the original problem [10, 29]. On the other hand, the Tikhonov regularization method has been proposed as a powerful tool for solving the difficulties that arise with

Fredholm equations, [41-43], which has also been applied to calculate the linear relaxation spectrum of food emulsions [44, 45].

Franco et al. [10, 29] have used an empirical model, adapted from the one given by de Rosa and Winter [46] for polymer melts, to successfully describe the three experimental regions that appear in the linear relaxation spectra of these emulsions:

$$H(\lambda) = A \left[\left(\frac{\lambda}{\lambda_c} \right)^m + \left(\frac{\lambda}{\lambda_p} \right)^n \right] \quad \text{for } \lambda_{min} < \lambda < \lambda_p ,$$

$$H(\lambda) = A \left(\frac{\lambda}{\lambda_p} \right)^c \quad \text{for } \lambda_p < \lambda < \lambda_{max} , \quad \dots\dots\dots(5)$$

where λ_c and λ_p are the characteristic relaxation times for the onset of the plateau and terminal regions, respectively, λ_{max} and λ_{min} are the reciprocal of the minimum and maximum experimental frequencies attained, m , n and c are the power-law exponents for the three different regions, and A is an empirical constant.

Madiedo and Gallegos [47] have proposed a different empirical model that describes the three regions of the relaxation spectra of oil-in-water emulsions stabilized by a mixture of two sucrose esters with different HLB values:

$$H(\lambda) = \frac{\alpha\lambda^m + \beta\lambda^n}{1 + \left(\frac{\lambda}{\lambda_p} \right)^p} \quad \dots\dots\dots (6)$$

In this model, m , n and p are, respectively, the slopes of the transition, plateau and pseudo-terminal regions, λ_p is the pseudo-terminal relaxation time, and the parameters α and β are given by the following relationships:

$$\alpha = \frac{H_o m}{(m-n)\lambda_o^m} , \quad \dots\dots\dots (7)$$

$$\beta = \frac{1}{\lambda_o^n} \frac{nH_o}{(n-m)} , \quad \dots\dots\dots (8)$$

where H_o is the minimum value of the relaxation spectrum, which appears between the transition and the plateau regions, and λ_o is the relaxation time that corresponds to this minimum. This model was successfully applied to emulsions in which a smooth transition between the plateau and terminal regions was obtained [30].

Continuous or discrete linear relaxation spectra have been used to model the non-linear viscoelastic response of food emulsions. Thus, the Wagner constitutive model [48], which involves the time-strain separability, has been used to predict the transient and steady flow of commercial and model mayonnaise and salad dressings (see figures 6 and 7) by introducing either the Maxwell generalized model [23, 49, 50] or the continuous relaxation spectrum [44, 45, 51]. Thus, for instance, the Wagner model in simple shear gives for the transient viscosity:

$$\eta(t, \dot{\gamma}) = -\frac{1}{\dot{\gamma}} \int_{-\infty}^t \int_{-\infty}^{\infty} H(\lambda) \exp\left\{-\frac{(t-t')}{\lambda}\right\} h(\gamma) \gamma(t, t') d(\ln \lambda) dt' \quad \dots\dots\dots(9)$$

in which the most common forms of the damping function used were the Wagner and Soskey-Winter equations [48, 52].

In addition to this, the parameter values of these damping functions have been correlated with protein concentration of salad dressing type-emulsions. An increase in protein content resulted in higher values of both Wagner’s damping factor (*k*) and Soskey-Winter’s parameter (*a*). In general, a marked strain softening was detected which confirms the experimental observation that emulsion viscoelasticity is delicate, as well as limited to smaller strain deformations than polymer systems [51].

2.2 Studies on wall slip.

The issue of wall slip requires special attention in relation to the understanding of the behaviour of disperse systems under shear conditions. At present, it is accepted that true slip at the wall does not occur during the flow of colloidal systems and, as Barnes [53] has pointed out, the term “wall depletion” is the most accurate way to

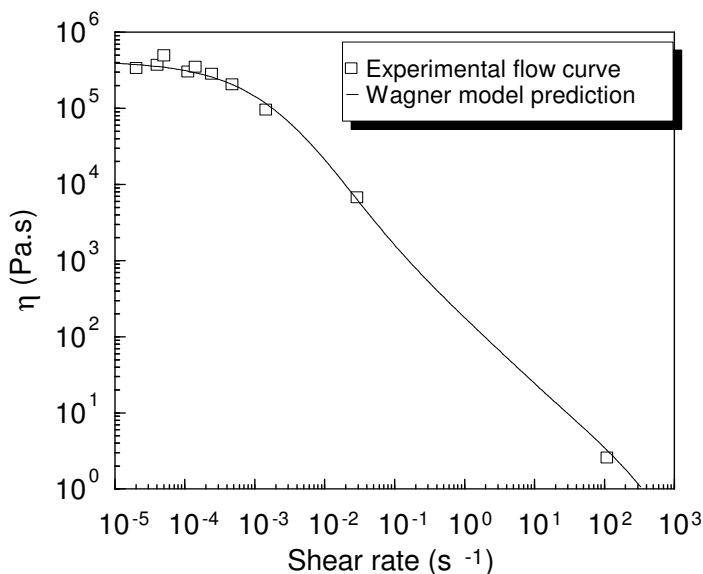


Figure 6. Prediction of steady viscous flow for an oil-in-water emulsion containing 65% oil and 3% lupin protein (reproduced from reference [51]).

describe this phenomenon in which the non-slip boundary conditions are not violated. Emulsions often show these effects due to the displacement of the dispersed phase away from solid boundaries, as for instance the walls of the sensor systems in a rheometer or the walls of pipes or tubes, giving a depleted layer of liquid, which then acts as a lubricant. This leads to an apparent decrease in the measured bulk viscosity. In the case of emulsions, the deformability of the droplets and creaming enhance this effect. As has been detected in several food emulsions [53-55] wall slip phenomenon is generally confined in a certain range of shear rates associated to constant values of shear stress or, in other words, around a critical stress at which a sudden drop in viscosity takes place. The use of roughened plates or the vane geometry has been proposed as effective techniques for eliminating slip effects in emulsions [53, 55, 56]. However, in complex systems, such as food emulsions, this phenomenon is until now not fully understood from a micro-structural point of view. Franco et al. [55] demonstrated that wall slip effects are strongly dependent on the composition and type of emulsion. Thus, for instance, a highly structured gel-like continuous phase dampens these effects, in contrast to oil-in-water emulsions with relatively low disperse phase volume fraction, in which creaming appears as a mechanism of instability. Sánchez et al. [57] proposed an empirical method to quantify the extension of wall slip as a function of several structural parameters such as disperse phase fraction, emulsifier concentration and droplet size (influenced also by processing), according to the differences found in the flow curves obtained with both serrated and smooth geometries along the experimental range of shear rate or shear stress studied. More recently, Bertola et al. [3] have related the slip phenomena to the yielding behaviour and flow instabilities of emulsions. In addition to this, they demonstrated that slip does not occur when using rough surfaces by withdrawing the calculated shear rate due to slip from the data obtained with smooth surfaces. Then, flow curves almost exactly correspond to those obtained using rough surfaces.

Although wall slip under the flow of food emulsions is a generally accepted phenomenon, some controversy appears in relation to the evidence of apparent wall slip in SAOS experiments. Ma and Barbosa-Cánovas [58] and Plucinski et al. [54] support the idea that no evidence of apparent wall slip in oscillatory shear is found for mayonnaises. On the contrary, Goshawk et al. [59], which performed several tests with different plate-plate separations, found that the values of the linear viscoelastic functions, at a given frequency, decrease as the plate-plate separation decreases, indicating that mayonnaise tested exhibits wall slip under SAOS, fact that is even surprising for the authors. Pal [56] also detected that the oscillatory response of emulsions is strongly influenced by slip effects not only quantitatively but also from a qualitative point of view since, in some cases, a solid like behaviour was found using the serrated plate geometry whereas a fluid-like response was obtained with smooth cone-plate geometries for the same emulsion. In addition to this, the linear viscoelastic range was clearly influenced by wall slip.

2.3 Effect of composition.

One of the main goals of emulsion technology is to find new alternatives for improving the stability and the physical properties. This research is usually centred on new surface-active agent suitable for replacing traditional egg and milk derivatives as

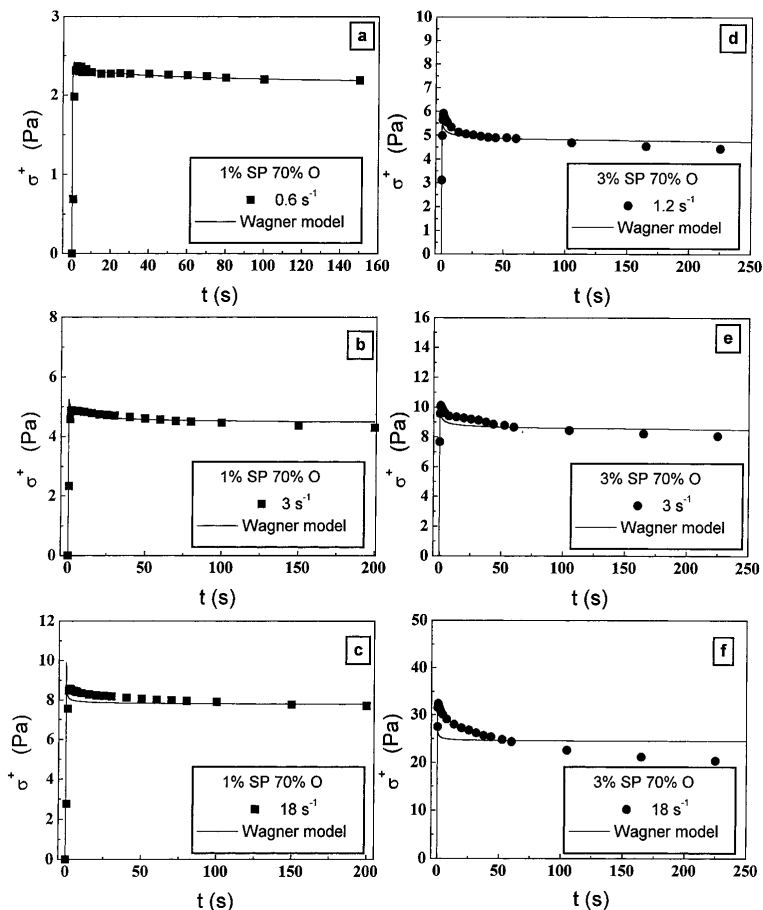


Figure 7. Predictions of transient shear stress for selected sucrose palmitate-stabilized emulsions (reproduced from reference [45])

emulsifier. Since the strength and nature of the interactions among droplets depend on the type and concentration of the emulsifiers used, emulsion stability and, consequently, the bulk rheology are also influenced [60]. Further stabilization may arise from the presence of low concentrations of water-soluble polysaccharides, hydrocolloids, which act as thickening or structuring agents in the continuous phase [61]. The main function of these hydrocolloids is to reduce the mobility of oil droplets, decreasing the extension of both flocculation and creaming processes.

Hen egg yolk is known as a reference ingredient in many food emulsions, such as mayonnaises or salad dressings, because it imparts desirable flavour, mouth-feel and colour. However, a problem associated with egg yolk is its high cholesterol content, which has been associated with a causative agent for heart disease. The use of organic solvents has been proposed as an effective way of removing cholesterol from egg yolk. Paraskevopoulou and Kiosseoglou [62] observed that extraction of yolk with petroleum ether resulted in a yolk-protein concentrate with emulsifying properties comparable to those of native egg yolk. In general, organic solvents, [63-65] remove all the lipids, including cholesterol, as well as the phospholipids responsible for the functional properties. On the other hand, a treatment with sub-critical or supercritical CO₂ offers a more attractive way of selectively extracting cholesterol from egg [66]. In general, these authors concluded that viscoelasticity of low-cholesterol egg yolk-stabilized emulsions is comparable to that of high cholesterol commercial mayonnaises and higher than that shown by the control spray-dried yolk [63, 65]. A more systematic study was developed by Moros et al., [67] in which the influence of different levels of cholesterol removing on the resulting egg yolk-stabilized emulsion was quantified. It was observed that the viscosity and the linear viscoelastic functions of low-cholesterol egg yolk-stabilized emulsions significantly decrease with egg-yolk cholesterol concentration for systems having a constant concentration of surface-active components. Thus, for instance, a reduction of more than 50% in the values of the plateau modulus was found for an emulsion stabilized by a highly cholesterol-reduced egg yolk (i.e. 81% wt cholesterol removed). Nevertheless, a different evolution was generally found in emulsions containing the same amount of cholesterol-reduced yolk. The generalised initial increase in viscoelastic parameters was explained by an increase in the concentration of surface-active components, as cholesterol and lipids were removed, but, in the same manner, a conformational alteration of lipoproteins induced by the cholesterol reduction seemed to affect emulsions predominantly using the maximum cholesterol-reduced egg yolk, especially at high oil content and low egg yolk concentrations (see figure 8).

Low-cholesterol products may be also achieved by replacing, total or partially, egg yolk by vegetable proteins. The influence of composition and processing conditions on the rheology of vegetable protein-stabilized emulsions have been widely studied by different authors [22, 68-70]. Most remarkable is the effect of pH [70]. An increase in the pH of the emulsion initially leads to an increase in emulsion viscosity and viscoelastic functions, as well as to a decrease in the mean droplet size, closely related to the lower diffusion rate of the protein to the oil-water interface due to a higher denaturation degree of the protein at low pH. At pH close to the protein isoelectric point, a singular rheological behaviour is found. Thus, high values of emulsion viscosity and viscoelastic parameters than those expected from its droplet size distribution were found, probably due to the formation of highly packed protein film at the interface which leads to a high surface viscoelasticity. The further slight decrease in the viscous and viscoelastic functions, at emulsion pH values above the isoelectric point, must be related to a decrease in interfacial viscoelasticity.

The evolution of viscosity and plateau modulus with pH are shown in figure 9.

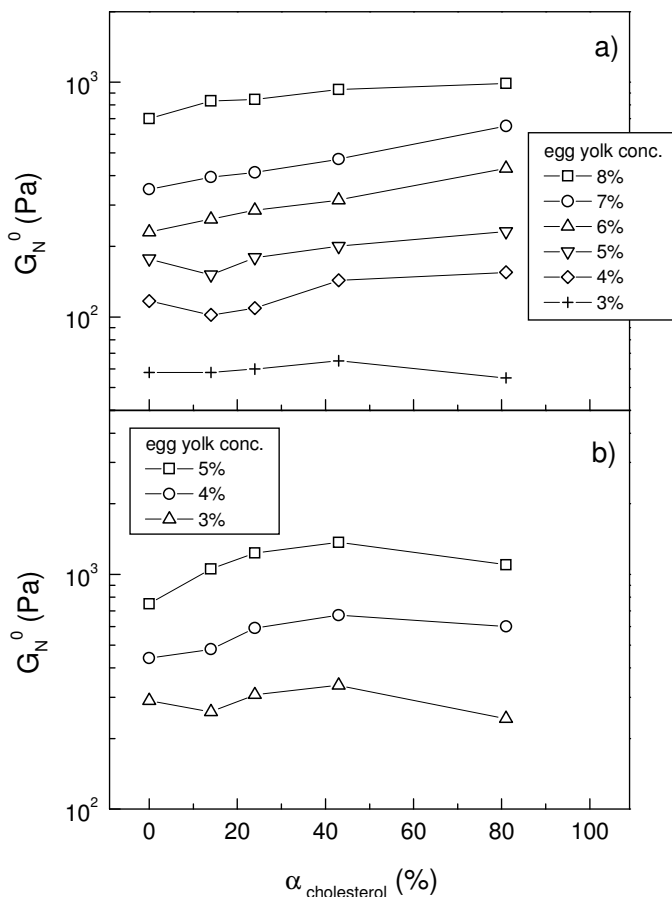


Figure 8. Influence of the level of cholesterol extraction on the plateau modulus for emulsions containing: (a) 70% wt oil, (b) 77.5% wt oil, and different cholesterol-reduced egg yolk concentrations.

Addition of a low-molecular-weight emulsifier may also yield an important stabilizing effect. Although, as a general rule, simple non-ionic surfactants displace proteins from the interface [71], some positive surfactant-protein interactions affecting not only emulsion or foam stability, but also rheology, have been reported [72-78]. Several physical mechanisms are responsible of the final emulsion characteristics mainly depending on the molar ratio of both kinds of emulsifiers. As Dickinson and

Hong [76] explained, at low surfactant concentrations, the surfactant is not available for disrupting the protein adsorbed layer or displacing protein from the interface, because is involved in complexation with the protein, yielding an increase in G' . This fact was explained on the basis of an enhancement of the local packing density in the adsorbed layer. However, increasing surfactant additions produce a dramatic decrease in G' . This linear viscoelasticity function may pass through a minimum and rise again, due to hydrophobic interactions, or show a continuous decay due to an irreversible loss of surface viscoelasticity, depending on the protein concentration. In addition to this, the phase behaviour of the surfactant/water systems must be taken into account. Thus, the formation of a liquid-crystalline, or a gel-like continuous phase, around oil droplets results in enhanced stability and considerably increased rheological parameters [77, 79]. Demetriades and McClements [80] indicated also the importance of pH in protein-surfactant interactions in emulsions stabilised by mixtures of sodium dodecyl sulfate (SDS) and whey proteins. Above the isoelectric point of the proteins, as expected, SDS binding enhances emulsions stability by increasing the electrostatic repulsion among droplets. However, below the isoelectric point an extensive flocculation occurs, which significantly increase the viscosity and decrease creaming stability.

On the other hand, the effect of using a mixture of different types of proteins in the properties of oil-in-water emulsions is open to discussion. Several authors showed that it might lead to a synergistic interaction, providing an improvement in the quality of the final product [74], whereas other authors showed that it might lead to some deterioration in performance, rather than an improvement. The origin of this

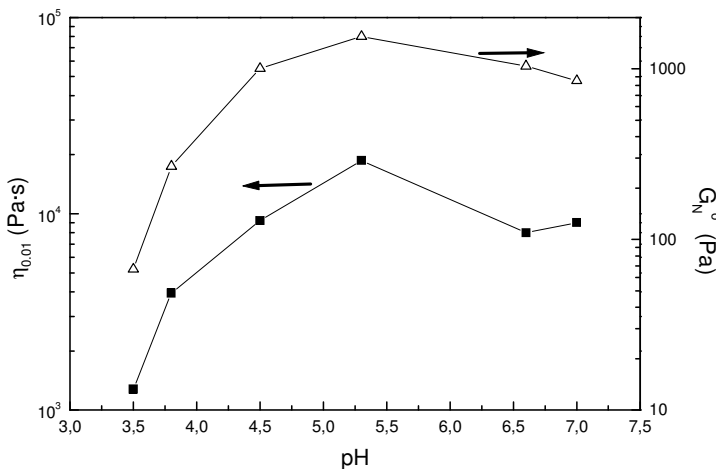


Figure 9. Evolution of the steady-state viscosity at 0.01 s^{-1} and the plateau modulus with emulsion pH for pea protein-stabilized emulsions (reproduced from reference [70]).

deterioration may be a more disarranged organisation of both kinds of protein at the interface [81-83], the manifestation of either thermodynamic incompatibility between them [84] or competitive adsorption of these protein molecules at the interface [85, 86]. Systematic rheological studies carried out in this sense indicates that partial replacement of egg yolk by milk or vegetable proteins as emulsifiers confers to the emulsions lower values of viscosity and viscoelastic functions than those obtained when egg yolk was the only emulsifier [86, 87]. However, at sufficiently high weight ratios of pea protein/egg yolk the tendency was inverted, increasing the viscoelastic functions as pea protein concentration increases.

Ionic strength also influences the stability and bulk rheology of food emulsions (specially protein-stabilised), since it modifies the structure of the electrical double layer surrounding the droplets. Thus, for instance, the apparent viscosity and the shear-thinning character increase with CaCl_2 concentration, indicative of droplet flocculation; although this phenomenon is reduced by lowering pH [88]. The addition of salt, in a SDS-stabilized emulsion enhances the shear-thinning behaviour but adding small amounts of sodium caseinate bring about a gradual lowering of the low-stress apparent viscosity. Further increases in caseinate content lead to a quasi-Newtonian behaviour. This fact was explained on the basis of a sequence of reversible flocculation, non-reversible flocculation and, finally, breaking up of flocs structures as caseinate content increases [89]. On the other hand, small amounts of ionic calcium initially decreases the viscosity of caseinate-stabilised emulsions, but starting from a critical calcium/caseinate molar ratio the viscosity increases, being much higher than the calcium-free emulsion and inhibiting depletion-flocculation. The addition of a non-ionic surfactant was found to have a synergistic effect but, in this case, a jump in the low-stress viscosity and the onset of substantial shear-thinning was attributed to emulsion destabilisation due to a surfactant-induced depletion flocculation [90].

In principle, the inclusion of a thickener agent increases emulsion stability and viscosity. Usually, the higher polysaccharide concentration, the higher the values of viscosity [91, 92] and viscoelastic functions [69] are. However, a thermodynamic incompatibility may occur in some protein-stabilised emulsions with added polysaccharides [93]. In addition to this, the use of mixtures of polysaccharides may result in a synergistic rheological effect, for instance xanthan gum together with guar gum, or a negative effect, as for instance adding xanthan gum to potato starch [23]. Finally, the presence of non-thickener polysaccharides as sucrose or glucose, used as sweeteners, may also affect emulsion rheology. Dickinson and Merino [94] found that, at high concentrations, the presence sugar leads to larger emulsion droplets, reduces the gelation time and increases the elastic modulus in caseinate-stabilised emulsions. Sugar was also found to affect large-deformation rheology, promoting strain-weakening and a shorter linear regime.

2.4 Processing and technological aspects.

Emulsification is a complex unit operation in which many variables influence the processing and the final rheological characteristics of the product. The manufacture of emulsions usually requires the application of considerable mechanical energy. The two critical steps are the consecutive disruption of droplets and their

coalescence, both of which are favoured by an intense agitation. Consequently, the improvement of the emulsification process requires the measurement of the droplet size of the dispersed phase and its polydispersity. Moreover, the emulsification process may be greatly affected by the viscous and viscoelastic properties of the continuous phase at which the disperse phase is added.

One of the first studies on the influence of mechanical variables during processing was reported by Franco et al., [10] for emulsions stabilized by a mixture of macromolecular and low-molecular-weight emulsifier. Figure 10 shows the linear relaxation spectra of emulsions prepared with a rotor-stator turbine as a function of rotational speed and residence time. As can be observed the slope of the plateau region increases with the processing mechanical variables, because of the development of a three-dimensional network. This is also enhanced by a decrease in mean droplet size and polydispersity of the emulsion, yielding stronger inter-droplet interactions. As a result, stability against creaming was improved. Different results were obtained later on for emulsions stabilized by a sucrose ester non-ionic surfactant [95], which forms a gel-like structure in the continuous phase for a wide range of concentrations and temperatures [43]. As was previously mentioned, an increase in agitation speed or emulsification time also produces a decrease in droplet size and polydispersity. However, in this case, an increase in the agitation speed produced a decrease in the values of the dynamic viscoelasticity functions. The opposite effect was found by

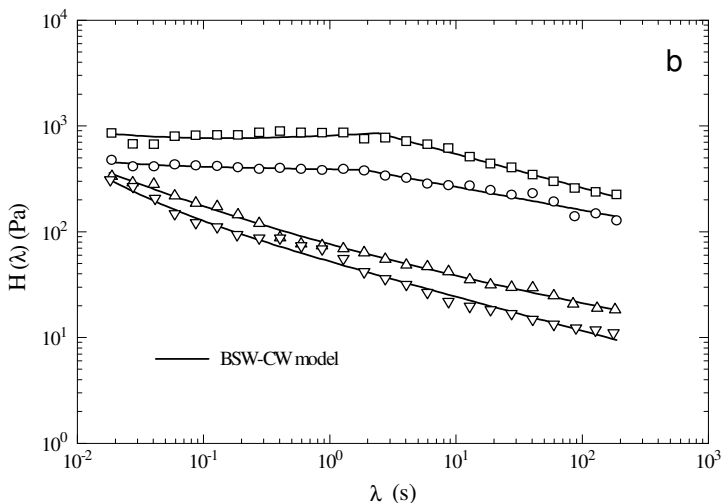


Figure 10. Influence of emulsification time and agitation speed on the relaxation time spectra of salad dressing emulsions: \square 8000 rpm – 5 min, \circ 8000 rpm – 3 min, Δ 5000 rpm – 5 min, ∇ 5000 rpm – 3 min. Adapted from reference [10].

increasing the emulsification time. Therefore, the viscoelastic properties of these emulsions depend on the balance between the formation of a larger interfacial surface and the breakdown of the gel-like structure of the continuous phase during processing.

The influence of mechanical processing variables on vegetable protein-stabilised emulsions is mainly affected by droplet size [22]. An increase in emulsification time and, specially, agitation speed produces a decrease in the Sauter diameter and favours the development of an entanglement network, noticed by an enhanced development of the plateau region in the mechanical spectrum and a significant increase in the values of the dynamic functions (i.e. see figure 11). These authors also found an increase in emulsion viscosity and other textural parameters like firmness and adhesiveness.

Temperature is a crucial variable to be controlled during the processing of protein-stabilised emulsions. For instance, an increase in the temperature during the emulsification, induced by the application of a severe mechanical energy, must affect the protein hydrophobicity [68] and, consequently, favours the inter-droplet

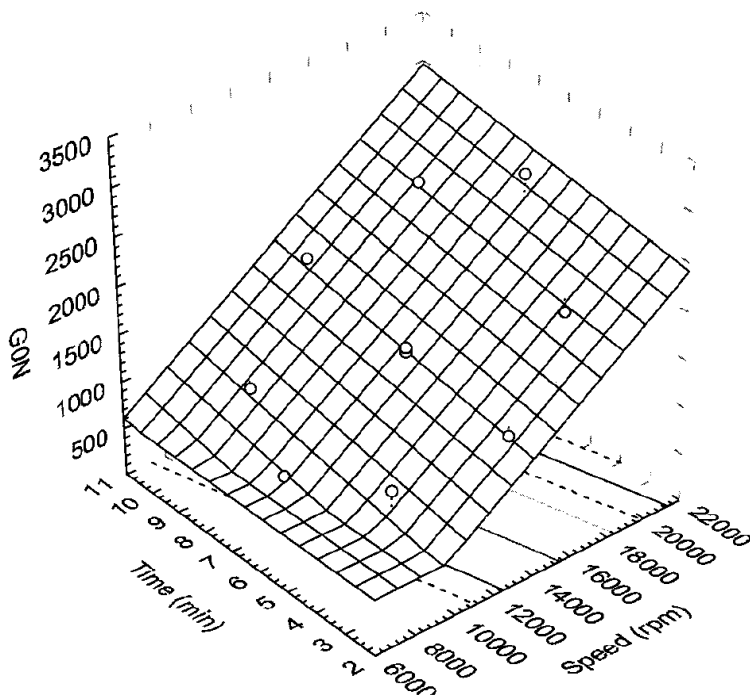


Figure 11. Evolution of the plateau modulus for lupin protein-stabilized emulsions prepared with different emulsification times and homogenization speeds (reproduced from reference [22]).

interactions. On the other hand, an increase in temperature or heating time favours the coalescence process, leading to larger droplet sizes and broader distributions, as found for pea-protein stabilised emulsions [70]. However, a severe thermal treatment previous to emulsification leads to more viscous emulsions. Thus, for instance, the viscosity and the plateau modulus increases with temperature, specially up to a temperature around 75° C and then remain almost constant, in spite of higher droplet sizes, a fact that is related to the achievement of the protein extensive denaturation. The application of high temperatures during the emulsification process produces similar effects [10].

An even more severe previous thermal treatment on native egg yolk is the spray-drying process, usually required to microbiologically preserve the final product, or as the first step previous to a cholesterol extraction process [67, 96]. The rheology of spray-dried yolk stabilized emulsions is dramatically different to that found with native egg yolk-stabilised emulsions due to a significant denaturation of egg yolk lipoproteins, which confers a marked gel-like behaviour and significantly higher values of the linear viscoelastic functions to these egg product-stabilized emulsions [97, 98].

The application of thermal treatments after emulsification may also have significant influence on the rheological behaviour of protein-stabilised emulsions. Dickinson and co-workers [75, 76, 99-102] have extensively studied, during the last few years, the rheological properties of heat-set whey protein-stabilised emulsion gels and the *in situ* gelation process through small-deformation oscillatory measurements. In all cases, the fresh emulsion was a very low viscous liquid-like system and became a gel network by increasing temperature. Thus, a crossover between G' and G'' was noticed at a relatively high temperature. Chen and Dickinson [102] investigated the effects of protein concentration and the volume fraction of oil phase on the viscoelastic properties of heat-set whey protein emulsion gels. They conclude that protein concentration is the main factor affecting gel strength. The dispersed oil droplets act as space fillers but also help to build up the gel matrix structure through interactions between protein molecules at the droplet surface and those in the gel matrix. The filler effects of oil droplets on the rheology of heat-set egg yolk, soy and milk protein-stabilised emulsion were respectively studied with some detail by Dickinson and Chen [103], Anton et al., [104] and Kim et al. [105]. Although a simplified van der Poel's equation [106] to estimate the shear modulus of a particulate composite has been used by the authors, the fitting fails due to both oil droplet flocculation and droplet deformability.

This thermorheological behaviour was shown by emulsions with relatively low volume fractions of oil phase. The improvement in the strength of highly concentrated gel-like emulsions, by means of thermorheological treatments, was also studied by Moros et al [107]. They show how highly flocculated egg yolk-stabilised emulsions, in principle with a soft gel-like behaviour achieved during the emulsification process, are susceptible to improve their gel-like behaviour by applying different thermal treatments on fresh emulsions. Thus, for instance, the application of upward/downward temperature cycles, setting the maximum temperature at 67° C, avoids emulsion breakdown and yield significantly higher values of the rheological

functions in comparison to those found with fresh emulsions, in spite of the thermal-induced droplet coalescence observed.

As may be observed in figure 12, in the first region, which corresponds to a temperature range comprised between 25 and 67° C, the evolution of G' is typical of that found during an upward temperature ramp, an initial decrease of the dynamic functions up to around 45° C and a subsequent increase up to around 70° C, related to a heat-induced rearrangement of the egg yolk lipoproteins located at the interface of oil droplets. In the second region, where temperature is kept constant at 67° C for different elapsed times, G' shows a rapid increase and then levels off. If temperature is kept constant at 67° C for 500 s (cycles B3 and B4) the values of G' are significantly higher than those obtained by cooling the sample immediately after the maximum temperature was reached (cycle B1). On the contrary, when the sample was maintained at 67° C for a much longer period of time, i.e. 1500 s (cycle B2), a slight decrease in G' is shown. These results were explained taking into account the aggregation of denatured lipoproteins, mainly livetins and LDL. However, if the sample is maintained at high temperature during an extended period (cycle B2) a subsequent significant coalescence of oil droplets may be observed (i.e. $d_{43} = 25.2 \mu\text{m}$ after the application of cycle B2 versus $d_{43} = 16.4 \mu\text{m}$ after the application of cycle B3).

Finally, a further sample cooling produces a new increase in G' , mainly due to hydrogen bonding. On the contrary, the cooling rate seems not to affect the final value of the linear viscoelastic functions, as may be deduced from the comparison of the final values of G' after the application of cycles B3 and B4 respectively. Afterwards, the values of G' do not change by keeping constant temperature at 25° C, which

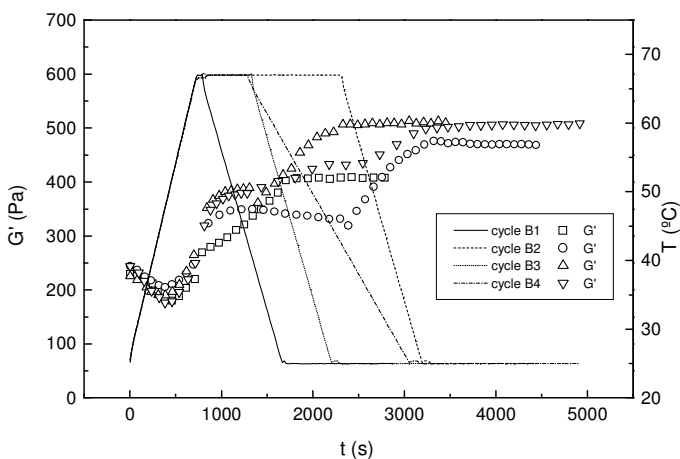


Figure 12. Evolution of G' with time, during the application of different cycles of temperatures, for an emulsion containing 70% (w/w) oil and 5% (w/w) egg yolk (reproduced from reference [107]).

indicates an irreversibility of the gel reinforcement process. However, absolute values of G' after the application of these thermal treatments were significantly lower as compared to those found by others [102, 103, 108], results that were obtained with milk protein-stabilized emulsions subjected to the same thermal treatments and containing similar protein concentrations, even with much lower fraction of dispersed phase, which indicates that egg yolk-stabilized emulsions are much less susceptible to enhance gel strength than milk protein systems.

The reversibility of heat-induced gelation was studied by Dickinson and co-workers, for caseinate-stabilised emulsions, through viscosimetry measurements [101, 109]. They showed that a thermo-reversible gelation in the temperature range of 30–45° C occurs mainly depending on pH and calcium ion content. They divided the emulsions, attending to the reversibility, in three categories (see figure 13): i) liquid-like emulsions which remains liquid when heated, ii) liquid-like emulsions which become gels when heated, exhibiting an increase in viscosity of, at least, one order of magnitude and decreasing viscosity again when it was cooling back down, and iii) emulsions that show already a gel-like behaviour when emerging from the homogeniser, which present an increase in viscosity of several orders of magnitude on heating above 30° C, without returning to low values on cooling back to ambient temperature. They presented a sort of phase diagram showing the different behaviours as a function of acid and calcium content. In addition to this, Chen and Dickinson [108] studied the effect of different programs of temperature on the reversibility of emulsions gels, attending to the evolution of the linear viscoelastic functions. As an

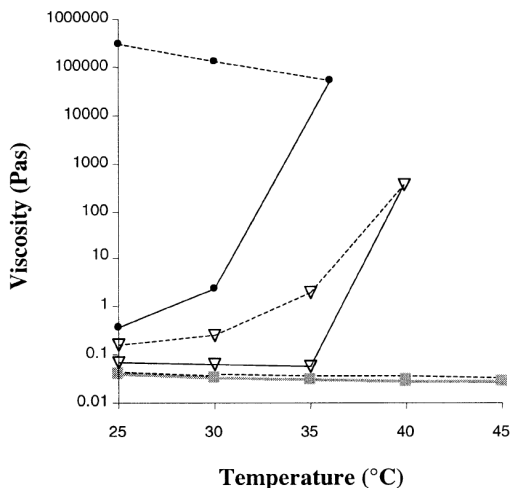


Figure 13. Examples of the three categories of emulsions attending to the thermoreversibility of the rheological behaviour. Solid lines: heating; dashed lines: back-cooling. ■: category i), ▽: category ii), ●: category iii). Reproduced from reference [109].

example, they concluded that the application of a program $45^{\circ}C \rightarrow 5^{\circ}C \rightarrow 45^{\circ}C$ on the emulsions leads to a temperature-reversible behaviour. G' and G'' increase on cooling to $5^{\circ}C$ and recover their original values on reheating to $45^{\circ}C$. On the contrary, the program $5^{\circ}C \rightarrow 45^{\circ}C \rightarrow 5^{\circ}C$ produces a non-reversible rheological behaviour. Thus, they found G' values around 10 times higher than values before the application of the thermal treatment.

An alternative to heat treatments is the high-pressure technology. The emulsifying and stabilising ability of some high-pressure treated vegetable and milk proteins were found inferior to those shown by the native proteins, which was attributed to an enhanced dissociation and/or aggregation through disulphide bridging [110, 111]. However, the viscoelastic parameters, i.e. the complex modulus, of emulsions prepared with severely pressure-treated (up to 800 MPa) β -lactoglobulin are higher in a wide range of pH than those found with untreated systems, even more when a thickener agent was included in the formulation, probably due to the development of high-pressure-induced interdroplet macromolecular linkages [111]. In any case, high-pressure processing seems to be a gentler processing operation in terms of changes in droplet size and instability [112]. On the contrary, high-pressure treatments prior to emulsification (600 and 400 MPa, respectively) on ovoalbumin [113] or lupin protein [114] clearly improve the emulsifying efficiency and stabilizing properties of emulsions. Concerning the rheological behaviour, Chapleau and de Lamballerie-Anton [114] found that viscosity and G' and G'' values slightly increase with pressure, although the viscoelastic behaviour, typical of flocculated emulsions, was essentially the same.

The influence of processing variables may be also studied by means of an *in situ* rheological monitoring of the emulsification process [115]. The *in situ* rheological measurements were carried out in a small-scale semi-batch reactor, so called rheo-reactor, equipped with a helical ribbon impeller adapted to a rheometer. An analytical method based on the Couette analogy allows to quantify correctly the torque-rotational speed to be transformed in the absolute rheological response, either under steady-state flow or in oscillatory regime [116]. The rheo-reactor not only provided real-time information during processing, but also allowed a complete rheological characterization of the final product without any sampling. Edgar Chavez-Montes et al. [115] followed-up *in situ* the processing of one of the most complex food systems such as ice cream, consisting of an emulsion of milk-fat globules in a highly viscous continuous phase containing sugars, proteins and stabilizers together with ice crystals and air bubbles. Processing was divided in two crucial steps, foaming and subsequent freezing of mixes. They found that rheology of the incipient product was mainly influenced by the type and concentration of stabilisers. Figure 14 shows the evolution of specific viscosity with time during the foaming step for different blends of stabilisers and emulsifiers. In addition to this, a combination of two emulsifiers (i.e. Tween 20 and mono- and diglycerides) was necessary to produce a desired partial coalescence of fat globules, which is related to the melting resistance of ice creams.

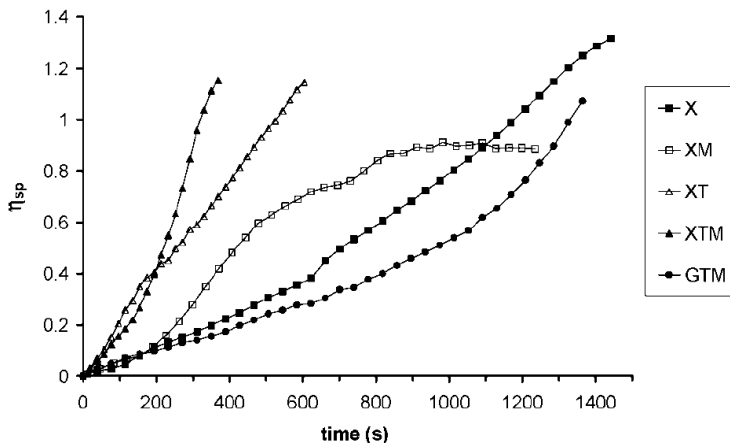


Figure 14. Evolution of specific viscosity during foaming of mixes stabilized with different thickeners and emulsifiers (reproduced from reference [115]).

3. RHEOLOGY OF CONCENTRATED PLANT FOOD SUSPENSIONS

The viscous flow behaviour of many concentrated plant food dispersions has been extensively studied during many years. It appears that most, if not all, of them exhibit shear-thinning flow behaviour, although in many cases the minimum shear rate applied was rather high. Consequently, the Ostwald-de-Waele model has been used extensively for characterising the viscous flow properties of plant food dispersions, although different authors have sustained that many plant food dispersions also exhibit a yield stress. Power-law parameters and yield stress values for selected plant food dispersions are shown in Table 2. Nevertheless, some comprehensive compilations of these parameters can be found in the literature [117, 118].

Several important differences between plant food and non-food suspensions should be mentioned [2]:

- the solid particles in food suspensions are not of simple shapes;
- they are flexible and have multimodal size distributions [131];
- the particles are hydrated and are in physical and chemical equilibrium with the continuous medium;
- the continuous medium of a typical food suspension, usually called serum, is an aqueous solution of sugars, organic acids, salts and pectic substances;

- the chemical composition of the continuous medium depends on the product, the cultivar and factors such as the extent of ripening.

The above mentioned characteristics can lead to significant inter-particle interactions compared to viscous forces, resulting in different flow behaviour.

Product	% Solids	T (°C)	n	K (Ns ⁿ /m ²)	τ_0 (Pa)	Comment	Reference
Apple Sauce	86.8 – 99.3	25	0.15 - 0.24	40.6 - 76.9	18.4 – 46.4	Three yield stress mode: Casson., Herschel-Bulkley ad Mizrahi-Berk	Qiu and Rao (1988) [119]
Apple puree	Three samples	25 - 60	0.4	112 - 58		Power law model	Schaller et al. (1970) [120]
Apple sauce	12° Brix	25	0.297 - 0.399	7.38 - 19.95		Power law model Viscosity/ °Brix/ pectin relation	Rao et al. (1986) [121]
Apricot puree	69 – 72	4.5 - 60	0.28 - 0.46	3.5 - 86.0		Variation of K and n with T	Watson (1968) [122]
Apricot puree	Four samples	22.5	0.59 - 0.79	0.82 - 1.65	8.04 – 22.11	Casson, Steiner and author's model Thixotropic	Costell and Duran (1978)[123]
Banana puree	26.5	40	0.34	8.575		Power Law model	García et al. (1974) [124]
Banana puree	17.7	22	0.28	12.3		Power Law model	Rao et al. (1974) [125] Qiu and Rao (1990) [126]
Blackcurrant juice	35 - 64.5	5 - 60	1.0	2.4 - 500		Newtonian model effect of temperature and composition	Ibarz et al. (1992b) [127]
Grape juice	55 – 68	-10 to 40				Newtonian model temperature effects	Rao et al. (1986) [128]
Lemon products	9.5 – 62		0.72 - 1	0.43 - 1.69	2.07	Power law and Herschel Bulkley models temperature effects	Saenz and Costell (1987) [129]
Orange juice concentrated	59 – 65	30	0.302 - 0.4	0.26 - 0.45	0.49 - 0.78	Mizrahi-Berk model (Modified Casson model)	Rao et al., (1984) [130]

Table 2. Power-law parameters and yield stress values of some plant food dispersions.

In addition to this, the amount and the size distribution of the insoluble solid matter in the plant food suspensions depend to some extent on the size of the screen employed in the finishing operation during their manufacture [131]. Therefore, food suspensions are complex materials whose characteristics with respect to the nature of the insoluble solids, as well as those of the fluid media, must be determined prior to experimentation. Consequently, to understand the role of the continuous and dispersed media, the two media should be separated by centrifugation and their characteristics studied separately.

Because of the compressible nature of plant food dispersions, the direct determination of the magnitude of the volume fraction is difficult as it depends on the centrifugal force employed in the separation of the phases. Therefore, standard centrifugal forces must be employed for determining the pulp content of a given plant food dispersion [132].

Very good examples of typical plant food dispersions are the wide variety of industrial tomato products manufactured: tomato paste, puree and concentrate, tomato ketchup and fried tomato sauce.

3.1 Viscous flow of tomato dispersions.

Tomato paste is a dispersion of solid particles (pulp) in aqueous media (serum) [133] resulting from the concentration of tomato pulp, after the removal of skin and seeds, and contains 24% or more natural soluble solids [134]. Tomato puree is the term applied to lower concentrations of tomato paste (containing 8% to less than 24% natural soluble solids). Tomato paste can be produced either by the cold break or by the hot break process [135]. In a hot break process the chopped tomatoes are pumped into a heat exchanger and immediately preheated to a temperature of at least 85° C, by which the pectolytic enzymes polygalacturonase (PG) and pectin methyl-esterase (PME), present in the tomatoes, are inactivated [136]. In a cold break process the chopped tomatoes are preheated to temperatures of around 60° C. Then the pectolytic enzymes retain a large part of their activity and are able to degrade the cell wall pectin during subsequent processing. During pulping/finishing [137] the preheated tomato pulp passes two or three sieves, with pore sizes normally ranging from 0.5 to 1.5 mm, to remove skins and seeds. Subsequently, the resultant juice is concentrated, by evaporation under partial vacuum, to tomato paste with a refractive index of 28-30° Brix. A flow diagram of tomato paste processing is presented in figure 15.

One of the main quality attributes of tomato concentrate products is viscosity [136]. The apparent viscosity of tomato concentrates is influenced by different factors: tomato variety and maturity; water-insoluble (WIS) and water-soluble (WSS) solids content; particle size distribution and particle shape; and processing variables [134]. Different empirical models have been used to characterize the flow behaviour of tomato concentrate [132, 138]. Thus, tomato concentrate viscous behaviour has been usually described by a power-law model [133, 139, 140] and this assumption has been reported as satisfactory for engineering design purposes [141]. Values of the flow index range from 0.18 to 0.26 for tomato concentrates [140, 142].

Fito et al. [143] confirmed the shear thinning nature of concentrates and measured both the flow and the consistency indexes as a function of temperature for concentrates produced by both hot- and cold-break methods. The variation of the flow index with temperature was not found to be significant. In contrast, Trifiro et al. [141] found both the consistency index and the flow index to vary with temperature and suggested the following relationships:

$$K = K_0 a^{1000/T} \quad \dots\dots\dots(10)$$

$$n = n_0 + 1000/T, \quad \dots\dots\dots(11)$$

where K_0 , a , n_0 and b are material specific constants and T is the absolute temperature. The power law and temperature dependent values of K and n were then used to estimate the pressure drop in continuous “tube-in-tube” heat exchangers, used for heat

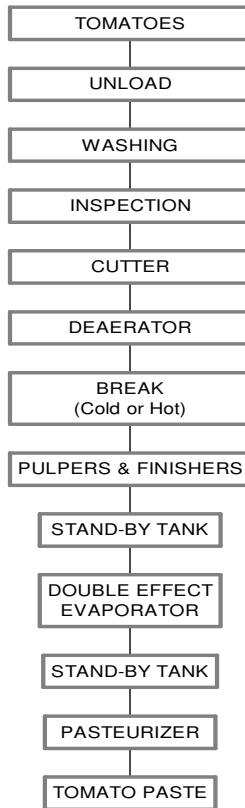


Figure 15. Flow diagram of tomato paste processing.

sterilization of tomato paste.

In addition to this, different models that include the yield stress as a fitting parameter, such as the Herschel-Bulkley and the Casson models [133, 144] have been also used to describe the viscous behaviour of tomato concentrates. In some cases, the yield stress was obtained by using the vane method [145]. Rao et al. [146] reported values of the flow index in the Herschel-Bulkley model ranging from 0.27 to 0.66, depending on tomato variety. Dervisoglu and Kokini [147] fitted data from tomato paste also to the Herschel-Bulkley model, and found yield stresses of the order of 45 Pa. The flow index was in broad agreement with other measured values.

A large number of papers have been published relating apparent viscosity, yield stress and power-law parameters to solid concentration and particle size [133, 144, 146, 148-151] and to processing conditions, as well, such as breaking temperature, finishing, concentration and homogenisation of tomato juice and tomato paste [131, 143, 145, 148, 152-153]. In fact, these processing conditions have an indirect effect on the apparent viscosity and flow parameters, by influencing the physico-chemical characteristics of the WIS particles, WIS concentration and serum viscosity.

Bhasin and Bains [154] sustained that neither the tomato variety nor the method of juice extraction had any significant effect on the flow index values. In the same way, Rao et al. [146] showed that the flow index was not significantly influenced by solids concentration. Molwane and Gunjal [155] found lower values of the flow index for hot-break than cold-break concentrates, although this index did no change appreciably by increasing solids concentration or temperature.

Rao et al. [146] found that the consistency index increases as total solids of the concentrates do. Both exponential and power type relations were found to be suitable for describing the relationship between total solids and the consistency index:

$$K = a_1 \exp(b_1 \cdot \text{total solids}) \quad \dots\dots\dots(12)$$

$$K = \alpha (\text{total solids})^\beta \quad \dots\dots\dots(13)$$

Table 3 shows the values of the power-law relationship between the consistency index and solids concentration for selected plan food dispersions.

Rao and Cooley [157] proposed that the logarithm of the apparent yield stress and total solids of tomato concentrates are related by a quadratic equation:

$$\ln \tau_0 = a + b(TS) + c(TS)^2 \quad \dots\dots\dots(14)$$

On the contrary, Sharma et al. [144] have related the yield stress and the water insoluble solids (WIS) using an exponential equation:

$$\tau_0 = a \exp [b(WIS)] \quad \dots\dots\dots(15)$$

In the same way, Xu et al. [153] found that the viscosity of tomato concentrates was higher for hot-break than cold-break samples. Thus, they evaluated the rheological properties of tomato paste produced from three varieties at breaking temperatures of 85, 96 and 107° C. Apparent viscosity depended both on tomato variety and process temperature, with the highest viscosity achieved through use of the 107° C breaking temperature.

Tanglertpaibul and Rao [131] proposed the apparent viscosity at a shear rate of 100 s^{-1} as a suitable rheological characteristic for tomato concentrates. The apparent viscosity was found to depend on the total solids concentration of tomato concentrates raised to a power in the range of 2.0 to 2.5. A more detailed study [148] involved separating serum from hot-break tomato juice by centrifugation and adding varying levels of pulp to the serum, to determine if a simple relationship existed between apparent viscosity and pulp content. Expressing the pulp content of the tomato concentrate as a pulp/serum wet weight ratio (PS), the following relationship resulted:

$$\eta_{100} = \eta_{\text{serum}} + A(PS)^{\beta} \quad \dots\dots\dots(16)$$

$$\eta_{\text{serum}} = C + D p^E \quad \dots\dots\dots(17)$$

<u>Dispersion</u>	α	β	<u>Reference</u>
Tomato juice	81.4	2.4	Harper and El Sahrighi (1965) [156]
Tomato concentrate	0.022	2.35	Rao et al. (1981) [146] Rao and Cooley (1983) [157]
Tomato concentrate	0.03	2.37	Fito et al. (1983) [143]
Apple concentrate	$2.8 \cdot 10^{-15}$	7.5	Rao et al. (1984) [130]
Apple juice	$2.2 \cdot 10^{-15}$	7.6	Ibarz et al. (1987) [158]
Babaco concentrate	0.519	2.44	Castaldo et al. (1990) [159]
Banana juice	$4.33 \cdot 10^{-34}$	19.0	Khalil et al. (1989) [160]
Grape concentrate	$6.9 \cdot 10^{-15}$	7.43	Rao et al. (1984) [130]
Mango pulp	$3.5 \cdot 10^{-4}$	1.36	Manohar et al. (1990) [161]
Pear juice	$9.3 \cdot 10^{-11}$	4.9	Ibarz et al. (1987) [158]
Pear purée	$3.6 \cdot 10^{-3}$	3.0	Harper and Lebermann (1962) [162]
Raspberry juice	0.1	6.4	Ibarz and Pagan (1987) [163]
Blackcurrant juice	$2.21 \cdot 10^{-9} - 8.87 \cdot 10^{-6}$	6.2 – 3.47	Ibarz et al. (1992) [127]

Table 3. Values of the parameters of the power-law relationship between the consistency index and solids concentration for different plant food dispersions.

The coefficient *A* indicates the contribution to viscosity of a unit amount of pulp and the coefficient *B* reflects the influence of pulp content on viscosity of concentrates from different tomato cultivars and/or processes. “*p*” is the pectin content expressed as pectic substances wt % of serum.

Dale et al. [164] concerned with the specification of viscosity for use in reverse osmosis system design, developed an empirical equation for the apparent viscosity of tomato concentrates based on the mass fractions of protein, solids and fibre, and absolute temperature.

Tanglertpaibul and Rao [131] used a carefully designed plan to compare the apparent viscosities of pastes made by the traditional method of hot break juice evaporation (JE) to those obtained by serum evaporation (SE) or reverse osmosis (SRO). Although apparent viscosities of SRO and SE concentrates were not significantly different at low concentrations, at higher concentrations the viscosity of the less temperature-affected SRO pastes was higher. The apparent viscosities of pastes made by evaporation of hot break tomato juice were always lower than those obtained by centrifugation followed by either evaporation or reverse osmosis of the separated serum and remixing. Therefore, there may be improvements in textural properties realised through separation of tomato juice serum and preferably non-thermal concentration, followed by recombination with pulp.

Particle size dramatically influences the consistency of tomato paste. As a general rule, a decrease in particle size yields a larger interfacial area which results in stronger inter-particle interactions and, consequently, higher viscosity values [133]. However, several authors have reported opposite results [151]. Thus, an increase in particle size yielded larger tomato paste viscosity values [131, 140, 165]. For instance, Yoo and Rao [166] found that the Casson viscosities of concentrates from tomato juice using 0.84 mm screen were higher than those made using 0.69 mm finisher screen. It is worth pointing out that tomato paste processing may change spheroidal particles into elongated particles, due to a rupture of the cell wall structure, which offer a greater resistance to flow [134].

Yoo and Rao [133] have related the relative viscosity (η_r) of tomato puree samples to the pulp weight fraction of solids (*P*), in place of the volume fraction due to the fact that tomato particles are deformable (see figure 16). With this aim, the Maron-Pierce equation was used:

$$\eta_r = [1 - (P/A)]^2, \quad \dots\dots\dots(18)$$

where *A* is an empirical parameter.

As Metzner [167] has pointed out for rigid particles, the value of *A* decreases as the aspect ratio (length to diameter ratio) of the suspended particles increases. Consequently, a stronger particle anisometry will result in a higher apparent viscosity. Tomato particles have a rather irregular shape, caused by factors such as tearing of the tissues during manufacture [133, 168]. As Yoo and Rao [133] have demonstrated, the value of *A* decreases as the average particle size increases, due to a larger aspect ratio.

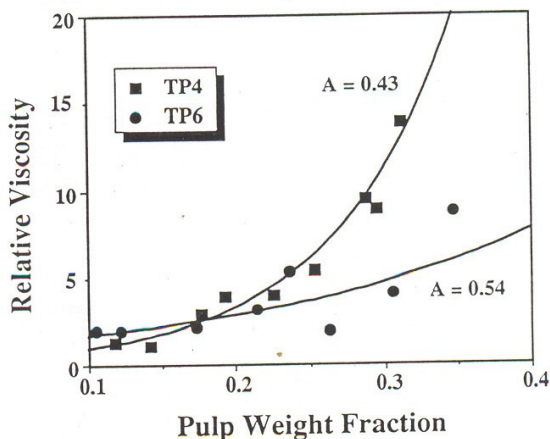


Figure 16. Relative viscosity-pulp weight fraction data of two particles sizes (TP4 = 0.71 mm and TP6 = 0.34 mm. Curves are predictions by the modified Maron-Pierce equation). Reproduced from reference [133].

3.2 Linear viscoelasticity of tomato products: influence of processing.

Much less work has been done on the characterization of the linear viscoelastic properties of these tomato products [142, 145, 169], which are of a great importance in relation to the characterisation of the microstructure of the tomato concentrate products and, also, for the prediction of the viscous flow of these products through the development of suitable non-linear viscoelasticity models. Thus, Rao and Cooley [142] carried out oscillatory tests, in the linear viscoelastic range, on tomato paste samples. They found that the Cox-Merz rule was not applicable, but sustained that the steady and dynamic shear data conformed with the use of a shift factor on frequency.

The linear viscoelastic behaviour shown by tomato paste was similar to that found for other concentrated suspension [170]. All of them showed a similar evolution of the storage and loss moduli with frequency as may be observed in figures 17 and 18. Based on the above-mentioned linear viscoelastic properties, it was suggested that they may be classified as weak gels [142]. Thus, the storage modulus values, G' , were always superior to the loss modulus values, G'' , in the whole range of frequency studied. Nevertheless, they showed a clear tendency to a crossover at low frequencies (beginning of the terminal region of the relaxation spectrum) and also at high frequencies.

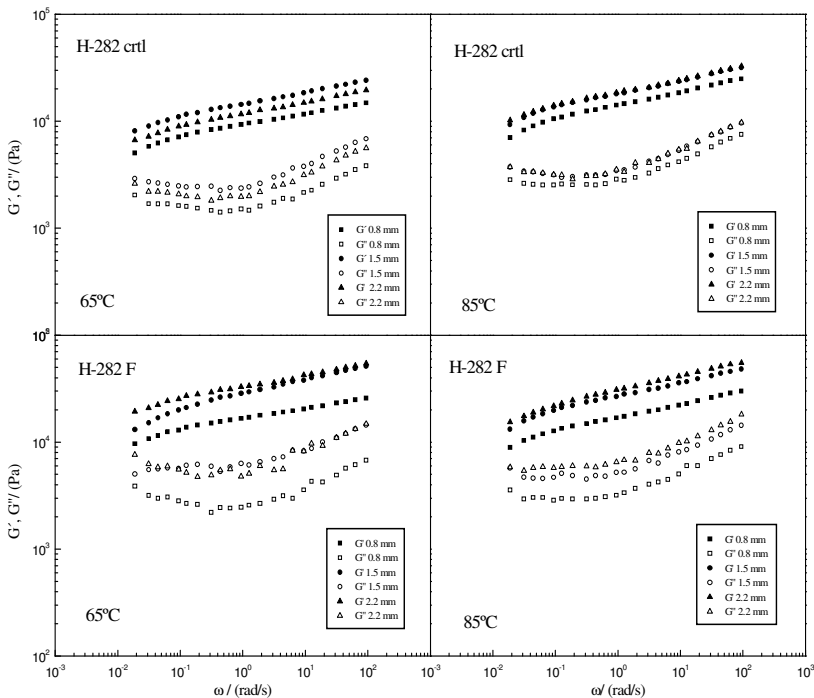


Figure 17. Influence of finisher screen opening on evolution of storage and loss moduli with frequency for different tomato paste samples (reproduced from [171]).

Nevertheless, most of the work carried out, up to now, has been focused on the relationship between rheology and processing of tomato paste. Nevertheless, the results obtained allowed to establish the influence that solids content and particle size exert on the linear viscoelasticity properties of tomato paste. Thus, Sánchez et al. [171] have studied the influence that some processing variables (sieve pore size and breaking temperature) and tomato variety exert on the linear viscoelastic properties of tomato paste. The study was carried out on tomato paste samples coming from different tomato varieties (with different content in pectolytic enzymes polygalacturonase and pectin methylesterase), manufactured at different temperatures of breaking (65-85° C) and screen sizes (0.8-2.2 mm). Tomato varieties H-282 ctrl and 1401-C were commercially available. Tomato variety H-282 F was a modification of variety H-282 ctrl, having a lower content in pectolytic enzyme polygalacturonase (PG). On the other hand, variety 1401-J was a modification of variety 1401-C, based on a significant reduction in the pectolytic enzyme pectin methylesterase (PME).

As other authors reported [148] with viscous flow measurements, contradictory results concerning the influence of the finisher screen opening were found. Thus, they reported maximum values of the apparent viscosity for tomato juices and concentrates at an intermediate finisher screen opening. An increase in sieve pore size, for example, from 0.8 up to 1.5 mm always yielded a tomato paste sample with higher WIS content. The above-mentioned increase in screen opening also produced larger mean particle size, d_{43} , for samples processed at a breaking temperature of 65° C, but the values were quite similar when the samples were processed at a breaking temperature of 85° C. Nevertheless, the values of the linear viscoelasticity functions always showed a significantly increase in the whole frequency range studied, at both breaking temperatures (see figure 17). These results were explained, taking into account that the consistency of tomato paste is dramatically influenced by the WIS content, which always increased as screen opening did. Thus, different authors [133, 146, 148, 149, 172] have reported that viscosity shows a power law dependence of pulp or total solids content of the concentrated tomato products, although some of them sustained that the contribution of the disperse solids was much more important [140].

A further increase in screen size, from 1.5 to 2.2 mm generally yielded slightly lower WIS content in the tomato paste samples. On the contrary, the values of the volume diameter were larger. Consequently, two opposite variables influenced the rheological results obtained. For example, the sample manufactured from variety H-282 ctrl, processed at 65° C and using 1.5 mm screen size showed higher values of the linear viscoelasticity functions (see figure 17) than the sample processed at the same temperature but using 2.2 mm screen size. In this case, the values of the volume diameter were quite similar for both samples. Consequently, the influence of the WIS content appears decisive. However, the samples manufactured from variety H-282 F,

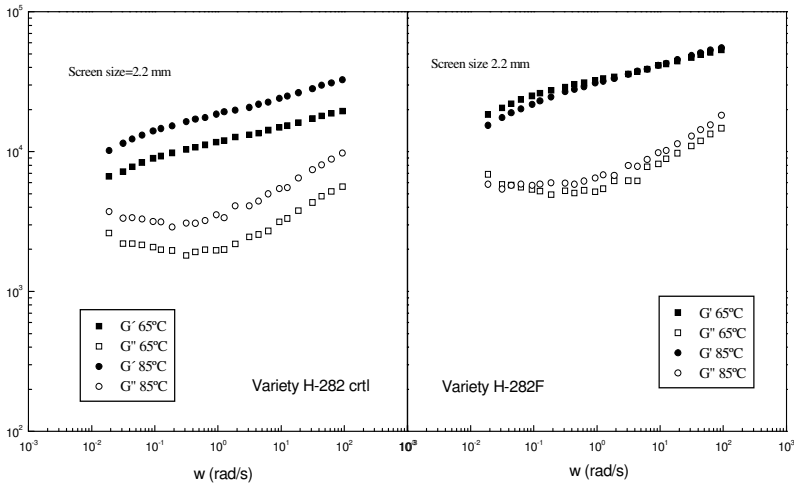


Figure 18. Influence of breaking temperature on evolution of storage and loss moduli with frequency for different tomato paste samples.

in the same conditions, showed different results. Thus, the values of the linear viscoelasticity functions (figure 17) slightly increased with the finisher screen opening. This was a consequence of a quite similar *WIS* content of both samples and an apparent increase in volume diameter for the sample processed with the larger screen size. Finally, the values of the linear viscoelasticity functions for the samples obtained from variety H-282 ctrl (see figure 17), processed at 85° C and using the above mentioned screen sizes (1.5 and 2.2 mm) were very similar. At this breaking temperature the volume diameter for the sample manufactured using 2.2 mm screen size is larger than the one obtained with 1.5 mm screen opening. Consequently, the influence of the *WIS* content, which decreases as screen size increases, is dampened by this increase in particle size. This increase in particle size is even predominant when the decrease in *WIS* content is less significant, as has been found in variety H-282 F samples, yielding a slight increase in the linear viscoelasticity functions with screen opening.

The influence of breaking temperature on the linear viscoelastic properties of tomato paste depends on tomato variety. An increase in breaking temperature generally results in tomato paste samples with a higher *WIS* content, due to both inactivation of the pectic enzymes and more efficient extraction of pectic substances [173]. The above-mentioned increase in temperature generally produces tomato paste samples with smaller particle size.

For samples manufactured from tomato variety H-282 ctrl and using the same finisher screen opening, an increase in breaking temperature always produced higher values of the linear viscoelasticity functions (figure 18). On the contrary, the influence of breaking temperature on the linear viscoelastic characteristics of tomato paste samples manufactured from tomato variety H-282 F was quite different. Thus, the opposite influences of a higher *WIS* content and smaller particle size always yielded very similar values of the linear viscoelasticity functions for samples processed using the same screen size, as can be observed in figure 19, where the values of the plateau modulus are plotted as a power-law function of particle size (μm) and water insoluble solids content (% wt).

This power-law relationship did not work with tomato pastes from variety H-282 ctrl. Nevertheless, the plateau modulus values were progressively closer to those obtained with tomato paste sample H-282 F, as breaking temperature was raised. It is worth pointing out that tomato paste H-282 F had a reduced content in PG. This reduction is reflected by a much reduced depolymerisation of the pectic substances [174]. This explains the much larger *WIS* content of these samples, at the same processing conditions. At a breaking temperature of 85° C, the influence of the pectolytic enzymes is quite similar for both tomato varieties, due to a progressive inactivation of both types of enzymes (PG and PME), which yielded a lower difference in the values of the linear viscoelasticity functions.

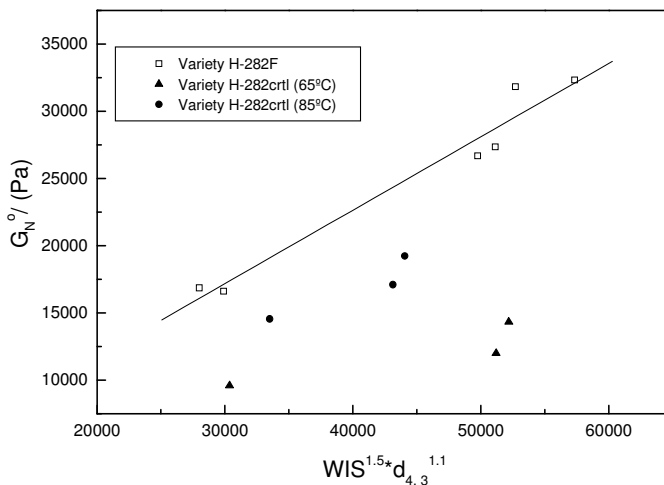


Figure 19. Plateau modulus values as a function of volume diameter and water-insoluble solids content (*WIS*) for different tomato paste samples (reproduced from reference [171]).

However, at 65° C, both enzymes are acting during the processing of the tomato paste samples manufactured from tomato variety H-282 ctrl. In this case, the main effect of the pectin methyl-esterases is to decrease the esterification degree of the pectin, which is transformed to pectic acid, highly insoluble in water. Nevertheless, this decrease in the esterification degree of the pectins favours a further action of the polygalacturonase, which transforms them in low-molecular weight soluble compounds. In addition to this, it is worth pointing out the lower values of the linear viscoelasticity functions of the samples manufactured at 65° C, taking into account their *WIS* content and particle size values. These results were explained on the basis of an extensive degradation of the wall cell structure, for tomato paste samples H-282 ctrl, as a consequence of the polygalacturonase activity [174], and the consequent reduction in their viscoelastic characteristics, due to the enhanced pectin depolymerisation. Furthermore, the influence of the pectin methyl-esterase (decreasing the esterification degree of the pectins) on the charge of the cell walls should be also taken into account. Thus, for samples having a reduced content in PG, an increase in the negative charge of the wall cells, due to the above-mentioned action, may enhance cell to cell adhesion via calcium bridging, which would increase the viscoelastic characteristics of the tomato paste samples.

The same authors [171] studied the evolution of the linear viscoelasticity functions with frequency for tomato paste samples coming from tomato varieties 1401-C and 1401-J (reduced content in PME). The evolution with frequency of G' and G'' was clearly dependent on tomato variety. Thus, the slopes of the storage and loss

moduli curves were higher for tomato paste samples manufactured using tomato variety 1401-J, which had a reduced PME content. This lower content in PME also yielded tomato serum viscosities much higher than those found in tomato serum from variety 1401-C, and, also, a Maxwell-like linear viscoelastic behaviour. These results were consistent with a significant increase in the concentration of water-soluble pectins, due to the reduced content in PME, that results in a much higher esterification degree of the tomato paste pectins and, consequently, in a lower pectic acid and *WIS* content. This reduced *WIS* content explains the lower values of the linear viscoelasticity functions found in tomato paste samples manufactured from tomato variety 1401-J.

Tomatoes usually contain from 7 to 8.5% total solids, of which about 1% are skins and seeds. The tomato skin consists of four or five layers of cells under a thin cuticle. In all the vegetable cell walls, polysaccharides are the predominant constituents. The general composition is considered to be approximately 30% cellulose, 30% hemicellulose, 35% pectin and 5% proteins; in the later ripening stages, lignine can also be found in great quantities [175]. As was previously mentioned, during processing of tomato paste, tomato pulp is passed through juice extractors, step that eliminates as residues (tomato slurry) 2-5% of the original tomato solids. Sánchez et al. [176] have studied the influence that the addition of “treated tomato slurry” into tomato juice exerts on the viscous flow and linear viscoelastic behaviour of the final tomato paste. “Tomato slurry” designates a mixture of tomato pulp, skin, seeds and

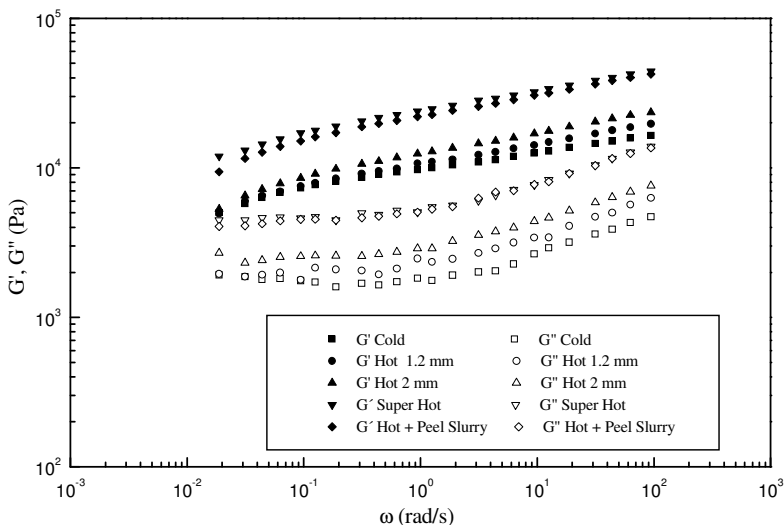


Figure 20. Evolution of the storage and loss moduli with frequency for different tomato paste samples, at 25° C (reproduced from reference [176]).

fibres originating from tomato cell walls and which are of a sufficient big size to be rejected from standard tomato juice extractors [177]. Tomato paste samples with addition of “treated tomato slurry” were manufactured using a breaking temperature of 80° C and a sieve screen size of 1.2 mm.

As may be observed in figure 20, the addition of tomato slurry produced a significant increase in the linear viscoelasticity functions, as compared to the values obtained with a tomato paste sample manufactured at the same breaking temperature (80° C), but quite similar to those shown by a tomato paste sample manufactured at a breaking temperature of 90° C (Super-hot sample). These results were explained taking into account the influences that tomato paste *WIS* content and particle size exert on the rheological parameters of the above-mentioned samples. Thus, the tomato paste sample manufactured with tomato slurry had a higher *WIS* content than the other two samples manufactured at the same breaking temperature (Hot 2.0 mm and Hot 1.2 mm), although lower particle size. On the contrary, the addition of “treated tomato slurry” yielded tomato paste samples with similar *WIS* content to that obtained by submitting a regular tomato juice (without tomato slurry addition) to a super-hot process (breaking temperature of 90° C).

The addition of tomato slurry brings also about an increase in the lycopene content of tomato paste, as a consequence of the larger lycopene content of the tomato slurry. This fact yields an improvement of colour, as well as an increase in its potential antioxidant and nutritional properties.

The results previously shown suggest that the addition of “treated tomato slurry” may be of great interest for tomato paste production and very important from a technical and economical point of view. Thus, it would be possible to reach the standard specifications, i.e. viscosity, with lower breaking temperatures. This reduction would not damage the product as during a super-hot tomato paste process, obtaining a tomato paste with even better colour and nutritional value [177]. It is worth pointing out that tomato paste with a higher consistency can lead to a significant cost saving in the production of tomato-based finished products, both by reducing the quantity of thickeners and/or the amount of tomato paste to be used in the recipe, factors that have a dramatic influence on the final consistency of the product. These advantages may be achieved without changing crucial processing parameters, i.e. finisher screen opening, hot-break holding time and temperature.

Valencia et al. [178] have studied the influence that some tomato paste processing variables (finisher screen opening and breaking temperature) and tomato variety exert on the linear viscoelastic properties of tomato ketchup. They concluded that an increase in screen size during tomato paste manufacture does not produce a systematic influence on the rheological response of tomato ketchup, as could be expected. On the contrary, the influence of tomato paste breaking temperature on the linear viscoelasticity properties of tomato ketchup was very uniform. Thus, an increase in the storage and loss moduli of tomato ketchup samples with tomato paste breaking temperature was observed for samples processed using the same screen opening (see figure 21). This increase in the linear viscoelasticity functions was related to the higher *WIS* content of the tomato paste processed at 85° C and, in some cases, to a larger particle size of the tomato ketchup samples. In addition to this, the lower values of the linear viscoelasticity functions of the samples manufactured with tomato paste

processed at 65° C were also related to a degradation of the cell wall structure of the tomato, due to pectin depolymerisation caused by polygalacturonase activity [174].

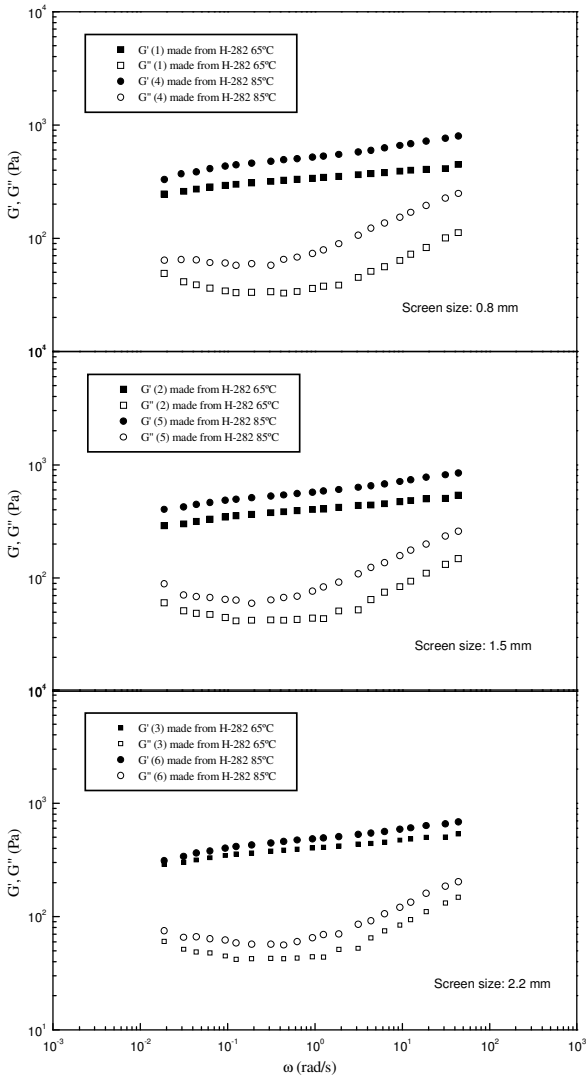


Figure 21. Influence of tomato paste breaking temperature on the linear viscoelasticity functions of tomato ketchup, at 25° C (reproduced from reference [178]).

Valencia et al. [179] have also studied the influence of the same variables on the linear viscoelastic properties of tomato sauce products. It was observed that the influence of the screen size, used during the manufacture of tomato paste, on the rheological properties of the resulting tomato sauce samples was even more complex than that found with tomato paste, due to the presence of a thickener (starch) in the formulation. Thus, the particle size distribution curves for all the tomato sauce products studied showed a bimodal distribution. On the other hand, an increase in the linear viscoelasticity functions and plateau modulus with tomato paste breaking temperature was again observed for samples processed using the same screen opening.

3.3 Non-linear viscoelasticity modelling of tomato products.

Valencia et al. [180] carried out also the characterization and modelling of the non-linear rheological properties of tomato paste, manufactured under different processing conditions (sieve pore size and breaking temperature). With this aim, flow measurements, dynamic linear viscoelastic and linear and non-linear stress relaxation tests were performed. Different geometries with smooth and serrated surfaces were used to optimise the viscous flow measurements and avoid wall-depletion phenomena.

Figure 22A shows the evolution of the storage (G') and the loss (G'') moduli with frequency, within the linear viscoelasticity range, for a selected tomato paste sample (processed at 65° C and using 1.5 mm screen size). Figure 22B shows the evolution of $H(\lambda)$ obtained by the application of regularization methods [40, 42,43]. In this case, the linear relaxation spectrum only has two regions: the plateau region, with an almost nil slope, and the beginning of the transition region in the low relaxation time range [181]. Figure 22A shows the recalculation of the dynamic linear viscoelasticity functions, which indicates that the continuous relaxation spectrum calculated by means of regularization techniques gives a good description of the linear relaxation behaviour of these systems.

In order to obtain the damping function, $h(\gamma)$, stress relaxation tests were performed in the non-linear viscoelasticity range. Figure 22C shows the evolution of the relaxation modulus with the elapsed time after shear, for a range of shear strains inside and outside the linear viscoelasticity region. As may be seen in this figure, the non-linear relaxation modulus, $G(\gamma, t - t')$ and the linear relaxation modulus, $G(t - t')$ undergo a continuous decrease within the time scale studied. The shape of $G(\gamma, t - t')$ is independent of the strain previously applied on the sample. Time-strain separability for the non-linear viscoelasticity function was then assumed. As may be deduced, a quite large structural destruction takes place due to shear in these systems.

The values of $h(\gamma)$ versus strain together with the corresponding fits for a tomato paste sample are shown in figure 22D. Three types of damping functions were tested in order to obtain the best predictions of the Wagner model: the Wagner damping function [48] containing only one empirical parameter, k , which quantifies the level of non-linearity in the material:

$$h(\gamma) = \exp(-k\gamma), \quad \dots\dots\dots(19)$$

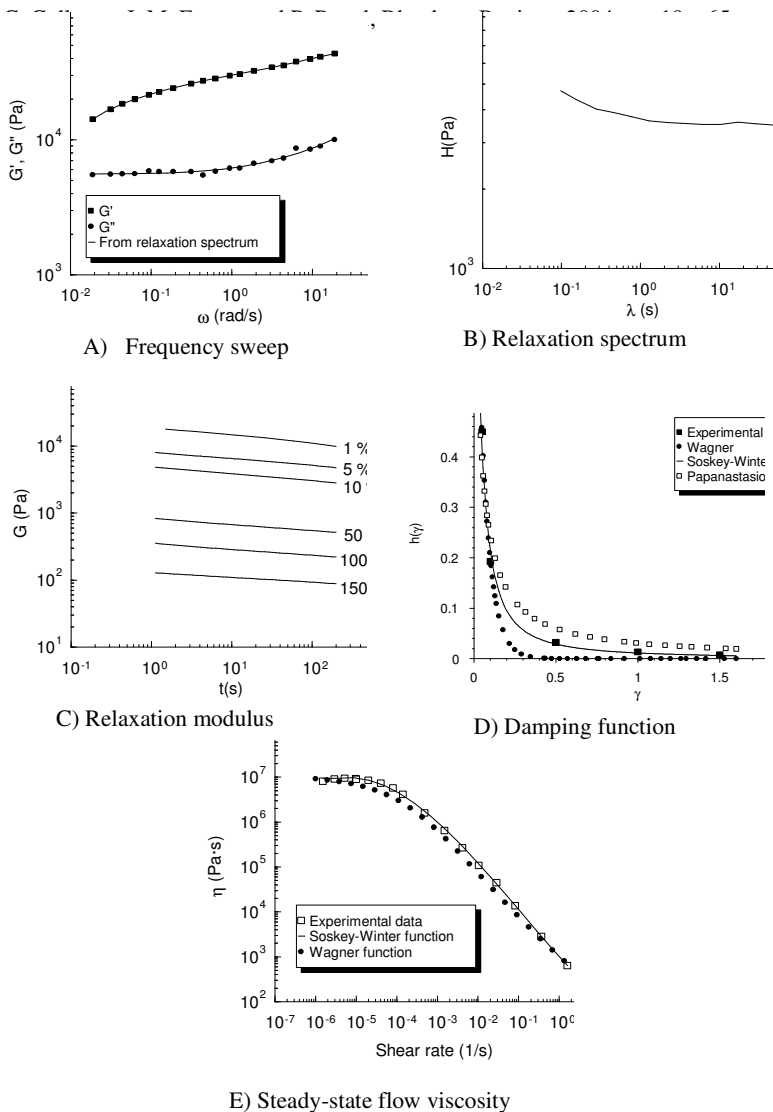


Figure 22. (A) Evolution of the storage and loss moduli with frequency and recalculation from the linear relaxation spectrum. (B) Linear relaxation spectrum. (C) Evolution of the linear and non-linear relaxation moduli with the elapsed time after shear; (D) Values of different damping functions. (E) Experimental and predicted values of the steady-state viscosity, at 25° C, for a selected tomato paste sample (H-282 F, breaking temperature: 65° C; screen opening: 1.5 mm). Reproduced from [180].

the Soskey-Winter equation [52], with two empirical parameters:

$$h(\dot{\gamma}) = \frac{I}{I+a\dot{\gamma}^b} , \quad \dots\dots\dots(20)$$

and the Papanastasiou damping function [182], with just one empirical parameter:

$$h(\dot{\gamma}) = \frac{\alpha}{\alpha+\dot{\gamma}^2} . \quad \dots\dots\dots(21)$$

As can be seen in figure 22D, Soskey-Winter’s model provides a better fit than the Wagner and the Papanastasiou model.

Figure 22E shows the experimental viscous flow curve for a tomato paste sample. This behavior was predicted by using a non-linear viscoelasticity constitutive equation, the Wagner model. Introducing the Soskey-Winter damping function, the steady-state viscosity is then given by the following equation, which must be solved numerically:

$$\eta(\dot{\gamma}) = - \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} H(\lambda) \exp\left\{ \frac{-(t-t')}{\lambda} \right\} \frac{\dot{\gamma}(t-t')}{1+a[\dot{\gamma}(t-t')]^b} d(\ln \lambda) dt' \quad \dots\dots\dots(22)$$

As can be observed in figure 22E, the use of the Soskey-Winter damping function provides the best predictions of the viscous flow curves. In general, the viscous flow curves for all the tomato paste samples studied by these authors were predicted with an acceptable accuracy, using a combination of the continuous linear relaxation spectrum and the Soskey-Winter damping function.

The Soskey-Winter parameter “*a*” and the Wagner damping factor “*k*” slightly increase as sieve pore size does. This evolution was related to a larger strain-softening as tomato paste mean particle size increases. On the contrary, an increase in breaking temperature produced a large decrease in both damping parameters. This indicates that the microstructure of tomato paste samples processed at a breaking temperature of 85° C is less strain-dependent.

4. CONCLUDING REMARKS

The rheology of concentrated food dispersions has been reviewed. As has been reflected, many structural factors influence the rheology of these complex foodstuffs. In addition to this, a change in processing variables influences the above-mentioned structural factors, leading to very different behaviours for the same formulation. Although the linear viscoelasticity data obtained with these products are quite feasible, special care has to be given to the measurement of the non-linear behaviour due to the appearance of flow instabilities in a significant shear rate (or stress) range. Finally, it is worth pointing out that much more work is needed to understand the relationship among rheology-microstructure-processing of food dispersions.

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