Single Drop Dynamics under Shearing Flow in Systems with a Viscoelastic Phase

Vincenzo Sibillo,[1] *Stefano Guido,*[1] *Francesco Greco,**[2] *Pier Luca Maffettone*[3]

[1]Dipartimento di Ingegneria Chimica, Università di Napoli "Federico II", Piazzale Tecchio 80, 80125 Napoli, Italy
[2]Istituto per i Materiali Compositi e Biomedici (IMCB) – CNR, Piazzale Tecchio 80, 80125 Napoli, Italy
[3]Dipartimento di Scienza dei Materiali ed Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

Summary: In this article, we discuss the dynamics of a single drop immersed in an immiscible liquid, under an imposed shear flow. The two situations of a viscoelastic matrix with a Newtonian drop and of a viscoelastic drop in a Newtonian matrix are considered, both systems being characterized by a viscosity ratio equal to one, and by the same elasticity parameter. Experimental data are taken with a rheo-optical computer-assisted shearing device, allowing for drop observation from the vorticity direction of the shear flow. Data favourably compare with predictions of the recently proposed Maffettone-Greco model, where the drop is described as a deforming ellipsoid.

Keywords: rheology; viscoelastic properties

INTRODUCTION

Immiscible liquid-liquid suspensions are very often encountered in nature and in industrial processes, so the understanding and control of their structure and flow properties is of great importance. In general terms, suspension behaviour under flow conditions is determined by the rheology of the components *plus* the morphology of the interface, and can be very difficult to study. The simplest possible case, namely, the infinite-dilution single-drop problem, appears then to be a reasonable starting point, as a "prototype" problem, to investigate on the basic features of suspension rheology.

A rather rich literature is dedicated to the single drop system, which is summarized in several reviews[1-3]. It should be emphasized, however, that the ample majority of the research papers on this topic dealt with fully Newtonian systems, where both the phases are Newtonian liquids. Instead, relatively few papers were devoted to non-Newtonian systems, i.e., with viscoelastic components. In many experiments, moreover, the fluids investigated included both viscosity and normal stresses "thinning" with the flow rate, hence a clear identification of separate elastic and viscous non-Newtonian effects had not

 DOI: 10.1002/masy.200551003

been obtained.

Recently, an exact theoretical analysis of the non-Newtonian case has been performed, for constant viscosity elastic liquids (second-order fluids), and for small deformations of the drop, and predictions from that analysis have been shown to be in very good agreement with experimental data taken on so-called “Boger fluids” in slow shear[3,4]. Away from the small deformation limit, a simple phenomenological model has also been proposed very recently by Maffettone and Greco[5], based on the assumption that the drop always retains an ellipsoidal shape. The phenomenological parameters of the Maffettone-Greco model (MG henceafter) were determined in the small deformation limit only, by comparison with the analytic asymptotic theory. The few sparse available steady-state and transient data with Boger fluids single drop systems were reasonably well predicted through the MG model, at least for intermediate drop deformations, and for not too highly elastic fluids.

In this paper, new experimental data of drop deformation and orientation taken under shear flows are presented, both at steady state and in time-dependent situations (start-up). For the first time, two properly chosen “inverse” non-Newtonian systems are considered, namely, a Newtonian drop immersed in a Boger fluid, and vice versa. Thus, the respective effects of outer/inner elasticity are examined. The MG model is used again to obtain predictions for drop deformations. It will be shown that the model performs nicely for both the non-Newtonian configurations, giving quantitative predictions in most cases, up to moderate drop deformations.

THE PHENOMENOLOGICAL MODEL

In the MG model of drop dynamics[5], the drop is assumed to be always an ellipsoid. Thus, at any time t, the drop surface is always described by the equation $\mathbf{Q}(t):\mathbf{rr} = r_0^2$, with r_0 the equilibrium radius, $\mathbf{r}$ the position vector spanning the deforming surface, and $\mathbf{Q}(t)$ a second rank symmetric, positive definite, and time dependent tensor. Drop dynamics, i.e., the evolution of $\mathbf{Q}(t)$, is ruled by the competing actions of flow-induced deformations and of relaxation towards a spherical shape, the former being driven by the flow field “at infinity”, the latter by the interfacial tension σ of the liquid pair. The proposed evolutive equation for tensor $\mathbf{Q}$ is:

$$\frac{d\mathbf{Q}}{dt}-(\boldsymbol{\Omega}\cdot\mathbf{Q}-\mathbf{Q}\cdot\boldsymbol{\Omega})+a(\mathbf{D}\cdot\mathbf{Q}+\mathbf{Q}\cdot\mathbf{D})+c\mathrm{Tr}(\mathbf{Q})\mathbf{D}=-\frac{f_1}{\tau_{em}}(\mathbf{Q}-g\mathbf{I}) \qquad (1)$$

(**I** is the unit tensor, and Tr(·) represents the trace operator.) In eq.(1), **D** and **Ω** are the deformation rate and the vorticity tensors, respectively, of the externally imposed flow field. The RHS of eq.(1) is a relaxation term, containing the so-called "emulsion time" $\tau_{em} \equiv r_0\eta/\sigma$ (η is the viscosity of the suspending liquid), and with g(**Q**, **D**) the function

$$g(\mathbf{Q},\mathbf{D})=\frac{3-\frac{\tau_{em}}{f_1}c\mathrm{Tr}(\mathbf{Q})\mathbf{D}:\mathbf{Q}^{-1}}{II_{\mathbf{Q}}} \qquad (2)$$

which is needed to preserve drop volume at all times. ($II_{\mathbf{Q}}$ in eq.(2) is the second scalar invariant of tensor **Q**.)

The nondimensional scalar coefficients a, c, and f_1 in eqs.(1),(2) depend on all the constitutive parameters of the two component fluids. In the general non-Newtonian case, when both the fluids are viscoelastic, at least five fully constitutive nondimensional quantities are obtained, namely: i) the viscosity ratio $\lambda = \eta_d/\eta$ (η_d is the drop viscosity); ii) the parameters $p \equiv \tau/\tau_{em}$ and $p_d \equiv \tau_d/\tau_{em}$, i.e., the ratios of the constitutive relaxation times τ and τ_d of the external and the inner fluid, respectively, to the emulsion time τ_{em}; iii) the ratios $\Psi \equiv -\Psi_2/\Psi_1$ and $\Psi_d \equiv -\Psi_{2d}/\Psi_{1d}$, where Ψ_1 and Ψ_2 and Ψ_{1d} and Ψ_{2d} are the first and second normal stress coefficients of the matrix and the drop fluid, respectively. Concerning ii), note that the constitutive relaxation time of the viscoelastic phase is here estimated from the well-known relationship (e.g., for the outer phase) $\tau = \Psi_1/2\eta$. Concerning iii), it should be recognized that the parameters Ψ and Ψ_d are not solely linked to shearing flow: in fact, in the limit of vanishing flow rate, they are constitutive properties of the component fluids. Formulae for coefficients a, c, and f_1 in terms of the constitutive parameters λ, p, p_d, Ψ, and Ψ_d (assumed to stay constant) are reported in Maffettone and Greco[5], and will be used unaltered in the present paper.

Equations (1),(2) can be made nondimensional through the so-called "capillary number" $Ca \equiv \tau_{em}|\nabla\mathbf{v}|$, with $|\nabla\mathbf{v}|$ the magnitude of the imposed velocity gradient. It should be emphasized that, within the equations of the phenomenological model, the flow strength only appears in the capillary number, whereas the other parameters are fully constitutive in nature, describing either single fluid properties (Ψ and Ψ_d) or properties of the fluid pair (λ, p, and p_d). Thus, for any given capillary number, and with λ fixed, predictions are different for different elastic fluid pairs, i.e., pairs with different non-Newtonian parameters Ψ, Ψ_d, p, and p_d. The purpose of this paper is just that of quantitatively testing this latter feature of the MG phenomenological model, through properly designed experiments in shear flows.

MATERIALS AND METHODS

The fluids to be used in the experiments were carefully selected in order to explore both the case of a Newtonian drop in a viscoelastic matrix and the reversed situation of a viscoelastic drop in a Newtonian matrix. In all the experiments, the viscoelastic phase was a constant-viscosity, elastic polymer solution (Boger fluid), and the Newtonian phase a silicone oil (Dow Corning). The Boger fluids were prepared by mixing a Newtonian polyisobutylene (PIB) sample (Napvis 5 and 10, BP Chemicals) with a small amount of a high molecular weight grade of the same polymer (Aldrich), preliminarily dissolved in kerosene at the concentration of 4% wt. In the case of a viscoelastic drop, special care was paid to make sure that no diffusion of the Newtonian PIB component took place in the continuous phase. In fact, it has been already reported that diffusion from a PIB drop into a silicone oil matrix can lead to a significant change of the interfacial and rheological properties of the drop phase, due to selective migration of molecular weights[6]. To overcome this problem, the two phases were preliminarily mixed and then let to equilibrate with respect to mass transfer. The so formed blend was ultracentrifuged to separate the two equilibrium phases. The Boger fluid rich phase was used to create the viscoelastic drop, and the silicone oil rich phase was loaded in the apparatus as the matrix. Phase equilibrium was checked by monitoring drop size as a function of time. No significant change was observed on the time scale of the experiments, thus ensuring that diffusion effects were negligible.

The rheological properties of all the fluids investigated were measured by means of a constant-stress rheometer equipped with a normal stress transducer (Bohlin, CVO 120), in the cone-and-plate configuration. As far as the Boger fluids are concerned, the viscosity was essentially constant in the range of shear rate investigated (up to 20 s^{-1}), and rather large values of the first normal stress difference were found. Furthermore, the slope of the first normal stress difference vs. shear rate in log scale was equal to 2 within experimental error, in agreement with the assumption of second order fluids made in the theoretical analysis. For what matters the drop fluids (i.e., the silicone oils), no normal stresses could be measured within the instrumental sensitivity. For the case of the viscoelastic matrix, relevant data are: η=6.6 Pa s, Ψ_1=3.5 Pa s^2, σ=1.3 mN/m, r_0=45 μm. For the case of the viscoelastic drop, relevant data are: η_d=65 Pa s, Ψ_{1d}=122 Pa s^2, σ=2.8 mN/m, r_0=37 μm.

The parallel plate apparatus used to generate simple shear flow has been described in detail elsewhere[7]. Briefly, one plate was displaced with respect to the other by a 2-axis translating stage, driven by two computer-controlled stepper motors. Parallelism between the two plates was adjusted by exploiting the reflections of a laser beam from the plate surfaces. Temperature was measured in situ by immersing a fine wire thermocouple in the sample between the two plates. Observations, along either the velocity gradient or the vorticity axis, were performed by using an optical microscope endowed with a monochromatic CCD video camera and a motorized focus system. The microscope itself was mounted on a motorized stage, to follow the deformed drop during motion.

The drop was injected in the continuous phase by means of a tiny glass capillary. A micromanipulator was used for a precise positioning of the capillary inside the gap. Since drop diameter was at least ten times smaller than the gap (~1 mm), wall effects were negligible. Images from the experimental runs were both recorded on videotape and stored on hard disk after digitization by a frame grabber installed on a personal computer. The maximum (L) and minimun (B) drop axis in the shear plane and the angle α between the maximum axis and the flow direction were measured in each image by an automated image analysis procedure, based on an edge-detection algorithm to identify the side-view drop contour. Drop shape under transient and steady conditions was characterized by the "deformation parameter" $D = (L-B)/(L+B)$ and the angle α.

RESULTS AND DISCUSSION

In this section the experimental results and the corresponding model predictions are presented and commented. Two situations are studied: a viscoelastic matrix with a Newtonian drop, and a Newtonian matrix with a viscoelastic drop. The viscoelastic phases are characterized by the same degree of elasticity $p=p_d=1.1$. Since no information is available on the value of the Ψ parameter, we always assume Ψ=0 in the calculations. (The value of Ψ is numerically irrelevant, however, for the observables considered in this paper.) Both the systems are at a viscosity ratio $\lambda = 1$. Steady state and transient behaviour of the deformation parameter and the orientation angle under shear flow are analyzed. For the sake of comparison, the steady state results are also contrasted with model predictions for the fully Newtonian system, at the same $\lambda = 1$. Indeed, such predictions are known to compare satisfactorily with the experimental data in the parameter range investigated (see Maffettone and Greco[5]).

Figure 1 shows the deformation parameter D at steady state as a function of the capillary number. The agreement between experimental results and theory predictions is good in the explored range of capillary numbers, and excellent for the viscoelastic drop case. It can be noted that both the non-Newtonian systems behave as the fully Newtonian one at low Ca-values. This feature confirms that the small deformation limit can be studied to derive interfacial tension independently of possible viscoelasticity of one phase. As the capillary number is increased, the system with the viscoelastic matrix first deviates appreciably from the Newtonian behaviour (Ca~0.1). The system with the viscoelastic drop detaches from the Newtonian behaviour at a slightly larger Ca-value (~0.2). Both the viscoelastic systems display a less deformed drop with respect to the fully Newtonian case, i.e., $D < D_{NEWT}$.

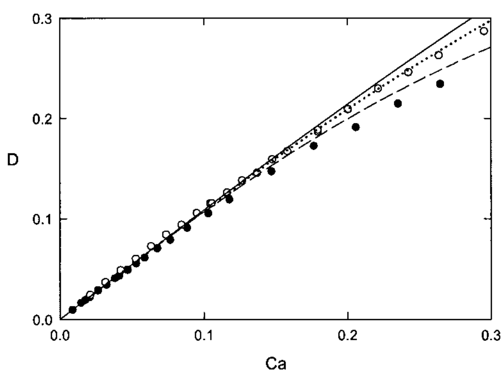

FIGURE 1 – The deformation parameter vs. the capillary number at steady state, for λ=1. Lines are model predictions, symbols are experimental data. Solid line: fully Newtonian system; Dashed line and ●: viscoelastic matrix and Newtonian drop (p=1.1, Ψ=0, p_d=0); Dotted line and ○ : Newtonian matrix and viscoelastic drop (p=0, p_d=1.1, Ψ_d=0).

Figure 2 shows the drop orientation angle α with respect to the velocity direction at steady state. It clearly appears that the model prediction is in good agreement with experiments in the case of a viscoelastic matrix, up to Ca~0.15, while fair agreement is found only at very small capillary number for the case of a viscoelastic drop. At larger Ca-values, the predictions deteriorate, underestimating the orientation angle in the case of the viscoelastic matrix, and, conversely, overestimating data in the viscoelastic drop case. Both viscoelastic systems show a drop closer to the velocity direction than for the fully Newtonian case, i.e., $\alpha < \alpha_{NEWT}$. At small Ca-values, the viscoelastic drop is closer to the Newtonian behaviour, as also predicted from theory. On the other hand, the experimental sets of data collapse on each other at larger Ca-values, at variance with predictions.

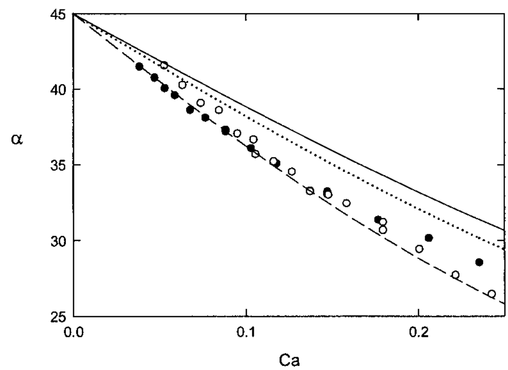

FIGURE 2 - The drop orientation angle α with respect to the velocity direction at steady state vs. the capillary number, for λ=1. Lines are model predictions, symbols are experimental data. Solid line: fully a Newtonian system; Dashed line and •: viscoelastic matrix and Newtonian drop (p=1.1, Ψ=0, p_d=0); Dotted line and ○: Newtonian matrix and viscoelastic drop (p=0, p_d=1.1, Ψ_d=0).

Transient behaviour for D and α are reported in Figs. 3-4. (Time in these figures is made nondimensional through the emulsion time τ_{em}.) Again, a good agreement is found between theory and experiments for the deformation parameter. At low capillary number the deformation parameter monotonically increases towards the steady state. As the Ca-value increases, the Newtonian drop in the viscoelastic matrix shows the appearance of an overshoot, which is more pronounced at Ca=0.25. This feature is qualitatively captured by the model. The viscoelastic drop in the Newtonian matrix shows a hint of an overshoot only at Ca=0.25. For this system, model prediction are very close to the experiments.

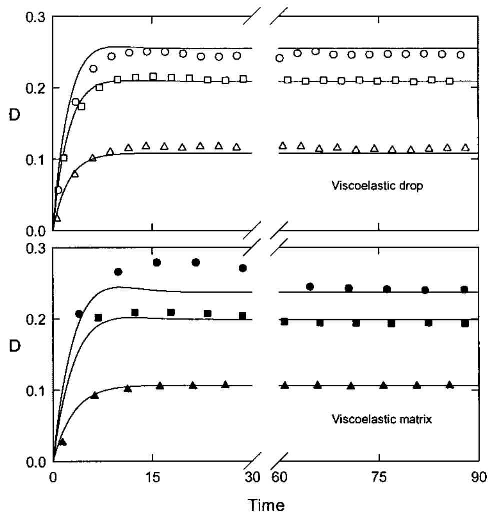

FIGURE 3 – Transient behaviour of the deformation parameter D vs. dimensionless time, at various Ca, for λ=1. Upper panel: Viscoelastic drop in Newtonian matrix (p=0, p_d=1.1, Ψ_d=0); Lower panel: Newtonian drop in viscoelastic matrix (p=1.1, Ψ=0, p_d=0). ▲,△ Ca=0.1; ■,□ Ca=0.2; ●,○ Ca=0.25. Lines are the corresponding model predictions.

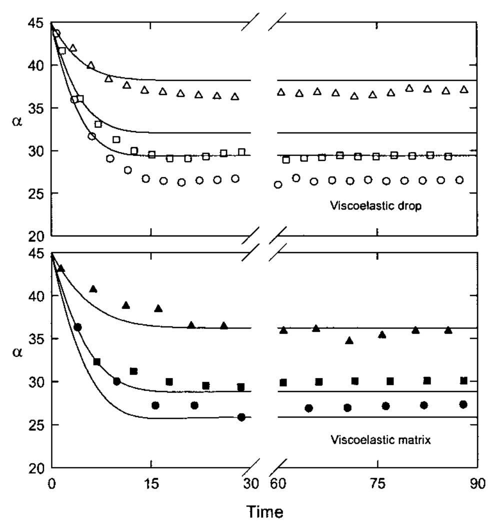

FIGURE 4 – Transient behaviour of the orientation angle α vs. dimensionless time, at various Ca, for λ=1. Upper panel: Viscoelastic drop in Newtonian matrix (p=0, p_d=1.1, Ψ_d=0); Lower panel: Newtonian drop in viscoelastic matrix (p=1.1, Ψ=0, p_d=0). ▲,△ Ca=0.1; ■,□ Ca=0.2; ●,○ Ca=0.25. Lines are the corresponding model predictions.

Figure 4 shows the transient behaviour of drop orientation angle α. Agreement between theory and experiments is less satisfactory for this quantity than for the deformation parameter D, as it already was at steady state (see fig.2). Of the two systems, the one with the viscoelastic matrix is here better described by the model.

CONCLUSIONS

In this paper, single drop dynamics under shear upon inception of flow have been studied, both experimentally and theoretically, for systems with a viscoelastic component. For the first time, two "inverse" non-Newtonian systems are considered, namely, with a Newtonian drop immersed in a Boger fluid, and vice versa. To highlight the effects of outer/inner elasticity, the two systems are so chosen as to have the same Newtonian parameter λ, and the same degree of elasticity, either carried by the matrix, or by the drop phase. Experimental data have been taken with computer-assisted video microscopy, observing the drop from the vorticity direction of the shear flow. Data have been compared with the predictions from a recently proposed model (Maffettone and Greco[5]). It has been shown that the model is capable of describing both the non-Newtonian configurations adequately, giving quantitative predictions in most cases, up to moderate drop deformations. It has been found that the presence of a viscoelastic component inhibits drop deformation and enhances orientation towards the shear direction, when compared to the equivalent (i.e., at the same λ) fully Newtonian system.

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