Microfluidic mixing of low viscosity Boger fluids

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Abstract This study is focused on the development of low viscosity Boger fluids and on the investigation of their elasticity on emulsion formation. Non-Newtonian continuous phases (Boger fluids) made of two different molecular weight Polyacrylamide in water plus glycerol solutions were used. While, as Newtonian continuous phase, a water plus glycerol solution showing the same viscosity as the non-Newtonian one was prepared and as dispersed phase silicon oil was used. Visualization of these emulsions flowing through a micromixer was useful in order to extract quantitative informations of their behavior, such as the velocity profile and droplets' size distribution. Then the formation of vortex upstream of a divergent-convergent configuration has been shown as the wall migration effect, which drives droplets away from the walls and toward the center of the microcapillary investigated.

Keywords: Mixing, non-Newtonian, Boger fluids, Microfluidics

1. Introduction

Liquid-liquid mixing is a common industrial practice, widely used in a variety of application, ranging from polymer synthesis and processing to biotechnology. Despite the extensive literature available on the topic, liquid-liquid mixing is still one of the most difficult and least understood mixing problems, especially when one of the two phases shows a non-Newtonian behavior; in fact the case of a Newtonian drops, in terms of deformation, relaxation and breakup in a Newtonian fluid has been extensively studied, both numerically and experimentally as in the pioneering works of Taylor (1934), Grace (1982) and Rallison (1984) but most of the fluids used in the industries show non-Newtonian behavior. It is also well known that the viscoelasticity of one of the phases can prevent the break-up of a single drop in a controlled flow as studied by Guido (2003) and Sibillo (2004), but very little is known about the mixing of non-diluted emulsion, when one or both the liquid phases show non-Newtonian behavior. A comprehensive characterization of liquid-liquid mixing in these systems is still missing and their application is based more on intuition and vendors claims than on scientific data.
Moreover since non-Newtonian fluids can have elastic behavior and at the same time exhibit nonlinear viscous effects like shear-thinning of the viscosity, it is particularly difficult to study viscoelastic flows in isolation from other effects. However, there's a class of viscoelastic fluids, known as Boger fluids, in which the viscosity is nearly constant with the shear rate. These fluids are particularly important because they enable elastic effects to be probed separately from shear thinning effects; comparing the viscosity behavior of a Boger fluid flow with that of a Newtonian fluid allows one to assess the influence of elasticity. In order to estimate the magnitude of non-Newtonian effects, a dimensionless

number, the Weissenberg number Wi, has to be considered. It is defined as the ratio between the first normal stress difference and the shear stress and represents a measure for elastic versus viscous forces in a viscoelastic medium.

$$\mathrm{Wi} = \lambda\gamma_{dot} \qquad 1)$$

The importance of Weissenberg number is even more clear at microscale because it can achieve high values also for low elastic fluids whilst also maintaining small Reynolds numbers. On the other hand, on the macroscale in order to induce relevant elastic responses (high *Wi*), tipically high *Re* numbers are also obtained, as a consequence the effects of viscoelasticity can be dampened by the competing effects of fluid inertia.
The importance of the device length scale and its effect on fluid elasticity is reflected in the definition of the elasticity number, El, which is dependent only on fluid properties (relaxation time λ, solution viscosity η, and fluid density ρ) and the characteristic length scale of the device,

$$\mathrm{El} = \frac{\lambda\eta}{\rho l^2} \qquad 2)$$

In literature has been demonstrated by (Groisman and Quake, 2004; James and Saringer, 1982) and in the more recent work of (Rodd et al., 2007) that the reduced length scales associated with microfluidic devices can enhance the magnitude of viscoelastic effects in dilute polymer solutions but very few experiments have been conducted specifically to test the effect of the elasticity number on complex viscoelastic flows.
Many works on the topic regards fluid dynamic behavior of viscoelastic fluids in convergent geometries, mostly contractions 4:1, because the flow of viscoelastic fluids through sudden contractions generates complex flow pattern, high shear rate close to the walls and high extension rate along the centerline upstream and downstream of the contraction, then in such geometries fluid properties, such as the elasticity, can be studied.
Contraction flows have been the subject matter of numerous experimental and numerical works since 1966 when (Vrentas et al., 1966) studied the Newtonian fluid behavior through an axisymmetric contraction and then have been the subject of detailed review by (Boger, 1987) and (White et al., 1987), in which the complex effect of flow geometry and fluid rheology were considered or more recent works as (Hulsen, 1993), (Genieser et al., 2003; Hulsen, 1993; Nigen and Walters, 2002; Rodd et al., 2005; Sunarso et al., 2007).
Another effect that has to take into account in fluid dynamic behavior of droplets in a continuous phase in a capillary is the migration away from the walls towards the center; effect that is very complex and depends both on flow and on fluid characteristics. The migration of emulsion droplets remains a largely unexplored area of study, despite the existence of an extensive literature on the analogous problem of solid particles migration (D'Avino et al., 2013; Segre and Silberberg, 1961). The case of migration of multiple droplets was studied theoretically by (Loewenberg and Hinch, 1997) but very few experiments were performed to validate the theory (Hudson, 2003; King and Leighton Jr, 2001).
In the present work the setup of a microsystem for the formation of emulsions made of silicon droplets as dispersed phase and as continuous phase a Newtonian and non-Newtonian matrix has been performed. Then the effect of elasticity on liquid-liquid mixing comparing fluid dynamic behavior of Newtonian droplets in a Newtonian and non-Newtonian matrix has been analyzed. Experiments are performed over a range of flow conditions corresponding to $0.1<\mathrm{Re}<1.5$ and $1<\mathrm{Wi}<12$. Then the behavior of two Boger fluids in 1.5:1 axisymmetric contraction geometry to investigate the role of fluid elasticity was studied and, as comparison, experiments on Newtonian liquids with the same shear viscosity as the Boger fluids are also carried out.

2. Materials and methods

As a continuous reference fluid, a system made of water and glycerin (79.74% wt) that shows a Newtonian behavior, then with a constant viscosity of 0.06 Pa·s, is used. For simplicity this fluid will be referred in the paper as NF.
In order to increase the elasticity and then to study the viscoelastic effect on mixing efficiency a polymer is added to the water plus glycerin solution, by forming low viscosity Boger fluids, that were used as continuous phase. These fluids consist of dilute concentrations of high molecular weight polymer in a Newtonian solvent, made of 76% glycerin-water. Two fluids have been formulated dissolving 75 ppm of two different anionic polyacrylamides (Dryfloc 974 by SNF Italy, Mw = 7000 KDa and by Sigma Aldrich Mw=5.000-6.000kDa) in a glycerin–water mixture.
The difference between the two PAA fluids is that the one from Sigma Aldrich, that has a lower molecular weight, shows a non-Newtonian behavior and low elasticity, and it will be named BF1, while the one purchased by SNF Italy shows a more elastic behavior, in the following as BF2.
The dispersed phase is a blend of 0.02 Pa·s and 0.01 Pa·s Newtonian silicon oil (Dow Corning) in order to maintain the same viscosity of the suspending fluid of 0.05 Pa·s.
Fig. 1 shows a drawing and a scheme of the experimental set-up. The reagents were injected into the microsystem with two glass syringes (supplied by Hamilton) placed on syringe pumps (Harvard PUMP 11 Plus Dual). The syringes are connected by plastic tubes to a stainless steel T-junction of 1 mm, where a premix of the phases takes place, and then the device is connected to two stainless steel frits in 20 μm porosity (all supplied by Upchurch scientific), that is where the efficient mixing occurs. Then the emulsion flows through a silica capillary of 320 μm inner diameter (Polymicro Technologies), that is placed on the motorized x-y stage of an inverted microscope (Zeiss Axiovert 100), that allows the fluid dynamic behavior of the emulsion to be observed and analyzed. The use of microcapillaries allows to generate large deformation rates and then high Weissenberg numbers also in low viscosity elastic fluids, whilst maintaining small Reynolds numbers, that is impossible in macroscale systems.
Images of the flowing emulsions were acquired by a high speed camera (Phantom 4.3, operated up to 4,000 frames/s) that can record clear images of drops in a continuous phase. Such sharp images of drops enable us to make a quantitative analysis of drops fluid dynamic in the silica microcapillary. The large arrays of images (around 15,000 for each run) recorded by the high speed camera were processed off-line by image analysis technique (Image Pro Plus 7) allowing to isolate the subsets of images with fluids passing through the field of view and then extracting quantitative features, such as the velocity profile. The experiments were carried out at room temperature, about 25°C for different matrix drop fluids with approximately the same viscosity and different elasticity.
In order to study the fluid dynamic behavior of the emulsion in a convergent system, a double capillary in a concentric configuration, with the silica capillary diameters' of 320 μm and 520 μm silica capillary was used, as shown in fig. 1

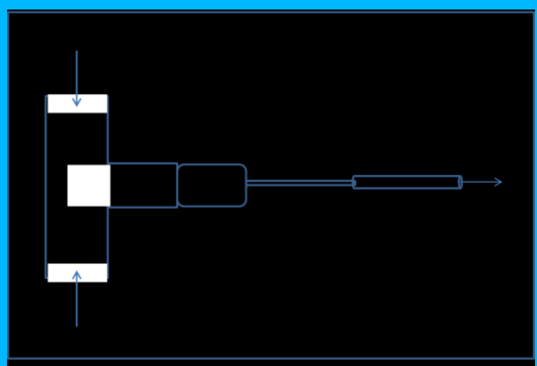

Fig.1 Experimental setup: micromixer with a double capillary

3. Results

The present study was focused on elasticity effects on liquid-liquid mixing.
The first step of this experimental work was the comparison of velocity profile observed using a Newtonian matrix, made of water plus glycerin 79.74%, and a non-Newtonian, made

of PAA75, in a single capillary of d_{in}=320μm (Fig.2).

During the experiment, at each pressure drop one movie is acquired. A movie usually contains a number of images (frames) depending on the frame rate imposed by the software; in this experiment the high speed camera operated at about 1000 frames/s. The images were analyzed by image processes techniques to extract quantitative information like the velocity profile. In particular by following droplets position frame by frame, an Euclidean distance versus time plot can be generated. The slope of this plot is emulsion velocity.

The experiment agrees well with theory confirming the newtonian behavior of NF, showing a parabolic-like behavior as described by Poiseuille's law. Moreover its velocity profile is observed to be rounder compared with the Boger one that shows a more flat trend and then behaves as a Bingham fluid at high velocities.

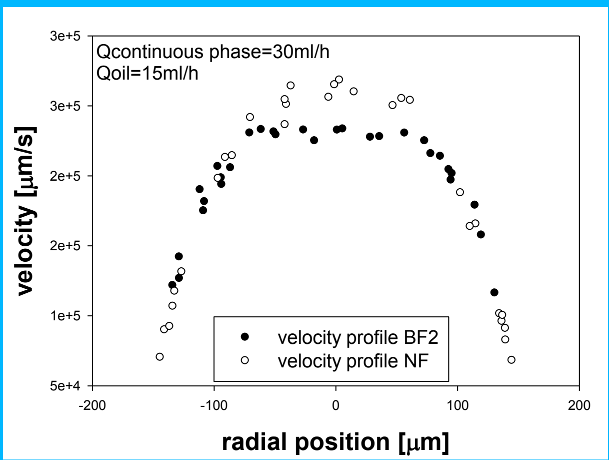

Fig.2 Velocity profile of NF and BF2

Then particle size distribution of droplets in matrix of different elasticity has been performed, showing that droplets in BF2 matrix are bigger than in NF one, as known in literature for single droplets where it has been demonstrated that the viscoelasticity of one of the phases can prevent the break-up.

Moreover entrance effects in a convergent system has been analyzed and the formation of vortex for Boger fluid at higher elasticity has been visualized as shown in Fig. 3. This effect does occur neither for Newtonian fluid nor for BF1, then it is attributable to the elasticity of the matrix phase.

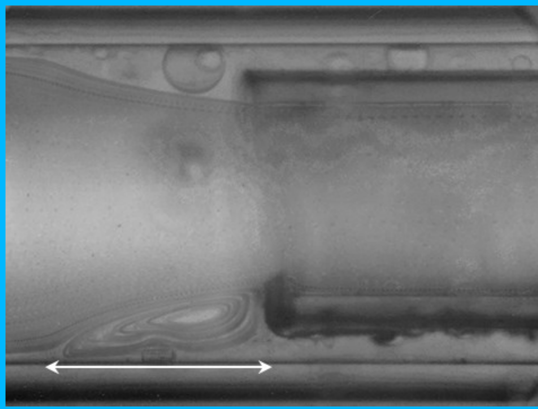

Fig.3 Formation of vortex for BF2

Finally another evidence of the influence of elasticity is the migration of droplets away from the walls of the capillary, creating the so called depletion layer that scales with Weissenberg and is much bigger for BF2, that confirms the more elastic character of the fluid.

Conclusions

In this work the set-up of a microfluidic system for liquid-liquid mixing was performed. It was used for mixing emulsions with the two phases showing a Newtonian behavior and when one of the two phases shows a non-Newtonian behavior. The presence of a Boger fluid that shows a non-Newtonian response in terms of different elasticity has a great impact on mixing and fills part of literature that is still lacking.

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