Non-Newtonian Liquid-Liquid Fluids in Kenics Static Mixers

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Immiscible liquid-liquid suspensions, such as emulsions and polymer blends, are frequently encountered in a variety of applications, e.g., cosmetics and pharmaceuticals design, food processing, and plastics technology. Mixing efficiency of such systems is greatly influenced by the property of the two phases. In particular, most of the fluids used by the industry show Non-Newtonian behaviour. This work is concerned with the application of static mixers to form biphasic liquid dispersions in the laminar flow regime; in particular the effects on the mixing efficiency of elasticity of one phase will be discussed. To this aim, appropriate fluids showing constant viscosity and weak elasticity, have been prepared. To analyze mixer performance, drop size distribution immediately after the last mixing element was measured via contrast enhanced video microscopy and image analysis. The stability of the emulsions was measured by Time Lapse microscopy, also in the presence of surfactants.

1. Introduction

Liquid-liquid mixing is a common industrial practice, widely used in a variety of application, ranging from polymer synthesis (Farzi et al., 2011) and processing (Middleman 1977) to biotechnology (Junker et al., 1994). Despite being one of the key issue of chemical engineering (Asprion et al., 2011) and the extensive literature available on the topic (Paul et al., 2003; Rauline et al., 2000; Hobbs & Muzzio, 1998), liquid-liquid mixing is still one of the most difficult and least understood mixing problems.

In general the flow can strongly influence the microstructure of multiphase systems, up to the formation of ordered structures (Caserta et al., 2008), that can be due to the fluid rheology Caserta and Guido, 2012), or induce migration of the inclusions due to non-Newtonian effects (Caserta et al. 2011).

Different technical solution are available for the mixing of liquid-liquid systems, depending on the type of processed fluids, ranging from the mechanical agitators to the in line static mixers. Static mixers consist of a series of motionless inserts installed in pipes or transfer tubes. Their purpose is to divide and redistribute the fluid streams sequentially until good mixing has been achieved. Indeed, they offer narrower residence time distribution, lower capital and operating costs and minimal maintenance requirements. In these devices, the energy of mixing is derived from the extra pressure loss needed to pump the fluids through the mixing elements, with respect to that needed if the fluid were flowing in the same tube, in absence of mixing elements. Various techniques have been used in the examination of static mixer performance: cross-section of mixtures of materials of two colors have been examined (Hall and Godfrey, 1965), conductivity profiles for the mixing of two streams identical except for conductivity (Chakrabarti, 1979) have been determined, fast competing reactions have been used to compare laminar flow micro-mixing in empty tubes and static mixers (Meyer et al., 1955). However, although predictive methods for mixture quality are often claimed, the basic understanding that governs static mixer performance is still quite limited. Most of the fluids used in the industries show non-Newtonian behaviour, it is well known that the viscoelasticity of one of the phases can prevent the break-up of a single drop in a controlled flow (Sibillo et al., 2004), but very few is known about the mixing of non-diluted emulsion, when of 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.

In this work we investigated the influence of the viscoelasticity of one of the phases on the mixing efficiency both using mechanical agitators and Kenics static mixers. Low viscosity water based Boger fluid has been ad hoc formulated in order to limit the pressure loss, the oil phase was chosen as Newtonian silicon oil. In order to stabilize the processed emulsion surfactants were added to the oil phase. Some preliminary results on the mixing efficiency and emulsion stability are here reported both for of water in oil and oil in water cases.

2. Materials & Methods

Low viscosity Boger fluids (Stokes et al., 2001a; Stokes et al., 2001b) were used as aqueous phase, the fluid consist of dilute concentrations of high molecular weight polymer in a Newtonian solvent, made of 76 wt% glycerin-water. Two different fluids have been formulated using polyacrylamide Separan (PAA) (Dow Chemical Ltd) and xanthan gum Keltrol (XGh) (Kelco) as high molecular weight polymer. The viscosity of the phases was kept low in order to reduce the pressure loss during the processing.

The polymer solutions were prepared by first dissolving the appropriate amount of polymer into deionized water to make a stock solution with a polymer concentration of 0.1 wt%. The water was warmed to about 40 °C and the polymer was added gradually to the water while continually swirling the container in order to disperse the polymer and avoid agglomeration. Sodium azide was added to the stock solution (< 0:02 wt %) to prevent bacterial contamination. The stock solutions were placed in a beaker with a magnetic stirrer at very low rotation rates for about 48 h and, once the polymer was fully dissolved, the solutions were stored in the refrigerator. The experimental solutions were made by adding the appropriate amounts of polymer stock solution to the required glycerol and sodium azide in order to obtain the desired final polymer concentration, the balance was made up with deionised water.

Rheological measurements were carried out using a stress controlled rheometer (Bohlin, CVO 120), due to the low viscosity and weak elasticity of the fluids; the rheometer sensibility was enhanced by using a double gap rotational geometry. In Figure 1 the viscosity is reported as function of shear rate for samples at different polymer concentration for Polyacrylamide (left) and Xantan gum (right), T= 20°C. Polyacrylamide fluid exhibits constant viscosity for all shear rates considered, while Xantan gum based fluids show a slight shear thinning for low shear rates (about 1 s^{-1}).
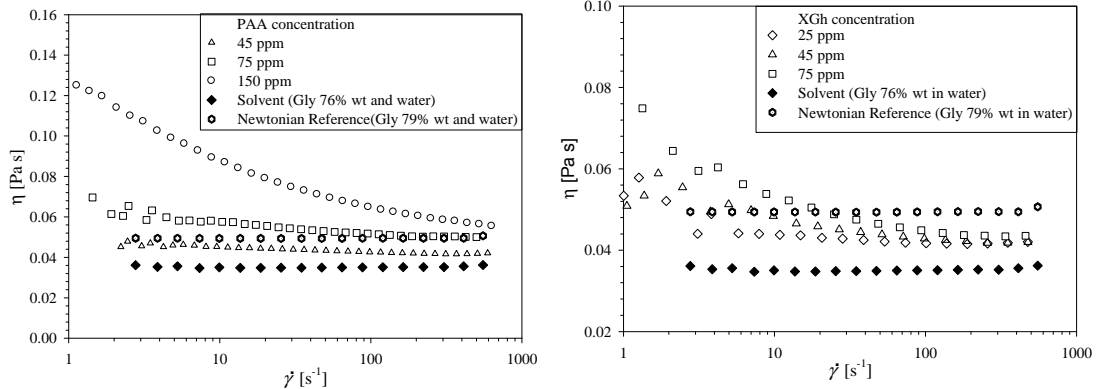

Figure 1. Viscosity vs shear rate at different polymer concentrations, T= 20°C. Left: Polyacrylamide, Right: Xantan Gum.

In order to quantify the first normal stress difference (N1), the first normal stress coefficient was estimated from dynamic measurements according to eq 1.

$$\Psi_1 = \frac{N_1}{\dot{\gamma}^2} = \lim_{\dot{\gamma} \to 0} \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2} = 2 \lim_{\omega \to 0} \frac{G'(\omega)}{\omega^2} \sim 2\,G' \tag{1}$$

In Figure 2 the elastic modulus (G') is reported as a function of the frequency for both PAA (left) and XG (right) at different solution. As first approximation N1 can be estimated assuming $\omega = \dot{\gamma} = 1$ s^{-1} and assuming the fluid as a second order one.
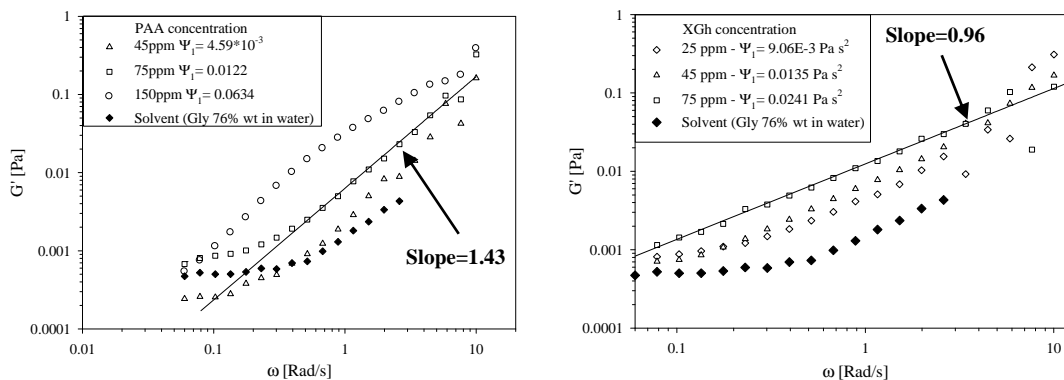
Figure 2: Storage modulus as function of oscillation frequency for different polymer concentration, T= 20°C. Left: Polyacrylamide, Right: Xantan Gum.

The fluids selected as non-newtonian phase for the mixing experiments were at 75 ppm both for the PAA and XGh fluid.

As oil phase, Newtonian silicon oils (SO) of different molecular weight (Dow Corning 20cst, 1000cst and 6000cst) were used. In this work Oil in Water and Water in Oil mixtures at 10 and 90 % of oil phase have been mixed, we will here present only results relative to the oil matrix case.

In order to quantify the influence of viscoelasticity on the mixing efficiency, a reference Newtonian fluid (GLY), obtained by mixing water and glycerin in an appropriate concentration (79.7%wt) to obtain the same viscosity of the non-Newtonian reference will be used.

The interfacial tensions σ of the mixtures used were measured observing the deformation of a single drop of water based phase in a matrix of SO6000, under simple shear flow at constant shear rate ($\dot{\gamma}$). The flow is realized by means of a parallel plate rheo-optical apparatus (Caserta et al., 2007). Images of deformed droplets, observed along the vorticity axis, are acquired by a high speed camera (Phantom 640) (Tomaiuolo et al.; 2012) mounted on an optical microscope (Zeiss Axioscope). For each system the drop deformation was fit according to the Shapira-Haber theory (Shapira & Haber, 1990), an extension of Taylor (Taylor, 1934) model to confined systems. (Eq. 2) relates the steady state deformation parameter D=(a-b)/(a+b), where a and b are respectively the major and minor axis of the ellipsoidal shape of the deformed droplet, to the capillary number $Ca = \frac{\eta_m \dot{\gamma} R}{\sigma}$, the ratio $\lambda = \frac{\eta_d}{\eta_m}$ of the droplet vs matrix viscosity; Cs is a geometrical parameter, R the droplet undeformed ratio, d is the gap between the plates.

$$D = \left[1 + C_S \frac{1+2.5\lambda}{1+\lambda} \left(\frac{R}{d} \right)^3 \right] \frac{19\lambda+16}{16\lambda+16} Ca \qquad (2)$$

In Figure 3 the experimental values are compared to Shapira-Haber prediction and to the Taylor unconfined equation.
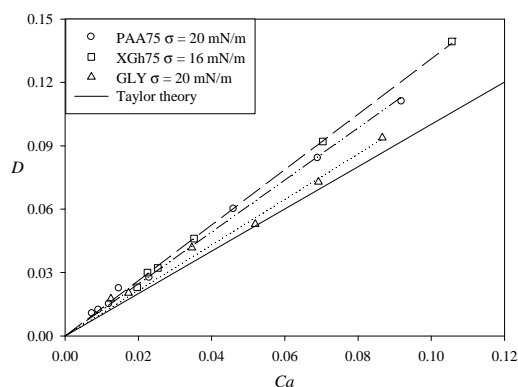

Figure 3 – Deformation parameter D vs Ca for the three systems. Continuous line is the Taylor unconfined prediction, dashed, dash-dot and dotted lines are he Shapira Haber theory for each system.

It's worth mentioning that the fluids selected are expected to show significant differences in terms of deformation and break-up of single drop in simple shear flow (Sibillo et al., 2004).

3. Results

It's known from the literature (Minale et al., 2010) that higher viscoelastic effects are expected when the viscoelastic phase is the continuous one, so we firstly chose to use water phase (Boger fluids or Newtonian GLY) as matrix and 20cSt silicon oil as drop phase. Due to the low viscosity of the matrix phase, a fast coalescence phenomena was observed, resulting in fast morphological changes over time. To suppress coalescence phenomena, surfactants (Tweed/Span) were added.

To further increase sample stability we used the 6000 cst oil as matrix phase, and water based Newtonian/Boger fluid as drop phase. In the following we report only some preliminary results obtained for the case of water in oil emulsion, mixed with kenics static mixers. To investigate the influence of the viscoelasticity of the drop phase three different disperse phases have been used: Newtonian GLY, PAA 75 ppm and XGh 75 ppm, the continuous phase was always the Newtonian Silicon Oil 6000 cst.

In figure 4 a mosaic of 16 images for the three emulsions (Newtonian GLY, PAA75 and XGh75) are compared, images were acquired by an automated video microscopy workstation (Vasaturo et al., 2012) equipped with a high sensitivity camera (Hamamatsu).
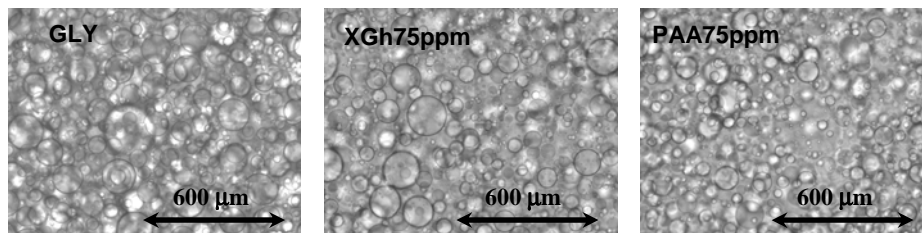

Figure 4. Images of emulsion obtained with kenics static mixers. Continuous phase is SO 6000 cst, disperse phase is Newtonian GLY (left), PAA 75ppm (middle), Xantan gum 75ppm (right).

The tree samples appear similar after a qualitative comparison of the images in Figure 4. In Figure 5 we report the drop size distributions for a quantitative comparison. The numerical distribution, (Figure 5a) show only minimal differences, in particular XGh 75 and GLY appear to be almost superimposed, while the PAA 75 appeared slightly better mixed. The cumulative volumetric, reported in Figure 5b, enhances the differences in the distributions at the higher diameters, this test is focused to investigate what is the size of the drop corresponding to most of the volume of the dispersed phase added to the mixture. The large diameters tail of the distribution show better mixing for the XGh 75.
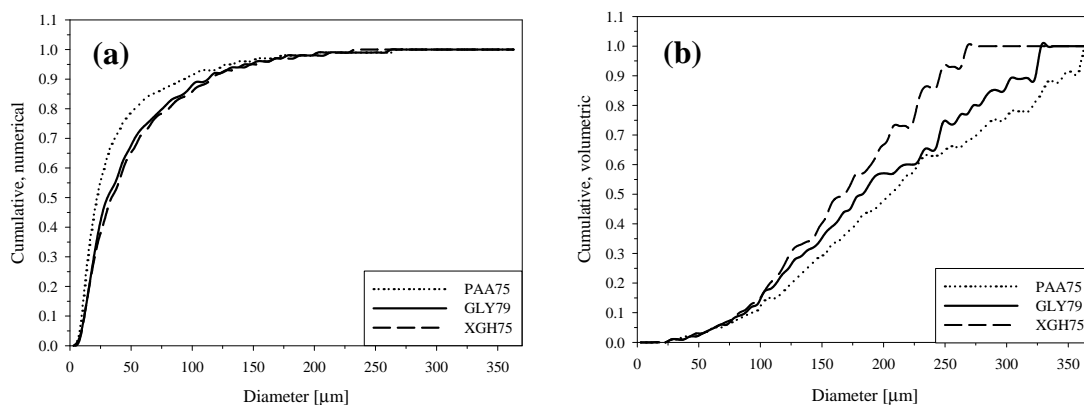

Figure 5. Particle size cumulative distribution for Newtonian and non Newtonian fluids. A) numeric, B) volumetric.

In Table 1 we report for the tree samples different average diameter, in microns. The reported error is the statistical relevance of the measure for numeric (Caserta et al., 2004) and volumetric mean diameters (Caserta et al., 2005). As expected from previous observations, most of the values are within the error bar for the three different samples, the only significant difference being for volume averaged diameter D43, representative of the higher diameter tail of the distribution. As observed in the charts, XGh75 shows a higher mixing efficiency.

The expected influence of the elasticity was to delay break-up phenomena, so resulting in a lower mixing efficiency. The effect was expected to be limited in the case the elasticity was only in the drop phase,

compared to the case of elastic matrix. In our case PAA75 shows substantially the same mixing efficiency compared to the Newtonian GLY, while XGg75 showed partial improvement in the mixing efficiency in the large diameter tail of the distribution. The higher mixing of the XGh75 could be due to the lower value of the interfacial tension, as reported in Figure 3. This is not unexpected since XGh is often used as emulsifying agent.

	D10	D32	D30	D43
GLY79	49±2	147±10	88±1	190±16
PAA75	38±7	156±6	81±6	208±15
XGh75	51±5	134±4	86±5	164±0.1

Table 1. Measured average diameters for mixtures with Newtonian and non-Newtonian disperse phase, values are in μm.

It is worth mentioning we cannot completely exclude the presence of coalescence phenomena (Caserta et al., 2006) or dynamic diffusion among the phases, even if they are immiscible (De Luca et al., 2008), due to possible poly-dispersities in the molecular weight distribution (Jonas et al., 2010), both during the mixing flow and during the sampling process, partially affecting our results.

The conclusion we can assume is that the differences induced by the viscoelasticity of the dispersed phase, in the range of values here investigated, are only limited and partially covered by the error induced by the presence of coalescence phenomena, partially by differences in the interfacial tension.

In order to further suppress coalescence phenomena, 0.5% wt Span20, a non-ionic surfactant, was added to the silicon oil phase. In Figure 6 we report the images of the system mixed using the Keincs apparatus. Comparing Figure 6 with the images in Figure 4 it is evident a strong influence of the surfactant (Pommella et al., 2012) to the mixing phenomena. The average drop size obtained in the presence of a limited quantity of Span 20 is certainly lower.
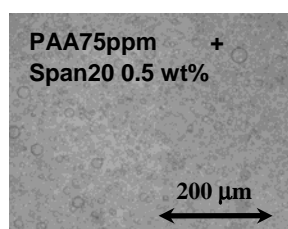

Figure 6. Images of emulsion obtained with kenics static mixers. Continuous phase is SO 6000 cst + 0.5 % wt Span21, disperse phase is PAA 75ppm.

In conclusion we presented here a methodology to investigate the influence of the viscoelasticity of one of the phases on the mixing phenomena. Some preliminary results show limited influence of the viscoelasticity of the dispersed phase, while a strong effect of the interfacial tension was observed. In particular even small quantities of surfactants can lead significant differences in the mixing efficiency. This particular aspect will be widely investigated in the future.

The presence of fast coalescence phenomena did not allowed a detailed investigation in the case of viscoelastic matrix, due to the limited viscosity of the phase. Further investigation will be done, formulating a Boger fluid with a viscosity high enough to reduce the effect of the coalescence, but not as high as to make the pressure loss in the mixing apparatus unaffordable.

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