Gel formation of low viscosity Boger fluids under high shear and extensional strain rate flow conditions

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Introduction

The flow of non-Newtonian fluids in microscale devices, especially those possessing an extensional component, are normally very complex to understand because of their shear rate dependent viscosity and elastic effects [1]. Boger fluids have a viscosity which is shear independent and therefore elastic behavior can be analyzed isolated from other non-linear effects.

Aqueous solutions of polyacrylamide (PAA) are very common fluids in microfluidics with complex fluids. Aitkadi and co-workers [2] conducted an experimental study to investigate the effect of the addition of salt on viscoelastic properties of partially hydrolyzed PAA in aqueous solutions showing that salt had a stabilizing effect on the solution viscosity. In this way it would be possible to prepare a Boger fluid, from polyacrylamide aqueous solutions, with some degree of elasticity and a nearly constant viscosity.

Several authors have also been dealing with the effect of polymer concentration [3,4], and the addition of NaCl [5,6] on the fluid rheology, and a more recent study investigates the flow of low viscosity Boger fluids through a microfluidic device [7].

It has been observed that when these Boger fluids flow through a porous medium, the pressure drop (Δp) across the bed varies linearly with the flow rate (Q), at low values of Q, as for Newtonian fluids. At a critical flow rate, elastic effects set in and Δp grows above the low-flow-rate linear regime. Subsequently, there is a more dramatic increase in the slope of the pressure drop curve at high deformation rates.

In this work, we try to elucidate the reason for this dramatic increase in the slope of the pressure gradient curve, which may be due to a spontaneous gelation of the polymer solutions subject to high shear and/or elongational strain rates.

Material and Methods

Boger Fluids

Polyacrylamide with a molecular weight M_w = 18x10^6 g/mol (Polysciences) was used to prepare the viscoelastic solutions by mixing the polymer into the solvent (de-ionized water) at different concentrations (50 and 125 ppm w/w) with 1% of NaCl (w/w), using magnetic stirrers at low speeds in order to prevent mechanical degradation of the polymer.

Fluid Rheology

Rheological characterization in shear flow was performed on a stress-controlled shear rheometer (Anton Paar, model Physica MCR301), with a plate-plate geometry of 50 mm diameter and a gap of 0.10 mm. Steady shear flow measurements in the range of shear rates, $0.1 \leq \dot{\gamma} / \mathrm{s}^{-1} \leq 10000$, were carried out at 20 ºC. In addition, large amplitude oscillatory shear experiments (LAOS) were performed in order to evaluate the progressive transition from linear to nonlinear rheological response.

Flow visualizations

The microchannel used to observe the flow effects at high elongational strain rates, is planar and

presents a hyperbolic contraction followed by an abrupt expansion. The total width of the channel is D_1 = 400 μm, the minimum width of the contraction is D_2 = 54 μm and the length of the hyperbolic contraction is L_c = 126 ± 1 μm, resulting in a total Hencky strain of $\varepsilon_H = \ln(D_1/D_2) = 2.0$ [7].
The depth of the microchannel is constant, h = 45 μm. Flow visualizations were obtained using streak photography. The optical setup consists of an inverted epi-fluorescence microscope (DMIL LED, Leica Microsystems GmbH) equipped with a CCD camera (DFC350 FX, Leica Microsystems GmbH), a light source (100 W mercury lamp) and a filter cube (Leica Microsystems GmbH, excitation filter BP 530-545 nm, dichroic 565 nm and barrier filter 610-675 nm). A syringe pump (PHD2000, Harvard Apparatus) was used to inject the fluid and control the flow rate in the microchannel, using syringes with different volumes (50μl - 100 μl), connected to the microgeometries by Tygon tubing of 0.44 mm internal diameter. The fluids were seeded with 1 μm fluorescent tracer particles (Nile Red, Molecular Probes, Invitrogen, Ex/Em: 520/580 nm). The microgeometry containing the seeded fluid was continuously illuminated and the light reflected by the fluorescent tracer particles was imaged through the microscope objective (10X, NA = 0.25) onto the CCD array of the camera using "long" exposure times (which were varied according to the flow rate) in order to capture the pathlines of the particles.

Porous medium

The porous medium used in this work consists of a packed bed column made from a hollow acrylic cylindrical tube (1.95 cm diameter) filled with unconsolidated sand of x_{32} = 400 μm. The liquid was introduced in the column from a pressurized reservoir; the inlet pressure could be varied and was measured with a manometer (Wika Instrument Corporation, model 332.50). The flow inlet was placed at the top of the column and the outlet was located at the bottom part, where the fluid was collected and weighed along time. The pressure drop measurements were carried out between two pressure taps in the column separated by a distance of 14.7 ± 0.1 cm using differential pressure sensors (Honeywell 26PC series) covering values up to ΔP = 200 kPa [8].
The porous medium analogue is represented as microfluidic conduits with a periodic arrangement, consisting of a continuous series of contractions and expansions (symmetric and asymmetric), fabricated in PDMS using standard soft-lithography techniques and SU-8 photo-resist molds. The flow behavior of Newtonian and non-Newtonian fluids was studied at room temperature (19.5 ± 0.9 °C) for a wide range of flow rates, which were imposed using a syringe pump and Hamilton syringes. The transient response of the pressure sensors was continuously recorded until steady-state was reached. To compare the results of the microchannels with the real porous media, we measured the pressure gradient *vs*. flow rate relationship in both systems [8].

Results and Discussion

Flow through porous medium

Figure 1 represents the evolution of the pressure gradient across the sand bed as a function of the interstitial velocity (i.e. different flow rates) for the various fluids tested.

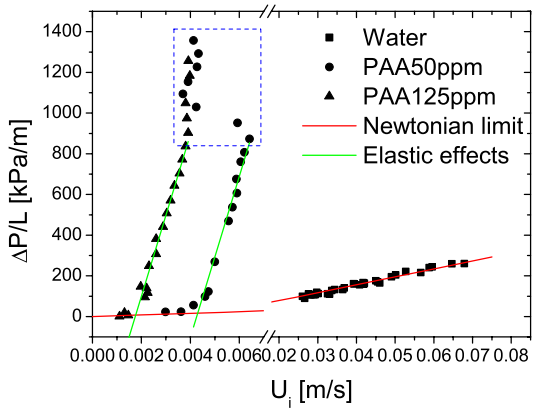

Figure 1. Influence of interstitial velocity on the measured pressure gradient through the porous medium for water, 50 and 125 ppm PAA aqueous solutions with 1% of NaCl, using sand of 400 μm.

At low velocities the evolution is linear, as for Newtonian fluids. At a critical velocity, elastic effects set in and Δp grows above the linear

regime. The solution of 125 ppm with salt requires lower interstitial velocities to trigger these elastic effects in comparison with the 50 ppm sample, which agrees with the fact that higher relaxation times are observed for high polymer concentration. Subsequently, a dramatic increase in the slope of the pressure drop curve at high flow rates is observed (delimited by a blue rectangle in Figure 1). This effect could be associated with a gelation process of the polymer solutions because of the high shear and/or extensional strain rates.

To clarify the origin of this possible gelation, different shear and extensional experiments were carried out at large deformation rates: (i) LAOS and steady-shear flow tests to measure the rheological properties at high shear rates; (ii) flow visualizations through a hyperbolic contraction microchannel (which induces a quasi-uniform extensional rate flow at the centerline of the microgeometry) to understand the effects of the high strain rates in extensional experiments.

Rheological characterization

The steady shear viscosity curves exhibit a nearly constant viscosity (Figure 2), as expected for Boger fluids, allowing in this way the study of the flow elasticity without the non-linear effects due to shear-thinning behavior.

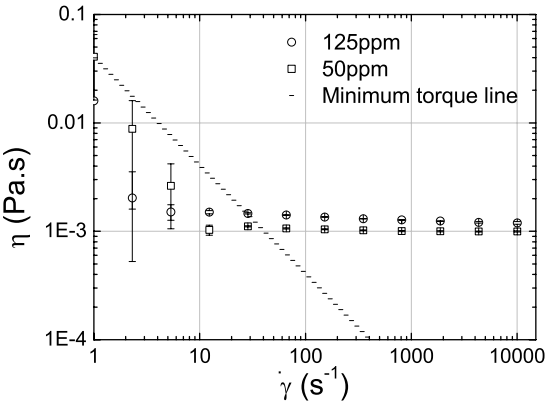

Figure 2. Viscosity curves for 125 and 50 ppm PAA aqueous solutions with 1% of NaCl.

LAOS measurements were carried out over a wide range of frequencies and strain amplitudes. Frequency sweep tests (data not shown here) show that both samples, 50 and 125 ppm, present a liquid-like behavior ($G''> G'$) in the reliability region of measurements. These results suggest that the gelation process is unrelated to the presence of high shear rates.

Flow visualizations

The flow patterns of the Boger fluid flow through the hyperbolic contraction were obtained (data not show here). Although, converging entry flows show complex flow patterns combining both shear and extensionally dominated regions, along the centerline the flow is primarily extensional and essentially shear-free. High flow rates were applied in order to induce a high extensional strain rate. No sign of gelation was observed at the highest flow rate ($Q \approx 100$ ml/hr). As a result, it is possible to conclude that pure extensional strain rates are not the sole responsible for the gelation of the solutions.

Flow through analogues of porous media

Flow visualizations and pressure drop measurements through the two microchannels analogues of the porous medium were carried out to investigate if the gel formation could be due to simultaneous shear and extensional deformations.

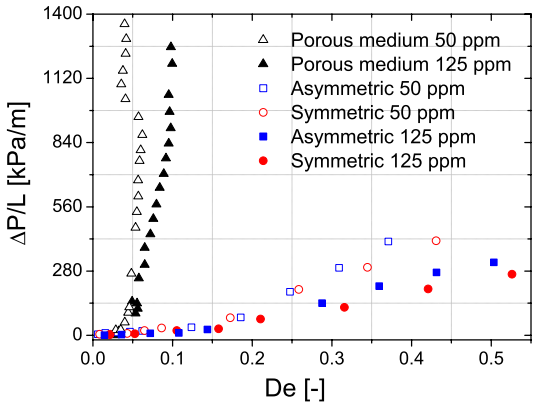

Figure 3. Influence of Deborah number on the pressure gradient through the real and the analogue porous media, for samples of 50 and 125 ppm PAA with 1% of NaCl.

In Figure 3, we compare the pressure drop measurements obtained in the porous medium analogue and in the real sand bed. In this case the pressure drop is plotted as a function of the

Deborah number, which is defined as: $De=\lambda(v/l)$, where λ is the longest relaxation time, l is a characteristic length scale (usually taken as the particle size) and v is a characteristic velocity, the interstitial velocity. The Deborah number represents a ratio of time scales of the material (λ) and of the flow process (l/v), allowing the comparison of the results obtained in the microchannels with those obtained with the sand bed. As can be seen in the results of Figure 3, as *De* is increased the analogue microchannels are no longer able to replicate the behavior of the flow in the real porous medium. In particular, the third slope observed in Figure 1, which is related to the possible formation of gel, is not achieved in the microchannels. Moreover, flow visualizations of the fluid flow through the asymmetric and symmetric configurations (Figure 4) did not provide new insights about the gelation phenomenon observed in the real porous medium.

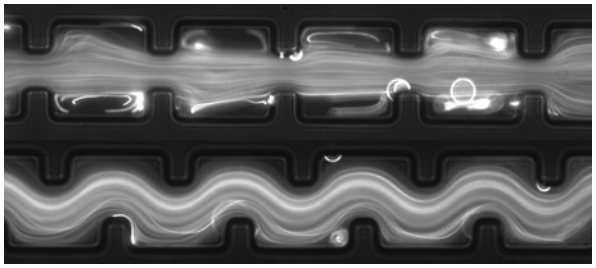

Figure 4. Flow visualizations of the highest polymer concentration (125ppm) through the symmetric (top) and asymmetric (bottom) configurations, Q=0.2 ml/hr.

We conclude that the 1D analogue porous media are not able to reproduce the gel formation of the viscoelastic fluid occurring in the real porous medium and, for that reason, further work is required in order to understand the flow conditions for gelification.

Acknowledgements

Authors acknowledge funding from Fundação para a Ciência e a Tecnologia (FCT), COMPETE and FEDER through projects PTDC/ EQU-FTT/ 71800/2006, PTDC/EQU-FTT/70727/2006, PTDC/ EME-MFE/99109/2008, PTDC/EME-MFE/114322/ 2009, REEQ/928/EME/2005 and REEQ/298/EME/ 2005. F.J. Galindo-Rosales acknowledges FCT for financial support (scholarship SFRH/BPD/ 69663/2010).

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