Chemical Engineering Science 64 (2009) 4537–4542

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Measurement of dynamic capillary pressure and viscosity via the multi-sample micro-slit rheometer

Doyoung Moon, Kalman B. Migler*

Polymers Division, 100 Bureau Drive, NIST, Gaithersburg, Maryland 20899, USA

ARTICLE INFO

Article history:
Received 14 October 2008
Received in revised form 30 January 2009
Accepted 18 February 2009
Available online 6 March 2009

Keywords:
Imbibition
Dynamic capillary pressure
Contact angle
Microfluidics
Viscosity
Rheometer

ABSTRACT

We develop two direct methods to simultaneously measure the dynamic capillary pressure and the viscosity of fluids by application of differential forces during flow into micro-channels. In the first method, a series of external pressures is applied in conjunction with the dynamic capillary pressure and a "Bagley analysis" is applied to the flow front velocity, and in the second, we utilize differential gravitational forces. By explicitly measuring the dynamic capillary pressure, the measurement window of the recently developed multi-sample micro-slit rheometer is extended to the regime where capillary forces are significant. These measurement methods will be useful in understanding filling flows encountered in diverse areas such as microfluidics, oil recovery and biological transport.

Published by Elsevier Ltd.

1. Introduction

[1]The flow of fluids into micro and nanoscale pores is critically important in many applications such as viscometry (Srivastava et al., 2005; Srivastava and Burns, 2006), microfluidics (Squires and Quake, 2005), oil recovery (Hatiboglu and Babadagli, 2008), ink printing (Ridgway and Gane, 2002), tribology, dip-pen nanolithography (Tas et al., 2002) and transport in plants and living organisms (Schneider et al., 2000). The dynamics of the filling process is governed by a balance of pressures: capillary, viscous, gravitational and external. While viscous and gravitational pressures are readily measured, the dynamic capillary pressure is difficult to measure because it is coupled with the fluid's contact angle with the wall and with flow induced changes in the fluid structure, both of which vary with shear rate (Degennes, 1985). In this manuscript, we demonstrate a simple method based on the "Bagley analysis" for extraction of the dynamic capillary pressure from an analysis of the velocity of the fluid flow front.

In a capillary driven flow of fluid into a pore, the capillary number (ratio of viscous to capillary forces—see Table 1) at the fluid-air-wall interface plays a critical role. In previous studies (Hoffman, 1975), the dynamic capillary pressure, P_{cap}, has been calculated by starting with the quiescent capillary pressure and adding a correction term that is induced by the dynamic contact angle

$$P_{cap} = 2\gamma \cos(\theta)\left(\frac{1}{h} + \frac{1}{w}\right) \quad (1)$$

(for the case of a rectangular capillary) where γ is the surface tension, θ is the contact angle, and h and w are rectangular channel depth and width, respectively. But in practice, θ and γ may not be possible to measure—θ is difficult to measure in non-circular or micro-geometries geometries (Ichikawa et al., 2004; Kim and Whitesides, 1997) and is generally shear rate dependent while γ may differ from its quiescent value if the fluid is multi-component (Nath, 1999).

There are several numerical and experimental results for filling flow analysis in micro-channels, but they wrestle with the issue of the dynamic contact angle and dynamic capillary pressure (Kim et al., 2002; Choi et al., 2006). Capillary pressure can be obtained by direct measurement (Weitz et al., 1987; Calvo et al., 1991; Degennes, 1988), but the methodologies have several limitations such as applicability only to liquid/liquid systems, requiring flow through porous media or requiring independent viscosity data. Alternatively, the dynamic contact angle (Hoffman, 1975; Fermigier and Jenffer, 1991) measurement can be obtained and then the dynamic capillary pressure are estimated indirectly with Eq. (1), but the method only applies to dimensions of mm's order that are accessible by simple optical techniques. This has the limitations described previously.

Our immediate need for an accurate and robust measurement of the dynamic capillary pressure stems from our development of an instrument to measure fluid rheology at low volumes. The recently developed multi-sample micro-slit rheometer (MMR) is a pressure driven slit rheometer with miniaturized dimensions (Moon et al., 2008). The principle of operation is to apply an external gas pressure to the reservoir of the fluid/polymer of interest and track the velocity of the flow front as it fills the micro-channel. As the fluid fills the channel, it slows down due to the increasing flow resistance. By relating the flow front velocity to the fluid shear rate, we measure the viscosity as a function of shear rate. The device has been

* Corresponding author.
E-mail address: Kalman.Migler@nist.gov (K.B. Migler).

[1] Official contribution of the National Institute of Standards and Technology; not subject to copyright in the United States.

0009-2509/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.ces.2009.02.039

Table 1
Dimensionless numbers for micro-channel flow and their meaning where h is the characteristic length (the slit channel height in our system), flow velocity V_f, viscosity η, density ρ, surface tension of the fluid γ.

Dimensionless number	Notation	Formula	Meaning
Capillary number	Ca	$Ca=\frac{\eta V_f}{\gamma}$	$\frac{\text{Viscous Force}}{\text{Capillary Force}}$
Bond number	Bo	$Bo=\frac{\rho g h^2}{\gamma}$	$\frac{\text{Gravity Force}}{\text{Capillary Force}}$
Reynolds number	Re	$Re=\frac{\rho V_f h}{\eta}$	$\frac{\text{Inertia Force}}{\text{Viscous Force}}$
Weber number	We	$We=\frac{\rho V_f^2 h}{\gamma}$	$\frac{\text{Inertia Force}}{\text{Capillary Force}}$

demonstrated with volumes of 30 μL over a range of temperatures on polymer melts and solutions ranging in viscosity from 1 to 10^6 Pa s. In the previous demonstrations of the instrument, the applied minimum shear stress is much greater than that of theoretical maximum capillary force so the capillary pressure is safely ignored. However, in order to measure the rheological properties of fluids in the case of low capillary number (in practice, for viscosity less than 1 Pa s), the dynamic capillary pressure must be independently determined.

In this work we develop two methods to simultaneously determine P_{cap}, both based on the application of differential pressure. In the first case, we show that we can utilize a modified Bagley analysis (Bagley, 1957) to obtain the dynamic capillary pressure based on application of differential external pressure at the same shear rate. In the second, use the combined effect of capillary and gravity forces without an external pressure source. Once we determine P_{cap}, the viscosity calculation is straightforward.

2. Differential forces methods

For a steady flow of a Newtonian fluid in a unidirectional slit channel of length l, and height h, the viscosity η, can be measured by Agassant et al. (1991)

$$\eta=\frac{\tau_w}{\dot{\gamma}_a}=\frac{\frac{h}{2}\left(\frac{\Delta P}{l}\right)}{\frac{6}{h}V_f}=\frac{h^2\Delta P}{12}\frac{1}{lV_f} \tag{2}$$

where τ_w and $\dot{\gamma}_a$ are wall shear stress and apparent shear rate respectively, ΔP is the pressure drop along the channel and V_f is the average flow velocity. We assume the ratio of width w to depth, h, is sufficiently large enough that the side wall effect can be ignored and that inertial effects are negligible (Carreau et al., 1997). In a filling flow, where the fluid displaces air as it enters the channel, Eq. (2) can still be used provided that

$$\Delta P=P_{ext}+P_{cap}+P_{grav} \tag{3}$$

and that l is identified with the length of the fluid in the channel, rather than the total channel length.

2.1. Case I: differential external pressure

In the first method to measure the dynamic capillary pressure and viscosity, we utilize the Bagley analysis which was originally developed to separate out the pressure drop in capillary rheology of polymeric materials that stems from the extensional flow fields in the entry and exit regions from that which stems from the Poiseuille flow in the capillary itself. This is necessary in polymers because the extensional viscosity can differ greatly from the simple shear viscosity resulting in significant deviations between apparent viscosity and actual viscosity. The fundamental idea is to carry out a series of experiments where the shear rate is kept constant but the channel length varies. In the data analysis, plots of the total pressure drop at constant shear rate as a function of length are extrapolated to the pressure drop at zero length. This extrapolated pressure drop at zero flow length is due to the entrance and exit flow. In the previous MMR experiments on high viscosity melts and solutions, modification of the classic Bagley method was necessary because the MMR utilizes a filling flow rather than the more common flow through a filled capillary tube. The extrapolated pressure drop was identified with the sum of the entrance flow plus the drop due to velocity rearrangements at the flow front.

In the present case of low viscosity Newtonian fluids where the fluid can spontaneously flow into the micro-channel, we recognize that we can identify the pressure drop that occurs at the flow front with the dynamic capillary pressure. This is possible because the pressure drop in the entrance is negligible because the fluids have low elasticity and that experiments are conducted under conditions of large l/h. In our system, the range of the Reynolds number Re is 10^{-4}–1 for shear rate; $(1–10^3)\,s^{-1}$, fluid density; 10^3 kg/m^3, channel depth; 10^{-4} m, fluid viscosities; $(10^{-2}–10^{-1})$ Pa s. With these parameters, the maximum loss of fluid kinetic energy (inertia effect, $1/2\rho V_f^2$) is below 10 Pa in the entrance region which falls within the experimental uncertainty. Furthermore, once the capillary pressure as a function of shear rate is obtained, we can calculate the viscosity and deduce the dynamic contact angle as a function of shear rate.

2.2. Case II: differential gravitational pressure

For the second method to determine capillary pressure and viscosity, instead of varying the external pressure as in the above section, we add a gravitational pressure to either enhance or retard the capillary driven flow. The viscosity for a slit channel can be expressed as follows by adding gravitational force to the total pressure drop term of Eq. (2),

$$\text{Upward flow}: \quad \eta_{up}=\frac{\tau_w}{\dot{\gamma}_a}=\frac{h^2(P_{cap}^{up}-\rho g l_{up})}{12}\frac{1}{l_{up}V_{up}} \tag{4a}$$

$$\text{Downward flow}: \quad \eta_{dw}=\frac{\tau_w}{\dot{\gamma}_a}=\frac{h^2(P_{cap}^{dw}+\rho g l_{dw})}{12}\frac{1}{l_{dw}V_{dw}} \tag{4b}$$

where ρ is density of fluid, g is the gravitational acceleration constant, l_{dw}, l_{up} are the flow lengths in the downward and upward directions, respectively, ρgl is the hydraulic pressure due to gravitational force, V_{dw}, V_{up} are flow velocity, and P_{cap}^{dw}, P_{cap}^{up} are the dynamic capillary pressures. Several conditions must be met for these equations to be valid: the dynamic capillary number is sufficiently low ($Ca<1$), the gravitational force is comparable with dynamic capillary force (Bond number, $Bo\approx 1$), and the inertial force is sufficiently small compared with capillary and viscous force (Weber number, $We\ll 1$, Reynolds number, $Re<1$). The requirement that Bo is sufficiently large so that gravitational effects measurably perturb the flow has the practical constraint that only data at relatively large l is meaningful. This leads to a limited shear range over which we can make the measurements. Here, over the limited shear rate range, we introduce the assumption that the capillary pressure and the viscosity in the upward and downward flows are equal, and we then equate Eqs. (4a) and (4b) to yield

$$P_{cap}=\frac{\rho g(l_{up}+kl_{dw})}{(1-k)} \tag{5}$$

where $k=l_{up}V_{up}/l_{dw}V_{dw}$. Eq. (5) indicates that the capillary pressure can be obtained by a measurement of flow velocity as a function of length.

Finally, the viscosity can be determined by applying P_{cap} to the horizontal flow equation (Eq. (2)). This relation can be applied to a shear thinning fluid if the capillary pressure is evaluated at the same flow velocity for the two opposite vertical channels and can