

Optically monitored dip coating as a contactless viscometry method for liquid films

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Real-time interferometric monitoring of the dip coating process is applied to the study of properties of flowing liquids. Nonvolatile Newtonian oils are considered, allowing validity of a simple model after the steady state is reached where film physical thickness depends on time as $t^{-1/2}$. Measurement of two distinct mineral oil standards, under several withdrawing speeds, resulted in kinematic viscosities of 1.17 ± 0.03 and 9.9 ± 0.2 S ($1\text{ S} = 1\text{ cm}^2/\text{s}$). Agreement of these results with nominal values from the manufacturer suggests that interferometric monitoring of dip coating may become a valuable method for accurate, contactless viscometry of liquid films. Advantages and present limitations are discussed. © 2005 Optical Society of America

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1. Introduction

Production of films by the coating industry is largely based on wet bench processes, where better understanding of their temporal dynamics could facilitate control and optimization.

For the spin coating process, optical monitoring of liquid films in real time, by laser interferometry, has been in use since the past decade.¹⁻⁴

As to the dip coating process, interferometric measurements were reported by Nishida *et al.*⁵ and Qu *et al.*,⁶ both regarding the spatial profile of liquid films at fixed values of time. Temporal evolution was first reported as a result of optical interference monitoring of a multicomponent zirconyl chloride aqueous solution,⁷ where significant refractive-index variation made explicit interpretation difficult. More recently, we chose Newtonian nonvolatile mineral oils, with a constant refractive index throughout the process and allowing application of a simple model, to compare the theoretical and experimental results of temporal physical thickness evolution.⁸ The agreement that was reached has allowed us to pursue, as a continu-

ation in this research, a determination of liquid-film flow properties from the monitored dip coating process.

2. Experimental Results

The experiment, whose scheme is illustrated in Fig. 1(a), essentially consists of our measuring a diode laser beam, at a wavelength $\lambda = 660$ nm, after normal reflection by a liquid film flowing on a glass substrate. This reflected light, as in optospinography,^{1,2,4} is compared with a reference signal and later processed by a lock-in amplifier, which is connected to a computer through an analog-to-digital converter.

The high acquisition rate (typically 3.5 kHz) and the proper alignment of the optical system, leading to a small illuminated spot on the sample (diameter < 0.5 mm) at $x = x_0$, were carefully kept for detailed monitoring of the dip coating process. The bath container was routinely kept inside a transparent chamber that prevented contamination, as well as temperature inhomogeneities.

We evaluated transparent Newtonian nonvolatile mineral oils, OP60 and OP400, which are used as viscometry standards in industry and present distant viscosity values. Conversion from optical to physical thickness was possible after determination of oil refractive indices by measurement with a commercial Abbe refractometer.

3. Theoretical Results

Thickness evolution of a liquid film on a substrate with an infinite length (continuous process) can be described, under steady-state flow, by a simplified

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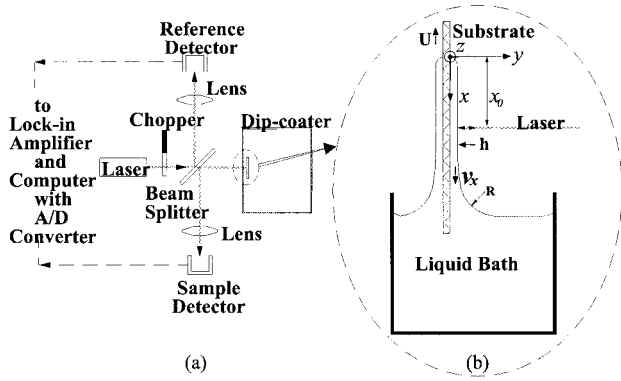


Fig. 1. (a) General scheme of the optical monitor. (b) Inset with illustration of the dip coating batch process, where laser probing is shown. A/D, analog-to-digital.

form of the Navier–Stokes equation, with regard to the coordinate system on the sample shown in Fig. 1(b)^{9,10}:

$$\sigma \frac{\partial^3 h}{\partial x^3} + \mu \frac{\partial^2 v_x}{\partial y^2} + \rho g = 0, \quad (1)$$

where major effects are considered on a fluid volume element with vertical velocity v_x as related to surface tension σ , gravity force ρg , and the coefficient of viscosity μ .

For an observer at rest on the substrate, the boundary conditions for this system are

$$v_x(y=0) = 0$$

$$\left. \frac{\partial v_x}{\partial y} \right|_{y=h} = 0. \quad (2)$$

Integration of Eq. (1) with the boundary condition of Eqs. (2) implies the following expression for the fluid flow velocity¹⁰:

$$v_x(y) = \frac{1}{\mu} \left(\sigma \frac{\partial^3 h}{\partial x^3} + \rho g \right) \left(hy - \frac{y^2}{2} \right). \quad (3)$$

The liquid flow q per film width unit, the latter shown along the z direction in Fig. 1, can be seen as the average drainage velocity $\langle v \rangle$ multiplied by the film thickness h [h_0 in Eq. (6) in Ref. 7]:

$$q = h \langle v \rangle = \int_0^h v_x(y) dy, \quad (4)$$

which then becomes

$$q = \frac{1}{\mu} \left(\sigma \frac{\partial^3 h}{\partial x^3} + \rho g \right) \frac{h^3}{3}. \quad (5)$$

The solution of Eq. (5) for continuous dip coating, when q is a constant, is described by several authors. For the batch process, however, q varies in accordance with the continuity equation¹³

$$\left(\frac{\partial h}{\partial t} \right)_x = - \left(\frac{\partial q}{\partial x} \right)_t, \quad (6)$$

which, combined with Eq. (5), leads to

$$\left(\frac{\partial h}{\partial t} \right)_x = \frac{1}{\mu} \left[\sigma \frac{h^3}{3} \frac{\partial h^4}{\partial x^4} + \left(\sigma \frac{\partial h^3}{\partial x^3} + \rho g \right) h^2 \frac{\partial h}{\partial x} \right]. \quad (7)$$

The terms with σ in Eq. (7) are associated with the pressure gradient P_σ caused by the curved meniscus surface tension. When this effect is much smaller than those from the gravity and viscosity forces (in connection with region 1 reported by Gutfinger and Tallmadge¹² as well as Spiers *et al.*¹¹), the radius of curvature R tends to infinity. Consequently,

$$P_\sigma = -\sigma \left(\frac{\partial^2 h}{\partial x^2} \right) \approx -\sigma \left(\frac{1}{R} \right) \approx 0, \quad (8)$$

and the force generated by the surface tension can be neglected, that is, $\partial P_\sigma / \partial x \approx 0$.

In the batch process, if the coincident origins of position and time are suitably chosen, and a finite substrate as shown in Fig. 1(b) is used, then the film thickness $h = h(x, t)$ can be obtained by separation of variables. This procedure leads to the solution¹²

$$h = B(x)A(t), \quad A(t) = Bt^{-1/2}; \quad B(x) = \sqrt{\frac{vx}{g}}, \quad (9)$$

where B contains the processing parameters, x is the probed position on the sample, and $\nu \equiv (\mu/\rho)$ is the kinematic viscosity.

Under more general conditions, in which the effect of the pressure gradient caused by the curved meniscus surface tension plays a significant role (in connection with region 2 reported by Gutfinger and Tallmadge¹²), several theories indicate a relationship similar to Eqs. (9), such that $B = T_0 \sqrt{vx/g}$. The extra proportionality factor T_0 is then a function of the capillarity number $Ca \equiv \mu U/\sigma$, where U is the withdrawing speed.¹¹ For $Ca < 0.01$, corresponding to low withdrawing speeds, the Landau–Levich numerical calculation led to a value $T_0 = 0.944 Ca^{1/6}$.^{9,10} As Ca increases to values larger than 1, experimental results with several liquids have shown saturation of T_0 at a constant value.¹¹ When the effects of surface tension become negligible, it has been shown by several authors that $T_0 \sim 1$, corresponding to a large Ca .^{11,14} This seems to be the case in the present study in which the withdrawing speed U was incremented until saturation of T_0 was reached, and the measure

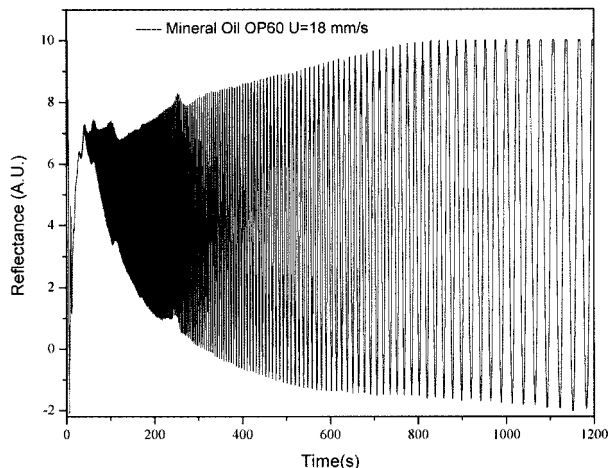


Fig. 2. Reflectance temporal evolution for mineral oil OP60 during dip coating. Refractive indices (n) at 660 nm: 1.503 ± 0.001 for a glass substrate (Brewster method) and 1.470 ± 0.001 for mineral oil OP60 (Abbe refractometry).

ment was positioned far from the curved meniscus region.

4. Results and Discussion

Using Newtonian, nonvolatile mineral oils with distinct viscosities, we performed experiments under

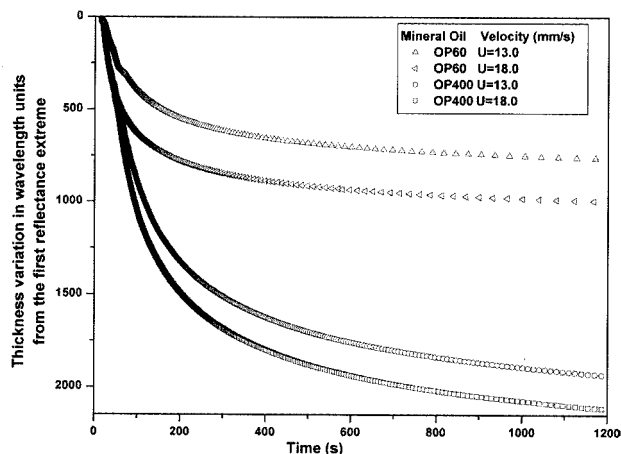


Fig. 3. Thickness variation in wavelength units ($\lambda = 660$ nm) for mineral oil (OP60 and OP400) films during dip coating at different withdrawing speeds (U). Although experimental points were obtained at each $\lambda/4$ variation, only data at each λ variation are shown for better visualization.

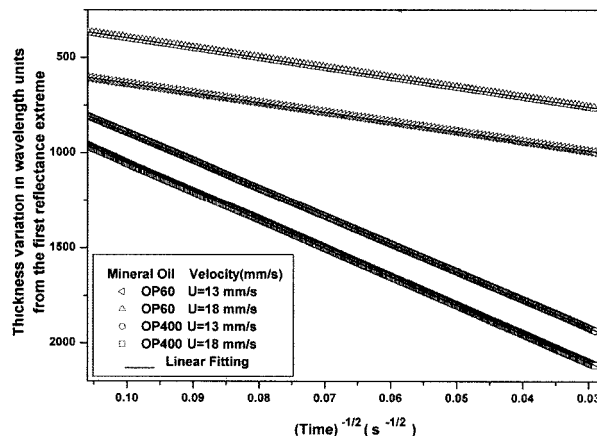


Fig. 4. Thickness variation of oil standards OP60 and OP400 versus inverse square root of processing time ($t^{-1/2}$) in open air. Although the experimental points were obtained at each $\lambda/4$ variation, only data at each λ variation are shown for better visualization ($\lambda = 660$ nm). Linear fitting corresponds to the model prediction for nonvolatile Newtonian fluids with resulting kinematic viscosity $\nu = 1.17 \pm 0.03$ S and 9.9 ± 0.2 S, respectively.

several withdrawing speeds. During processing of standard oil OP60 at 18 mm/s, for example, the interferogram shown in Fig. 2 was obtained.

Figure 3 follows from an analysis of the interferogram, considering that each interval between successive extremes corresponds to an optical thickness (physical thickness multiplied by refractive index) variation of $\lambda/4$. In Fig. 4 the same results are plotted as a function of the inverse square root of processing time.

After the initial steps of the process (when the model is not valid), the linear fitting with $t^{-1/2}$ predicted by the theoretical model (Section 3) is reached, with a standard deviation smaller than 0.04% of the slope magnitude B , as shown in Table 1.

For different liquids, B increases with increasing kinematic viscosity. At different withdrawing speeds, the slope is essentially the same for each liquid. Its kinematic viscosity is inferred from the slope of the curve fitted to the experimental data by use of Eqs. (9).

As shown in Table 1, agreement is attained between nominal values of viscosity, as provided by the manufacturer, and those obtained by the interferometric method, well within the experimental uncertainty (which also includes temperature fluctuations of ± 0.5 °C).

Table 1. Physical Properties of the Oils Under Analysis During Dip Coating

Oil	Refractive Index n	Probed Position x_0 (mm)	Slope B	Density ρ (kg/m ³)	Nominal ^a Kinematic Viscosity ν	Kinematic Viscosity Variation	Measured ^b Kinematic Viscosity ν
OP60	1.470 ± 0.001	27.0 ± 0.5	5057 ± 2	856.9	1.19	± 0.03	1.17 ± 0.03
OP400	1.492 ± 0.001	27.0 ± 0.5	$14,592 \pm 1$	894.1	10.1	± 0.4	9.9 ± 0.2

^aNominal values at 24 °C were obtained from interpolation, with second-order exponential decay fitting, from the supplier specifications at a set of temperatures.

^bFrom the interferometric method used in this study.

At lower speeds, in the same experiment, there was a need for a multiplicative factor T_0 in Eqs. (9), which increased with withdrawing speed. After 13 mm/s was reached, this constant tended to stabilize at unity, consistent with the theoretical expectation, as discussed in Section 3 for the steady-state flow and far from the curved meniscus region. This indicates that the simple theoretical model is valid, without significant influence of surface tension.

Furthermore, basic experimental conditions were satisfied, such as significant liquid-film transparency and refractive-index contrast at its interface with the substrate.

5. Concluding Remarks

In the dip coating batch process, optical interferometry was applied to the monitoring of flow properties of Newtonian, nonvolatile liquid films in real time.

Dependence of physical thickness variation on time, linear with $t^{-1/2}$, was observed experimentally in standard mineral oils with high precision (from quarter-wave variation steps, linear fitting was attained with a slope uncertainty of $\pm 0.04\%$), and Eqs. (9) could be directly applied in the region where there is no significant influence of surface tension for withdrawing speeds higher than 13 mm/s. The resulting kinematic viscosity values of 1.17 ± 0.03 s for OP60 and 9.9 ± 0.2 S for OP400 agree with those provided by the manufacturer, well within the experimental uncertainty.

This indicates the accuracy of the interferometric procedure for optical characterization of thin liquid films during dip coating, as long as experimental and modeling conditions are satisfied. In addition to transparency and refractive-index contrast at its interface with the substrate, the liquid film under measurement (withdrawing speeds sufficient for capillarity number independent flow, far from the curved meniscus region), at present for simplicity, must be nonvolatile, Newtonian, and present refractive-index invariance during the process. Further research is required to waive these restrictions toward wider applicability of optically monitored dip coating as a contactless viscometry method.

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