I&EC research
Industrial & Engineering Chemistry Research
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pubs.acs.org/IECR

Mathematical Modeling of a Dip-Coating Process Using a Generalized Newtonian Fluid. 1. Model Development

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ABSTRACT: Dip coating consists in the immersion of a substrate into a reservoir containing a film-forming fluid and then the withdrawing from the bath to produce the film. The objective of this work was to develop a mathematical model of the fluid-dynamic variables in a dip-coating process, considering that the film-forming fluid behaves as a generalized Newtonian fluid. An analytical and simple mathematical model that relates the main fluid parameters using a generalized Herschel−Bulkley model was proposed. This model was obtained on the basis of rigorous mass and momentum balances applied to a monophasic and non-evaporative system, where the main forces are viscous and gravitational. The parameters that can be estimated are velocity profile, average velocity, flow rate, local thickness, and average thickness of the coating film. Finally, the sufficient conditions for the model were obtained. The experimental validation and sensitivity analysis are presented in a complementary paper as part 2.

1. INTRODUCTION

Coating is an industrial process used to produce a continuous or discontinuous film of some nonvolatile material (usually a liquid) on a solid substrate.[1] Coating is used for several purposes such as material protection, magnetization, controlling refractive index, and lubrication.[2] Particularly in food industry, this process is used to modify the appearance of the products, to extend their shelf-life by decreasing the dehydration rate, to improve their mechanical resistance, and to incorporate specific additives, like nutrients and preservatives.[3]

While many different methods are employed in coating applications, one of the most simple, clear, and fundamentally important is the dip-coating technique.[4] Dip coating consists in the immersion of the substrate into a reservoir containing the film-forming fluid for a certain period of time that ensures its complete wetting and then the withdrawing of the substrate from the bath. Afterward, the fluid drainage by gravity completes the film formation.[5] In addition, a drying process can occur after (or eventually at the same time) the withdrawing and draining steps, consisting in the evaporation of volatile solvent and the concentration of solutes. The evaporation can be done by thermal or oxidative processes, while the progressive concentration of the dispersed or colloidal phase leads to polymerization, cross-linking, or aggregation phenomena that finalize the film deposition.[6−8] Furthermore, in the dip-coating process the substrate geometry can vary extensively (for example, the substrate can be a plate, a cylinder, or an irregular-shaped object), this being a distinguishing advantage of this coating technique.[2,9]

As discussed above, momentum, heat, and mass transfer phenomena are expected during film formation. However, if the coating process can be considered as occurring in isothermal and non-evaporative conditions, like in many practical situations, the problem can be reduced to study the fluid dynamics of the system.[5] From the literature reviewed, the film thickness obtained using the dip-coating technique (assuming a process where the effect of the surface tension on the studied variables is negligible) is influenced by several variables such as the withdrawal speed of the substrate, the external volumetric force (usually gravity), the size of the system, and the physical properties of the film-forming fluid (i.e., density and viscosity).[2,10−13] Therefore, to improve the control of the involved variables and to obtain an optimal design of the dip-coating process for food applications, mathematical modeling of the system fluid dynamics can be used for this purpose.

Some of the earliest theoretical studies in dip coating were done by Jeffreys,[14] Landau and Levich,[15] Derjaguin,[16] and White and Tallmadge.[17] Those authors used Newtonian fluids as the fluid-forming material. A natural step to improve the level of description with a convenient increase of the mathematical complexity of the problem is to use mathematical models that represent the fluid dynamics of a dip-coating process for materials with a generalized Newtonian fluid (GNF) behavior. The GNF is an extension of the Newtonian fluid that includes the idea of a shear-rate-dependent viscosity without taking into account normal stress or time-dependent elastic effects.[18,19] The GNF generally produces relatively simple constitutive equations, such as the Casson model,[20] the Bingham model,[21] the Herschel−Bulkley model,[22] and the Ostwald−de Waele model,[23] that are useful in many practical situations and industrial flow problems.[19] It is important to mention that a particular constitutive equation that can represent all the expressions described before is the model proposed by Ofoli et al.,[24] which is a generalization of the Herschel−Buckley equation originally developed for inelastic fluid foods. Specifically, this model involves several important rheological models (besides the generalized Herschel−Bulkley) such as Heinz−Casson,[25] Casson,[20] Mizrahi−Berk,[26] Herschel−Bulkley,[22] Ostwald−de Waele,[23] Bingham,[21] and Newtonian models.

Received: January 28, 2014
Revised: March 18, 2014
Accepted: March 20, 2014
Published: March 20, 2014

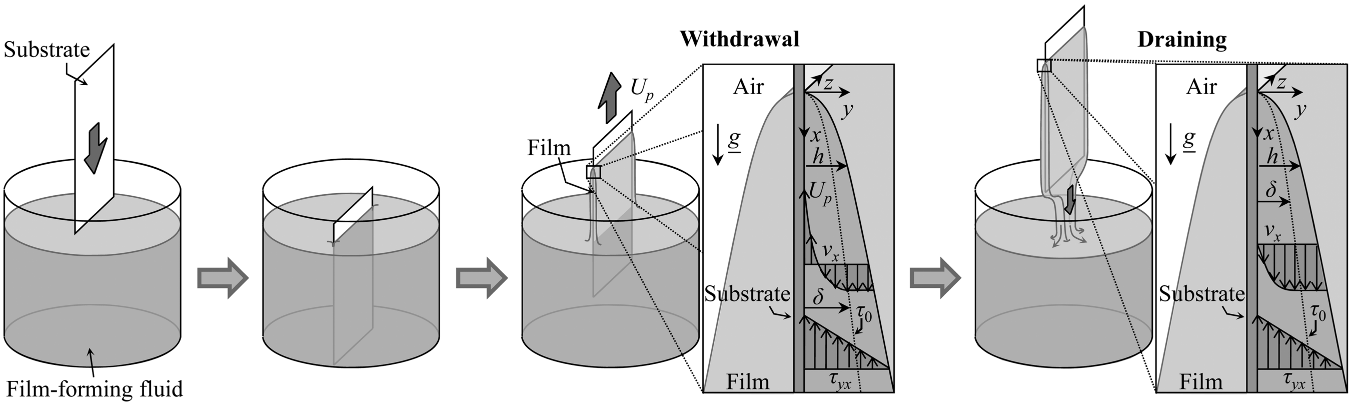

Figure 1. Schematic diagram of dip-coating process showing the withdrawal and draining stages.

A theoretical study of the dip-coating process that includes the mathematical modeling with their analytical solution and that takes into account a generalized rheological behavior of the film-forming fluid as proposed by Ofoli et al.[24] was not found in literature. Therefore, the objective of this work was to develop a mathematical model of the fluid-dynamic variables in a dip-coating process, considering that the film-forming fluid behaves as a generalized Newtonian fluid. The experimental validation and sensitivity analysis are presented in a complementary paper as part 2.[27]

2. THEORETICAL APPROACH

2.1. Equations of Change. A schematic diagram of the studied dip-coating process is shown in Figure 1. It is important to mention that the studied phenomena occur far away from the meniscus that is formed at the surface of the fluid-forming reservoir. The equations of change that describe the phenomena in an isothermal and non-evaporative dip-coating process are as follows

Total mass balance (i.e., continuity equation):

$$\frac{\partial \rho}{\partial t} + \underline{\nabla}\cdot(\rho \underline{v}) = 0 \tag{1}$$

Momentum balance:

$$\rho\left(\frac{\partial \underline{v}}{\partial t} + \underline{v}\cdot\underline{\nabla}\,\underline{v}\right) = -\underline{\nabla}p - \underline{\nabla}\cdot\underline{\underline{\tau}} + \underline{F}_{\mathrm{e}} \tag{2}$$

Taking into account the following assumptions: (1) the film-forming fluid is incompressible ($\rho \neq f(\underline{x},t)$), (2) the external forces are mainly gravitational ($\underline{F}_{\mathrm{e}} = \rho\underline{g}$), (3) the surface forces are negligible ($Ca \to \infty$), (4) the system is open ($\nabla \underline{p} \cong 0$), 5) the system can be represented in Cartesian coordinates ($\underline{x} = \underline{e}_x x + \underline{e}_y y + \underline{e}_z z$), (6) the problem is mainly 2D (i.e., $v_z \cong 0$ and changes in z direction are negligible: $\partial/\partial z \cong 0$), and (7) gravity acts in x direction ($\underline{g} = \underline{e}_x g_x$),

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \tag{3}$$

$$\rho\left(\frac{\partial v_x}{\partial t} + v_x\frac{\partial v_x}{\partial x} + v_y\frac{\partial v_x}{\partial y}\right) = -\left(\frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y}\right) + \rho g_x \tag{4}$$

$$\rho\left(\frac{\partial v_y}{\partial t} + v_x\frac{\partial v_y}{\partial x} + v_y\frac{\partial v_y}{\partial y}\right) = -\left(\frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y}\right) \tag{5}$$

The complexity (i.e., nonlinear nature) of eqs 3−5 makes it difficult to obtain an analytical solution. Thus, a dimensional analysis is useful to obtain simpler expressions of eqs 3−5 that is also representative of the phenomena that take place in the studied process. The following dimensionless variables are defined:

$$\tilde{v}_x = \frac{v_x}{U} \tag{6}$$

$$\tilde{v}_y = \frac{v_y}{V} \tag{7}$$

$$\tilde{x} = \frac{x}{L} \tag{8}$$

$$\tilde{y} = \frac{y}{h_L} \tag{9}$$

$$\tilde{\tau}_{ij} = \frac{\tau_{ij}}{\eta_{\mathrm{ref}}(U/h_L)} \tag{10}$$

$$\tilde{t} = \frac{t}{(L/U)} \tag{11}$$

where U and V are the reference velocities for the x direction and y direction, respectively [m s^{-1}], L is the length of the plate [m], h_L is the local thickness of the film at L [m], η_{ref} is an apparent viscosity at a reference condition.

Using eqs 6−9 in eq 3:

$$\frac{\partial \tilde{v}_x}{\partial \tilde{x}} + \frac{VL}{h_L U}\frac{\partial \tilde{v}_y}{\partial \tilde{y}} = 0 \tag{12}$$

In a dimensional analysis of eq 12 presented by Denn[28] and used by Peralta et al.,[29] the order of magnitude of the factor multiplying the second term is $O[VL/(h_L U)] \cong 1$. It is important to note that if $O[VL/(h_L U)] \gg 1$, $\tilde{v}_y$ would be zero, which is physically impossible during film developing. Conversely, $\tilde{v}_x$ would be constant, contradicting the fact that $\tilde{v}_x$ varies with x as the film thickness changes. Defining $\varepsilon = h_L/L$, $O(V) \cong O(\varepsilon U)$ results. As Peralta et al.[29] stated, this relation shows a natural way to define V and the definition of V used here will be $V = \varepsilon U$. Equation 7 can then be rewritten as $\tilde{v}_y = v_y/(\varepsilon U)$. Using this definition and eqs 6−9 in eqs 4 and 5, and considering the symmetry of $\underline{\underline{\tau}}$:[19]

$$Re\,\varepsilon\left(\frac{\partial \tilde{v}_x}{\partial \tilde{t}}+\tilde{v}_x\frac{\partial \tilde{v}_x}{\partial \tilde{x}}+\tilde{v}_y\frac{\partial \tilde{v}_x}{\partial \tilde{y}}\right)=-\left(\varepsilon\frac{\partial \tilde{\tau}_{xx}}{\partial \tilde{x}}+\frac{\partial \tilde{\tau}_{yx}}{\partial \tilde{y}}\right)+St \tag{13}$$

$$Re\,\varepsilon^2\left(\frac{\partial \tilde{v}_y}{\partial \tilde{t}}+\tilde{v}_x\frac{\partial \tilde{v}_y}{\partial \tilde{x}}+\tilde{v}_y\frac{\partial \tilde{v}_y}{\partial \tilde{y}}\right)=-\left(\varepsilon\frac{\partial \tilde{\tau}_{yx}}{\partial \tilde{x}}+\frac{\partial \tilde{\tau}_{yy}}{\partial \tilde{y}}\right) \tag{14}$$

where $St = Re/Fr$ is the Stokes number,[30] $Re = \rho U h_L/\eta_{\text{ref}}$ and $Fr = U^2/(g_x h_L)$.

In the dip-coating process, a thin film is formed over the plate that is being withdrawn from a vessel containing the coating liquid. Taking into account that the length of the plate is much larger than the average thickness of the film, that is $\varepsilon \ll 1$, and the flow is in the laminar regime (usually the viscosity of the coating liquid is high) so that $Re\ \varepsilon \ll 1$, then eqs 12−14 become

$$\frac{\partial \tilde{v}_x}{\partial \tilde{x}}+\frac{\partial \tilde{v}_y}{\partial \tilde{y}}=0 \tag{15}$$

$$\frac{\partial \tilde{\tau}_{yx}}{\partial \tilde{y}}\cong St \tag{16}$$

$$\frac{\partial \tilde{\tau}_{yy}}{\partial \tilde{y}}\cong 0 \tag{17}$$

This set of equations, which may be found for a lubrication flow in a fluid system,[28] will be used to describe the flow of a coating film during the stages of unsteady withdrawal and removal. It should be pointed out that the order of magnitude of St should be 1 in order to obtain an analytical solution different from (1) a constant τ_{yx} across the film or (2) a solidlike behavior of the film.

2.2. Range of Theoretical Validity of the Approach. An important feature of the theoretical approach presented here is to verify the range of validity of the set of eqs 15−17. The following set of conditions was assumed to be true:

$$\varepsilon \ll 1 \tag{18}$$

$$Re\,\varepsilon \ll 1 \tag{19}$$

$$St \cong O(1) \tag{20}$$

There is an additional condition, $Re\ \varepsilon^2 \ll 1$ (associated with eq 14), that is not taken into account in the set of equations to be verified because it represents a more restrictive situation than eq 19.

It is noteworthy that in order to evaluate eqs 18−20, two parameters need to be defined: (1) η_{ref}, (2) U. The definition of the first parameter will depend on the stage of the process where the model is applied and the evaluation of the second parameter will depend on the rheological model adopted. Therefore, different final expressions will be obtained from eqs 18−20 and an analysis for each case will be performed later.

Finally, it is necessary to mention that as $Re\ \varepsilon \ll 1$, the transient terms (along with the inertial terms in eqs 13 and 14) were neglected. The validity of this assumption depends on the operative conditions usually found in the dip-coating process. This hypothesis was tested theoretically by Gutfinger and Tallmadge[31] for a Newtonian fluid drained from a vertical plate. Those authors found that the solutions for local thickness with and without the transient terms agreed within an error of 1% for conditions usually found in dip-coating processes, that is, times greater than 0.7 s and plate lengths less than 1 m.

2.3. Constitutive Equation for the Generalized Newtonian Fluid. The set of eqs 15−17, which describes the relationship among the main transport variables in the process studied in this work, needs an additional equation to close the problem. The necessary equation should give the information of how the rate of deformation (expressed as a function of the velocity gradients in the material) is related to the stress in the film.

A generalized Newtonian fluid (GNF) is a fluid material that can be described by:[18,19]

$$\underline{\underline{\tau}} = -\eta\underline{\underline{\dot{\gamma}}} \tag{21}$$

where $\underline{\underline{\tau}}$ is the shear stress tensor [Pa], $\underline{\underline{\dot{\gamma}}}$ is the rate of deformation tensor (i.e., shear rate tensor) [s^{-1}], $\eta = f(|\underline{\underline{\dot{\gamma}}}|,T,p,C)$ is the apparent viscosity (scalar quantity) [Pa s], $|\underline{\underline{\dot{\gamma}}}|$ is the second invariant or magnitude of $\underline{\underline{\dot{\gamma}}}$ [s^{-1}], T is the temperature [K], p is the thermodynamic pressure [Pa], and C is the concentration [kg m^{-3}].

Ofoli et al.[24] proposed a generalization of the three parameter Herschel−Buckley model for inelastic fluid foods by adding a fourth parameter to yield:

$$\eta = \frac{(\tau_0^m + K^m|\underline{\underline{\dot{\gamma}}}|^n)^{1/m}}{|\underline{\underline{\dot{\gamma}}}|} = (\tau_0^m|\underline{\underline{\dot{\gamma}}}|^{-m} + K^m|\underline{\underline{\dot{\gamma}}}|^{n-m})^{1/m} \tag{22}$$

where $\tau_0 = f_1(T,p,C)$ is the yield stress [Pa], $K = f_2(T,p,C)$ is the consistency index [Pa $s^{n/m}$], and $n = f_3(T,p,C)$ and $m = f_4(T,p,C)$ are dimensionless coefficients. It is important to mention that by choosing conveniently the values of n, m and τ_0, eq 22 can yield several models found in literature (for example, $n = m$, Heinz−Casson model;[25] $n = m = {}^1/_2$, Casson model;[20] $m = {}^1/_2$, Mizrahi−Berk model;[26] $m = 1$, Herschel−Bulkley model;[22] $n = m = 1$, Bingham model;[21] $m = 1$ and $\tau_0 = 0$, Ostwald−de Waele model (i.e., power law);[23] and $n = m = 1$ and $\tau_0 = 0$, Newtonian model). The consistency index is transformed into the apparent viscosity at infinite rate of deformation, that is $K = \eta_\infty$, when $n = m$.

2.4. Velocity Profile within the Film. Equations 21 and 22 can be simplified. First, bearing in mind that $|\underline{\underline{\dot{\gamma}}}|$ can be calculated through the second invariant of the rate of deformation tensor:[18]

$$|\underline{\underline{\dot{\gamma}}}| = \sqrt{\frac{1}{2}(\underline{\underline{\dot{\gamma}}}:\underline{\underline{\dot{\gamma}}})} = \sqrt{\frac{1}{2}\sum_i\sum_j \dot{\gamma}_{ij}\dot{\gamma}_{ji}} \tag{23}$$

where $\underline{\underline{\dot{\gamma}}} = \underline{\nabla}\underline{v} + (\underline{\nabla}\underline{v})^{\mathrm{T}}$ and $\dot{\gamma}_{ij} = \partial v_i/\partial x_j + \partial v_j/\partial x_i$.

At this time, a dimensional analysis is necessary to obtain a convenient expression of eq 23. Taking into account that the system can be described as a Cartesian 2D system, eq 23 can be written as:[19]

$$|\underline{\underline{\dot{\gamma}}}| = \sqrt{\frac{1}{2}\sum_i\sum_j \dot{\gamma}_{ij}^{\,2}} = \sqrt{2\left[\left(\frac{\partial v_x}{\partial x}\right)^2+\left(\frac{\partial v_y}{\partial y}\right)^2\right]+\left(\frac{\partial v_x}{\partial y}+\frac{\partial v_y}{\partial x}\right)^2} \tag{24}$$

Using eqs 6−9 in eq 24:

dx.doi.org/10.1021/ie500407t | Ind. Eng. Chem. Res. 2014, 53, 6521−6532

$$|\tilde{\underline{\underline{\dot{\gamma}}}}| = \sqrt{2\varepsilon^2\left[\left(\frac{\partial \tilde{v}_x}{\partial \tilde{x}}\right)^2 + \left(\frac{\partial \tilde{v}_y}{\partial \tilde{y}}\right)^2\right] + \left(\frac{\partial \tilde{v}_x}{\partial \tilde{y}} + \varepsilon^2\frac{\partial \tilde{v}_y}{\partial \tilde{x}}\right)^2} \tag{25}$$

where $|\tilde{\underline{\underline{\dot{\gamma}}}}| = |\underline{\underline{\dot{\gamma}}}|/(U/h_L)$.

Also, according to eq 16, the only component in $\underline{\underline{\tau}}$ that is necessary to calculate is τ_{yx}. Therefore, considering that[19]

$$\tau_{yx} = -\eta\left(\frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y}\right) \tag{26}$$

Using eqs 6−10 to nondimensionalize eq 26:

$$\tilde{\tau}_{yx} = -\tilde{\eta}\left(\varepsilon^2\frac{\partial \tilde{v}_y}{\partial \tilde{x}} + \frac{\partial \tilde{v}_x}{\partial \tilde{y}}\right) \tag{27}$$

where $\tilde{\eta} = \eta/\eta_{\text{ref}}$.

Considering that $\varepsilon \ll 1$ and therefore $\varepsilon^2 \ll 1$, eqs 25 and 27 yield, respectively:

$$|\tilde{\underline{\underline{\dot{\gamma}}}}| \cong \left|\frac{\partial \tilde{v}_x}{\partial \tilde{y}}\right| \tag{28}$$

$$\tilde{\tau}_{yx} \cong -\tilde{\eta}\frac{\partial \tilde{v}_x}{\partial \tilde{y}} \tag{29}$$

Now, integrating eq 16:

$$\tilde{\tau}_{yx} \cong St\,\tilde{y} + C_1 \tag{30}$$

Taking into account that the film will be surrounded at the top by air and that $\eta_{\text{air}} \ll \eta_{\text{film}}$, a feasible boundary condition will be $\tilde{\tau}_{yx} \cong 0$ in $\tilde{y} \cong \tilde{h}(\tilde{x})$, where $\tilde{h}(\tilde{x}) = h(x)/h_L$. Thus, eq 30 yields:

$$\tilde{\tau}_{yx} \cong -St(\tilde{h} - \tilde{y}) \tag{31}$$

This equation predicts a linear profile of the shear stress across the film with a slope that depends on the ratio between gravitational and viscous forces. The nature of eq 31 shows that it is independent of the type of the coating material (i.e., Newtonian, viscoelastic, etc.), and the maximum shear stress is expected at the plate surface: $(\tilde{\tau}_{yx})_{\max} \cong -St(\tilde{h})$.

Now, using previous definitions, the dimensionless form of eq 22 is

$$\tilde{\eta} = \frac{(\tilde{\tau}_o^m + \tilde{K}^m|\tilde{\underline{\underline{\dot{\gamma}}}}|^n)^{1/m}}{|\tilde{\underline{\underline{\dot{\gamma}}}}|} \tag{32}$$

where $\tilde{\tau}_0 = \tau_0 h_L/(\eta_{\text{ref}}U)$ and $\tilde{K} = KU^{n/m-1}/(\eta_{\text{ref}}\,h_L^{n/m-1})$.

Equating the momentum balance (eq 31) with the constitutive expression for the coating material (eqs 28, 29, and 32) yields:

$$\left(\tilde{\tau}_0^m + \tilde{K}^m\left|\frac{\partial \tilde{v}_x}{\partial \tilde{y}}\right|^n\right)^{1/m} \cong St(\tilde{h} - \tilde{y}) \tag{33}$$

Defining $s = 1 - [St\,(\tilde{h} - \tilde{y})/\tilde{\tau}_0]^m$ and integrating eq 33:

$$\tilde{v}_x \cong \left(\frac{\tilde{\tau}_0}{\tilde{K}}\right)^{m/n}\frac{\tilde{\tau}_0}{\text{St}}\frac{(-1)^{1/n}}{m}\int\frac{s^{1/n}}{(1-s)^{(m-1)/m}}\,ds + C_2 \tag{34}$$

The integral in eq 34 can be solved using the definition of the incomplete beta function $B[s,a,b]$ through the Chevyshev integral:[32,33]

$$B[s, a, b] = \int s^{a-1}(1-s)^{b-1}\,ds \tag{35}$$

Additionally, eq 34 should be rearranged to obtain a convenient form because the factor $(-1)^{1/n}$ can cause mathematical problems that arise from negative numbers powered to real numbers. Expressing eq 35 in terms of the Gauss hypergeometric function $_2F_1[a,b;c;s]$ using[32,34]

$$B[s, a, b] = \frac{(1-s)^{b-1}s^a}{a}\,{}_2F_1\left[1, 1-b; a+1; \frac{s}{s-1}\right] \tag{36}$$

Then, using eqs 35 and 36 with the boundary condition $\tilde{v}_x = \tilde{v}_{x,\tilde{y}=0} = U_p/U$ in $\tilde{y} = 0$, and taking into account that the velocity profile can be considered as composed by two regions: $\tau_{yx} \geq \tau_0$ and $\tau_{yx} \leq \tau_0$ where the location of the transition is $\tilde{\delta} = \tilde{h} - \tau_0/(\rho g_x h_L)$, eq 34 yields the following:

For $0 \leq \tilde{y} \leq \tilde{\delta}$:

$$\tilde{v}_x \cong \frac{n}{(n+1)m}\frac{[\psi(0) - \psi(\tilde{y})]}{S_K^{m/n}} - \tilde{v}_{x,\tilde{y}=0} \tag{37}$$

For $\tilde{y} > \tilde{\delta}$:

$$\tilde{v}_{x,\tilde{y}\geq\tilde{\delta}} \cong \frac{n}{(n+1)m}\frac{\psi(0)}{S_K^{m/n}} - \tilde{v}_{x,\tilde{y}=0} \tag{38}$$

where

$$\psi(\tilde{y}) = \left(1 - \frac{\tilde{y}}{\tilde{h}}\right)^{m/n+1}\left\{1 - \left\{\frac{S_{\tau_0}}{[1-(\tilde{y}/\tilde{h})]}\right\}^m\right\}^{(n+1)/n} {}_2F_1\left\{1, 1-\frac{1}{m}; 2+\frac{1}{n}; 1 - \left\{\frac{S_{\tau_0}}{[1-(\tilde{y}/\tilde{h})]}\right\}^m\right\} \tag{39}$$

$$\psi(0) = (1 - S_{\tau_0}^m)^{(n+1)/n}\,{}_2F_1\left(1, 1-\frac{1}{m}; 2+\frac{1}{n}; 1-S_{\tau_0}^m\right) \tag{40}$$

$$S_{\tau_0} = \frac{\text{yield stress}}{\text{maximum stress}} = \frac{\tau_0}{\rho g_x h} \tag{41}$$

$$S_K = \frac{\text{viscous stress}}{\text{maximum stress}} = \frac{K(U/h)^{n/m}}{\rho g_x h} \tag{42}$$

2.5. Average Velocity Profile. The average velocity in the thickness h can be estimated by

$$\langle v_x\rangle_y = \frac{1}{h}\int_0^h v_x\,dy \tag{43}$$

Non-dimensionalizing eq 43 and taking into account the separation of the velocity profile in two regions performed in eqs 37 and 38 gives

$$\langle\tilde{v}_x\rangle_y = \frac{1}{\tilde{h}}\int_0^{\tilde{\delta}}\tilde{v}_x d\tilde{y} + \frac{1}{\tilde{h}}\int_{\tilde{\delta}}^{\tilde{h}}\tilde{v}_x d\tilde{y} = \frac{1}{\tilde{h}}\int_0^{\tilde{\delta}}\tilde{v}_x d\tilde{y} + \tilde{v}_{x,\tilde{y}\geq\tilde{\delta}}\frac{(\tilde{h}-\tilde{\delta})}{\tilde{h}} \tag{44}$$

Replacing eqs 37 and 38 in eq 44:

$$\langle \tilde{v}_x \rangle_y = \frac{n}{(n+1)m} \frac{1}{S_K^{m/n}} \left[\psi(0) - \frac{1}{\tilde{h}} \int_0^{\tilde{\delta}} \psi(\tilde{y}) d\tilde{y} \right] - \tilde{v}_{x,\tilde{y}=0} \tag{45}$$

Equation 45 can be solved by combining the identities presented by Abramowitz and Stegun[32] and Weisstein[34] into the following expression:

$$\begin{aligned} &\int s^a (1-s)^b {}_2F_1[1, a+b+c; a+1; s]\, ds \\ &= \frac{s^a(1-s)^b}{(1-c)} \{ {}_2F_1[1, 1+a+b; a+1; s] \\ &\quad - {}_2F_1[1, a+b+c; a+1; s] \} \end{aligned} \tag{46}$$

where $-a \notin \mathbb{N}$.

Now, defining a new intermediate variable $s = 1 - [S_{\tau_0}/(1 - \tilde{y}/\tilde{h})]^m$ to transform the integral in eq 45 to the form of eq 46, the expression for the volumetric flow rate yields

$$\begin{aligned} \langle \tilde{v}_x \rangle_y = &\frac{n}{(n+1)m} S_K^{-m/n} (1 - S_{\tau_0}^m)^{(n+1)/n} \\ &{}_2F_1\left(1, 1 - \frac{2}{m}; 2 + \frac{1}{n}; 1 - S_{\tau_0}^m\right) - \tilde{v}_{x,\tilde{y}=0} \end{aligned} \tag{47}$$

In many practical situations involving fluid dynamics problems, the ratio of the average to the maximum velocity is necessary. This expression can be obtained from eqs 38 and 47. Therefore, the ratio of the average velocity to the velocity in the film−air interface (eq 38) is

$$\begin{aligned} \frac{\langle \tilde{v}_x \rangle_y}{\tilde{v}_{x,\tilde{y} \geq \tilde{\delta}}} = &\left[\frac{n}{(n+1)m} S_K^{-m/n} (1 - S_{\tau_0}^m)^{(n+1)/n} {}_2F_1 \right. \\ &\left. \left(1, 1 - \frac{2}{m}; 2 + \frac{1}{n}; 1 - S_{\tau_0}^m\right) - \tilde{v}_{x,\tilde{y}=0} \right] \\ &/ \left[\frac{n}{(n+1)m} S_K^{-m/n} (1 - S_{\tau_0}^m)^{(n+1)/n} {}_2F_1 \right. \\ &\left. \left(1, 1 - \frac{1}{m}; 2 + \frac{1}{n}; 1 - S_{\tau_0}^m\right) - \tilde{v}_{x,\tilde{y}=0} \right] \end{aligned} \tag{48}$$

2.6. Estimation of the Volumetric Flow Rate Per Unit of Width of the Film.

The volumetric flow rate per unit of width (Q_z) is one of the main macroscopic parameters that can be related to the rest of the local quantities (i.e., velocity, pressure, etc.). Applying a mass balance on the film, Q_z can be estimated in dimensionless form as

$$\tilde{Q}_z = \langle \tilde{v}_x \rangle_y \tilde{h} \tag{49}$$

where $\tilde{Q}_z = Q_z/(Uh_L)$.

Thus, combining eqs 47 and 49:

$$\begin{aligned} \tilde{Q}_z = &\frac{n}{(n+1)m} \tilde{h} S_K^{-m/n} (1 - S_{\tau_0}^m)^{(n+1)/n} \\ &{}_2F_1\left(1, 1 - \frac{2}{m}; 2 + \frac{1}{n}; 1 - S_{\tau_0}^m\right) - \tilde{h}\tilde{v}_{x,\tilde{y}=0} \end{aligned} \tag{50}$$

In some cases, useful information can be obtained when the net flux within the film is zero. That is, the mass of film that goes upward is equal to the mass that is descending. This situation can be obtained when the plate has a velocity $U_p > 0$ and a constant film thickness is expected.[5] In this case, the dimensionless plate velocity expressed as $\tilde{v}_{x,\tilde{y}=0}$ can be related to $\tilde{h}$ and the rest of the parameters by

$$\begin{aligned} \tilde{v}_{x,\tilde{y}=0} = &\frac{n}{(n+1)m} S_K^{-m/n} (1 - S_{\tau_0}^m)^{(n+1)/n} \\ &{}_2F_1\left(1, 1 - \frac{2}{m}; 2 + \frac{1}{n}; 1 - S_{\tau_0}^m\right) \end{aligned} \tag{51}$$

2.7. Estimation of the Film Thickness.

The local thickness of the film that is being drained from the plate can be estimated using some of the above expressions. The integration of eq 1 in the y axis can be made taking into account the Leibniz integration rule[35] and that (1) the process can be represented by a 2D Cartesian coordinate system, (2) the coating process can be fast enough to neglect any mass transfer due to evaporation of volatile components of the film (i.e., water) through the film−air interface and thus a kinematic boundary condition[36] can be used, and (3) the film is incompressible. The resulting equation in dimensionless form is

$$\frac{\partial \tilde{h}}{\partial \tilde{t}} + \frac{\partial (\langle \tilde{v}_x \rangle_y \tilde{h})}{\partial \tilde{x}} \cong 0 \tag{52}$$

where the quantity that is differentiated with respect to $\tilde{x}$ is the volumetric flow per unit of width.

Introducing eq 50 into eq 52 gives

$$\begin{aligned} \frac{\partial \tilde{h}}{\partial \tilde{t}} \cong &\frac{n}{(n+1)m} \frac{\partial}{\partial \tilde{x}} \left[S_K^{-m/n} \tilde{h} (1 - S_{\tau_0}^m)^{(n+1)/n} \right. \\ &\left. {}_2F_1\left(1, 1 - \frac{2}{m}; 2 + \frac{1}{n}; 1 - S_{\tau_0}^m\right) \right] - \tilde{v}_{x,\tilde{y}=0} \frac{\partial \tilde{h}}{\partial \tilde{x}} \end{aligned} \tag{53}$$

The derivative in eq 53 can be carried out by combining the identities from Abramowitz and Stegun[32] and Weisstein,[34] that is:

$$\begin{aligned} &\frac{\partial}{\partial s} \{ [f(s)]^a [1 - f(s)]^b {}_2F_1[1, a+b; a+1; f(s)] \} \\ &= a [f(s)]^{a-1} [1 - f(s)]^{b-1} \frac{df(s)}{ds} \end{aligned} \tag{54}$$

Taking into account that $\tilde{h} = \tilde{h}(\tilde{x})$ and considering $f(s) = 1 - S_{\tau_0}^m$, $a = 1 + 1/n$, and $b = -(2/m + 1/n)$, eq 53 yields

$$\frac{\partial \tilde{h}}{\partial \tilde{t}} + [S_K^{-m/n} (1 - S_{\tau_0}^m)^{1/n} - \tilde{v}_{x,\tilde{y}=0}] \frac{\partial \tilde{h}}{\partial \tilde{x}} \cong 0 \tag{55}$$

Equation 55 is the differential balance that describes the dynamics of the film thickness over the plate. The solution of eq 55 equation has the form:[37]

$$\tilde{x} \cong S_K^{-m/n} (1 - S_{\tau_0}^m)^{1/n} \tilde{t} - \tilde{v}_{x,\tilde{y}=0} \tilde{t} + \beta(\tilde{h}) \tag{56}$$

Taking into account that $\tilde{h}(\tilde{t},0) = 0$, the effect of the term $\beta(\tilde{h})$ is usually neglected (for long drainage times) or considered zero.[14,38−41] Thus, eq 56 yields

$$S_K^{-m/n} (1 - S_{\tau_0}^m)^{1/n} - \left(\frac{\tilde{x}}{\tilde{t}} + \tilde{v}_{x,\tilde{y}=0} \right) \cong 0 \tag{57}$$

It is important to mention that when eq 57 is applied for $\tilde{x} \to \infty$, the film thickness can be considered as nearly constant (an example of this case is a substrate that is being withdrawn constantly from a vessel containing the film-forming fluid[5] and the parameter $\beta(\tilde{h})$ is assumed as nonzero.[42,43]

dx.doi.org/10.1021/ie500407t | Ind. Eng. Chem. Res. 2014, 53, 6521−6532

2.8. Estimation of the Average Thickness. The uniformity of the film is one of the main properties to be evaluated. This quantity can be estimated by the ratio of the average thickness to the local thickness.[40] The average dimensionless film thickness at a distance $\tilde{x}$ is defined by

$$\langle\tilde{h}\rangle_x = \frac{1}{\tilde{x}}\int_0^{\tilde{x}} \tilde{h}\, d\tilde{x} \tag{58}$$

where $\langle\tilde{h}\rangle_x = \langle h\rangle_x/h_L$.

To integrate eq 58 and solve the problem of the implicit nature of eq 57 in terms of $\tilde{h}$, the method presented by Gutfinger and Tallmadge[40] will be used. Differentiating eq 57 with respect to $d\tilde{x}$:

$$d\tilde{x} = \frac{\tilde{t}}{\tilde{h}}\left[\frac{m}{n}S_K^{-m/n}(1 - S_{\tau_0}^m)^{1/n-1} + S_K^{-m/n}(1 - S_{\tau_0}^m)^{1/n}\right] d\tilde{h} \tag{59}$$

and using eqs 56 and 59 in eq 58 gives

$$\langle\tilde{h}\rangle_x \cong \frac{1}{[S_K^{-m/n}(1 - S_{\tau_0}^m)^{1/n} - \tilde{v}_{x,\tilde{y}=0}]}\int_0^{\tilde{h}}\left[\frac{m}{n}S_K^{-m/n}(1 - S_{\tau_0}^m)^{1/n-1} + S_K^{-m/n}(1 - S_{\tau_0}^m)^{1/n}\right] d\tilde{h} \tag{60}$$

A change of variable is necessary to solve eq 60. Defining $s = 1 - S_{\tau_0}^m$ and $ds = S_{\tau_0}^m(m/\tilde{h})\, d\tilde{h}$, leads to

$$\frac{\langle\tilde{h}\rangle_x}{\tilde{h}} \cong \frac{S_{\tau_0}}{\left[s^{1/n}(1 - s)^{-(1/n+1/m)} - \frac{S_K^{m/n}}{S_{\tau_0}^{m/n+1}}\tilde{v}_{x,\tilde{y}=0}\right]}\int_{s(0)}^{s(\tilde{h})}\left[\frac{1}{n}s^{1/n-1}(1 - s)^{-(1+1/n+2/m)} + \frac{1}{m}s^{1/n}(1 - s)^{-(1+1/n+2/m)}\right] ds \tag{61}$$

Using eqs 35 and 36 and taking into account only the positive real roots of eq 57, finally eq 61 yields

$$\frac{\langle\tilde{h}\rangle_x}{\tilde{h}} \cong [1 + S_K^{m/n}(1 - S_{\tau_0}^m)^{-1/n}\tilde{v}_{x,\tilde{y}=0}]^{-1}\left[{}_2F_1\left(1, -\frac{2}{m}; \frac{1}{n} + 1; 1 - S_{\tau_0}^m\right) + \frac{n}{m(n+1)}(1 - S_{\tau_0}^m)\,{}_2F_1\left(1, 1 - \frac{2}{m}; \frac{1}{n} + 2; 1 - S_{\tau_0}^m\right)\right] \tag{62}$$

2.9. Estimation of the Force Required to Withdraw the Plate. An interesting industrial parameter is the force required to withdraw the plate carrying the film of fluid. In this case, the total force (F_{total}) can be estimated by

$$F_{total} = F_{plate} + F_{film} \tag{63}$$

where F_{plate} is the force related to the plate mass [N] and F_{film} is the force related to the film on the plate [N].

The forces in eq 63 can be estimated by

$$F_{plate} = 2eWL\rho_p g_x \tag{64}$$

$$F_{film} = \int_A (\tau_{yx})_{max}\, dA \tag{65}$$

where e is the half thickness of the plate [m], W is the width of the plate [m], and ρ_p is the density of the plate [kg m^{-3}]. Using eq 31 evaluated on the plate surface (in dimensional form) and taking into account the dimensional form of eq 58, the total force can be estimated by

$$F_{total} \cong 2g_x WL(\rho_p e + \rho\langle h\rangle_x) \tag{66}$$

2.10. Application to Quasi-vertical Systems. The model developed in this work can be used for systems with a certain inclination of the axis along $\underline{g}$ is acting. This can be done using the expression:

$$g_x = |\underline{g}|\cos(\theta) \tag{67}$$

where $|\underline{g}|$ is the magnitude of $\underline{g}$ [m s^{-2}] and θ is the angle between the axis of the plate and the axis of $\underline{g}$ [deg]. It is important to mention that if another force is acting in the system, $\underline{g}$ should be changed accordingly.

3. RESULTS AND DISCUSSION

3.1. Theoretical Validity of the Model. As stated in section 2.2, η_{ref} and U should be defined. The basic criterion that was used to select the way to define those quantities is that they should be representative and easy to estimate for a given system.

In the first case, and taking into account eqs 22 and 33, η_{ref} is a function of the position. Furthermore, because the maximum gradient is found at the end of the plate (that is, $x = L$ and $y = 0$), η_{ref} is defined as

$$\eta_{ref} = [\tau_0^m|\dot{\underline{\underline{\gamma}}}|_{x=L,\,y=0}^{-m} + K^m|\dot{\underline{\underline{\gamma}}}|_{x=L,\,y=0}^{n-m}]^{1/m} \tag{68}$$

Using the dimensional form of eq 33 in eq 68:

$$\eta_{ref} = \rho g_x h_L\left[\left(\frac{\rho g_x h_L}{K}\right)^m - \left(\frac{\tau_0}{K}\right)^m\right]^{-1/n} \tag{69}$$

Using eq 69 gives the expression for the Reynolds number as

$$Re = \frac{U}{g_x}\left[\left(\frac{\rho g_x h_L}{K}\right)^m - \left(\frac{\tau_0}{K}\right)^m\right]^{1/n} \tag{70}$$

This expression is consistent with the idea of the existence of flow (i.e., $Re > 0$) if $\rho g_x h_L > \tau_0$.

In the second case, the characteristic velocity can be related to the stage of the process that is being studied. In the lifting or withdrawal (when the plate is withdrawn from the container of the film-forming fluid) the plate velocity is $U_p > 0$ and U can be defined as $U = U_p$. On the other hand, in the removing or draining the velocity of the plate cannot be used and the conditions at $x = L$ are conveniently used to yield $U = Q_z h_L^{-1}$.

Using eq 70 in eq 19 and taking into account the definition of Fr, S_{τ_0} and S_K, the second condition of section 2.2 yields

$$Re\,\varepsilon = Fr\,\varepsilon S_{K,L}^{-m/n}(1 - S_{\tau_0,L}^m)^{1/n} \ll 1 \tag{71}$$

where $S_{\tau_0,L} = \tau_0(\rho g_x h_L)^{-1}$ and $S_{K,L} = K(Uh_L^{-1})^{n/m}(\rho g_x h_L)^{-1}$. Then, eq 71 can be rearranged as

$$S_{K,L}^{-m/n}(1 - S_{\tau_0,L}^m)^{1/n} \ll \frac{1}{Fr\varepsilon} \tag{72}$$

On the other hand, using the definitions of $S_{\tau_0,L}$ and $S_{K,L}$ in eq 20 gives

$$St = S_{K,L}^{-m/n}(1 - S_{\tau_0,L}^{m})^{1/n} = O(1) \tag{73}$$

Conservatively assuming that $O(1) \cong 0.5$ to 5, combining eqs 18 and 19 to obtain $Re < 1$, and that $\varepsilon \ll 1$ can be regarded as $\varepsilon < 0.1$ allows eqs 72 and 73 to be written as

$$S_{K,L}^{-m/n}(1 - S_{\tau_0,L}^{m})^{1/n} < \frac{1}{10}\frac{1}{Fr\,\varepsilon} \tag{74}$$

$$\frac{1}{2} \le S_{K,L}^{-m/n}(1 - S_{\tau_0,L}^{m})^{1/n} \le 5 \tag{75}$$

Figure 2 shows the region of validity of the model based on eqs 74 and 75. It is worth mentioning that the region represents the sufficient conditions for the model proposed.

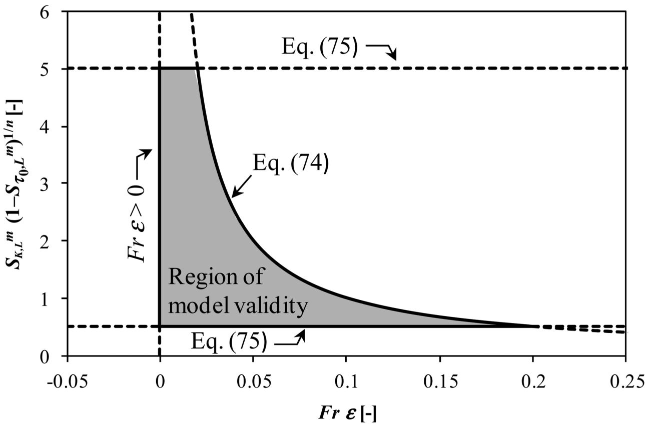

Figure 2. Region related to the sufficient conditions for the theoretical validity of the model.

3.2. Dimensional Forms of the Main Variables for Rheological Models Studied.

In previous sections, the model was presented in a dimensionless form, which is useful to analyze the physics of each equation. It is important to mention that the expressions obtained in this work can be simplified. These cases can be arranged taking into account the rheological models that can be derived from eq 22. Table 1–Table 8 present (in dimensional form) the expressions for velocity, average velocity, flow rate, local thickness, and average thickness for the following cases: (1) Generalized Herschel–Bulkley (Table 1), (2) Heinz–Casson (Table 2), (3) Casson (Table 3), (4) Herschel–Bulkley (Table 4), (5) Mizrahi–Berk (Table 5), (6) Ostwald–de Waele (Table 6), (7) Bingham (Table 7), and (8) Newtonian (Table 8). Some of the expressions presented in those tables are used in Part 2[27] to validate and analyze the developed model.

The simplifications were made by taking into account that in cases where m is an integer (for example: $m = 1$) or $m = {}^{1}/_{2}$, the function ${}_2F_1[a,b;c;s]$ can be simplified by using the symmetry property of ${}_2F_1[a,b;c;s]$[34]

$${}_2F_1[a, b; c; s] = {}_2F_1[b, a; c; s] \tag{76}$$

and the identity[33]

$${}_2F_1[-k, b; c; f(s)] = \frac{\Gamma(c)[f(s)]^{1-c}[1-f(s)]^{c+k-b}}{\Gamma(c+k)} \frac{\partial^k\{[f(s)]^{c+k-1}[1-f(s)]^{b-c}\}}{\partial s^k} \tag{77}$$

where $k \in \mathbb{N}$ and $\Gamma(s)$ is the gamma function of s.[44]

Also, in cases where $\tau_0 = 0$ (i.e., $S_{\tau_0} = 0$), the Gauss hypergeometric function can be simplified by using the following identity:[34]

$${}_2F_1[a, b; c; 1] = \frac{\Gamma(c)\Gamma(c-a-b)}{\Gamma(c-a)\Gamma(c-b)} \tag{78}$$

where $c - a - b > 0$.

Finally, a useful property of the gamma function is[44]

$$\Gamma(s+1) = s\Gamma(s) \tag{79}$$

Table 1. Dimensional Forms of Velocity, Average Velocity, Flow Rate, Local Thickness and Average Thickness for the Generalized Herschel–Bulkley Case: $\eta = (\tau_0^m|\dot{\underline{\underline{\gamma}}}|^{-m} + K^m|\dot{\underline{\underline{\gamma}}}|^{n-m})^{1/m}$

For $0 \le y \le \delta$:

$$v_x \cong \frac{n}{(n+1)m}\left(\frac{\rho g_x}{K}\right)^{m/n} h^{m/n+1}\left\{(1 - S_{\tau_0}^{m})^{(n+1)/n}\,{}_2F_1\left(1, 1-\frac{1}{m}; 2+\frac{1}{n}; 1-S_{\tau_0}^{m}\right) - \left(1-\frac{y}{h}\right)^{m/n+1}\left\{1 - \left[\frac{S_{\tau_0}}{1-(y/h)}\right]^{m}\right\}^{(n+1)/n}{}_2F_1\left\{1, 1-\frac{1}{m}; 2+\frac{1}{n}; 1-\left[\frac{S_{\tau_0}}{1-(y/h)}\right]^{m}\right\}\right\} - U_p \tag{80}$$

For $y > \delta$:

$$v_x \cong \frac{n}{(n+1)m}\left(\frac{\rho g_x}{K}\right)^{m/n} h^{m/n+1}(1 - S_{\tau_0}^{m})^{(n+1)/n}\,{}_2F_1\left(1, 1-\frac{1}{m}; 2+\frac{1}{n}; 1-S_{\tau_0}^{m}\right) - U_p \tag{81}$$

$$\langle v_x\rangle_y \cong \frac{n}{(n+1)m}\left(\frac{\rho g_x}{K}\right)^{m/n} h^{m/n+1}(1 - S_{\tau_0}^{m})^{(n+1)/n}\,{}_2F_1\left(1, 1-\frac{2}{m}; 2+\frac{1}{n}; 1-S_{\tau_0}^{m}\right) - U_p \tag{82}$$

$$Q_z \cong \frac{n}{(n+1)m}\left(\frac{\rho g_x}{K}\right)^{m/n} h^{m/n+2}(1 - S_{\tau_0}^{m})^{(n+1)/n}\,{}_2F_1\left(1, 1-\frac{2}{m}; 2+\frac{1}{n}; 1-S_{\tau_0}^{m}\right) - hU_p \tag{83}$$

$$\left(\frac{\rho g_x h}{K}\right)^{m} - \left(\frac{\tau_0}{K}\right)^{m} - \left[\left(\frac{x}{t} + U_p\right)\frac{1}{h}\right]^{n} \cong 0 \tag{84}$$

dx.doi.org/10.1021/ie500407t | Ind. Eng. Chem. Res. 2014, 53, 6521–6532

$$\frac{\langle h\rangle_x}{h} \cong \left[1+\left(\frac{K}{\rho g_x}\right)^{m/n}\frac{U_p}{h^{m/n+1}}(1-S_{\tau_0}^m)^{-1/n}\right]^{-1} \left[{}_2F_1\left(1,-\frac{2}{m};\frac{1}{n}+1;1-S_{\tau_0}^m\right)+\frac{n}{m(n+1)}(1-S_{\tau_0}^m){}_2F_1\left(1,1-\frac{2}{m};\frac{1}{n}+2;1-S_{\tau_0}^m\right)\right] \quad (85)$$

Table 2. Dimensional Forms of Velocity, Average Velocity, Flow Rate, Local Thickness and Average Thickness for the Heinz−Casson Case: $\eta = (\tau_0^m|\underline{\dot{\gamma}}|^{-m}+\eta_\infty^m)^{1/m}$

For $0 \le y \le \delta$:

$$v_x \cong \left[\frac{\rho g_x h^2}{(m+1)\eta_\infty}\right]\left\{(1-S_{\tau_0}^m)^{(m+1)/m}{}_2F_1\left(1,1-\frac{1}{m};2+\frac{1}{m};1-S_{\tau_0}^m\right)-\left(1-\frac{y}{h}\right)^2\left\{1-\left[\frac{S_{\tau_0}}{1-(y/h)}\right]^m\right\}^{(m+1)/m}{}_2F_1\left\{1,1-\frac{1}{m};2+\frac{1}{m};1-\left[\frac{S_{\tau_0}}{1-(y/h)}\right]^m\right\}\right\}-U_p \quad (86)$$

For $y > \delta$:

$$v_x \cong \frac{\rho g_x h^2}{(m+1)\eta_\infty}(1-S_{\tau_0}^m)^{(m+1)/m}{}_2F_1\left(1,1-\frac{1}{m};2+\frac{1}{m};1-S_{\tau_0}^m\right)-U_p \quad (87)$$

$$\langle v_x\rangle_y \cong \frac{\rho g_x h^2}{(m+1)\eta_\infty}(1-S_{\tau_0}^m)^{(m+1)/m}{}_2F_1\left(1,1-\frac{2}{m};2+\frac{1}{m};1-S_{\tau_0}^m\right)-U_p \quad (88)$$

$$Q_z \cong \frac{\rho g_x h^3}{(m+1)\eta_\infty}(1-S_{\tau_0}^m)^{(m+1)/m}{}_2F_1\left(1,1-\frac{2}{m};2+\frac{1}{m};1-S_{\tau_0}^m\right)-hU_p \quad (89)$$

$$\left(\frac{\rho g_x h}{\eta_\infty}\right)^m-\left(\frac{\tau_0}{\eta_\infty}\right)^m-\left[\left(\frac{x}{t}+U_p\right)\frac{1}{h}\right]^m \cong 0 \quad (90)$$

$$\frac{\langle h\rangle_x}{h} \cong \left[1+\frac{\eta_\infty U_p}{\rho g_x h^2}(1-S_{\tau_0}^m)^{-1/m}\right]^{-1}\left[{}_2F_1\left(1,-\frac{2}{m};\frac{1}{m}+1;1-S_{\tau_0}^m\right)+\frac{1}{(m+1)}(1-S_{\tau_0}^m){}_2F_1\left(1,1-\frac{2}{m};\frac{1}{m}+2;1-S_{\tau_0}^m\right)\right] \quad (91)$$

Table 3. Dimensional Forms of Velocity, Average Velocity, Flow Rate, Local Thickness and Average Thickness for the Casson Case: $\eta = (\tau_0^{1/2}|\underline{\dot{\gamma}}|^{-1/2}+\eta_\infty^{1/2})^2$

For $0 \le y \le \delta$:

$$v_x \cong \left(\frac{\rho g_x h^2}{6\eta_\infty}\right)\{(1-S_{\tau_0}^{1/2})^3(3+S_{\tau_0}^{1/2})-\{[1-(y/h)]^{1/2}-S_{\tau_0}^{1/2}\}^3\{3[1-(y/h)]^{1/2}+S_{\tau_0}^{1/2}\}\}-U_p \quad (92)$$

For $y > \delta$:

$$v_x \cong \left(\frac{\rho g_x h^2}{6\eta_\infty}\right)(1-S_{\tau_0}^{1/2})^3(3+S_{\tau_0}^{1/2})-U_p \quad (93)$$

$$\langle v_x\rangle_y \cong \frac{\rho g_x h^2}{3\eta_\infty}\frac{1}{10}(-S_{\tau_0}^3+15S_{\tau_0}-24S_{\tau_0}^{1/2}+10)-U_p \quad (94)$$

$$Q_z \cong \frac{\rho g_x h^3}{3\eta_\infty}\frac{1}{10}(-S_{\tau_0}^3+15S_{\tau_0}-24S_{\tau_0}^{1/2}+10)-hU_p \quad (95)$$

$$\left(\frac{\rho g_x h}{\eta_\infty}\right)^{1/2}-\left(\frac{\tau_0}{\eta_\infty}\right)^{1/2}-\left[\left(\frac{x}{t}+U_p\right)\frac{1}{h}\right]^{1/2} \cong 0 \quad (96)$$

$$\frac{\langle h\rangle_x}{h} \cong \frac{1}{30}\left[1+\frac{\eta_\infty U_p}{\rho g_x h^2}(1-S_{\tau_0}^{1/2})^{-2}\right]^{-1}(S_{\tau_0}^2+2S_{\tau_0}^{3/2}+3S_{\tau_0}+4S_{\tau_0}^{1/2}+20) \quad (97)$$

Table 4. Dimensional Forms of Velocity, Average Velocity, Flow Rate, Local Thickness, and Average Thickness for the Herschel−Bulkley Case: $\eta = (\tau_0|\underline{\dot{\gamma}}|^{-1}+K|\underline{\dot{\gamma}}|^{n-1}$

For $0 \le y \le \delta$:

$$v_x \cong \frac{n}{(n+1)}\left(\frac{\rho g_x}{K}\right)^{1/n}h^{1/n+1}\left[(1-S_{\tau_0})^{1/n+1}-\left(1-\frac{y}{h}-S_{\tau_0}\right)^{1/n+1}\right]-U_p \quad (98)$$

For $y > \delta$:

$$v_x \cong \frac{n}{(n+1)}\left(\frac{\rho g_x}{K}\right)^{1/n}h^{1/n+1}(1-S_{\tau_0})^{1/n+1}-U_p \quad (99)$$

$$\langle v_x\rangle_y \cong \frac{n}{(2n+1)}\left(\frac{\rho g_x}{K}\right)^{1/n}h^{1/n+1}(1-S_{\tau_0})^{1/n+1}\left[\frac{n}{(n+1)}S_{\tau_0}+1\right]-U_p \quad (100)$$

$$Q_z \cong \frac{n}{(2n+1)}\left(\frac{\rho g_x}{K}\right)^{1/n} h^{1/n+2}(1 - S_{\tau_0})^{1/n+1} \left[\frac{n}{(n+1)}S_{\tau_0} + 1\right] - hU_p \tag{101}$$

$$\frac{\rho g_x h}{K} - \frac{\tau_0}{K} - \left[\left(\frac{x}{t} + U_p\right)\frac{1}{h}\right]^n \cong 0 \tag{102}$$

$$\frac{\langle h\rangle_x}{h} \cong \frac{(n+1)}{(2n+1)}\left[1 + \left(\frac{K}{\rho g_x}\right)^{1/n}\frac{U_p}{h^{1/n+1}}(1 - S_{\tau_0})^{-1/n}\left[\frac{n^2}{(n+1)^2}S_{\tau_0}^2 + \frac{n}{(n+1)^2}S_{\tau_0} + 1\right]\right]^{-1} \tag{103}$$

Table 5. Dimensional Forms of Velocity, Average Velocity, Flow Rate, Local Thickness and Average Thickness for the Mizrahi–Berk Case: $\eta = (\tau_0^{1/2}|\underline{\underline{\dot\gamma}}|^{-1/2} + K^{1/2}|\underline{\underline{\dot\gamma}}|^{n-1/2})^2$

For $0 \le y \le \delta$:

$$v_x \cong \frac{2n}{(2n+1)}\left(\frac{\rho g_x}{K}\right)^{1/(2n)} h^{1/(2n)+1}\left\{(1 - S_{\tau_0}^{1/2})^{1/n+1}\left[\frac{n}{(n+1)}S_{\tau_0}^{1/2} + 1\right] - \left[\left(1 - \frac{y}{h}\right)^{1/2} - S_{\tau_0}^{1/2}\right]^{1/n+1}\left[\frac{n}{(n+1)}S_{\tau_0}^{1/2} + \left(1 - \frac{y}{h}\right)^{1/2}\right]\right\} - U_p \tag{104}$$

For $y > \delta$:

$$v_x \cong \frac{2n}{(2n+1)}\left(\frac{\rho g_x}{K}\right)^{1/(2n)} h^{1/(2n)+1}(1 - S_{\tau_0}^{1/2})^{1/n+1}\left[\frac{n}{(n+1)}S_{\tau_0}^{1/2} + 1\right] - U_p \tag{105}$$

$$\langle v_x\rangle_y \cong \frac{2n}{(2n+1)(4n+1)}\left(\frac{\rho g_x}{K}\right)^{1/(2n)} h^{1/(2n)+1}(1 - S_{\tau_0}^{1/2})^{1/n+1}\left[\frac{6n^3}{(n+1)(3n+1)}S_{\tau_0}^2 + \frac{6n^2}{(3n+1)}S_{\tau_0} + \frac{3n(2n+1)}{(3n+1)}S_{\tau_0}^{1/2} + (2n+1)\right] - U_p \tag{106}$$

$$Q_z \cong \frac{2n}{(2n+1)(4n+1)}\left(\frac{\rho g_x}{K}\right)^{1/(2n)} h^{1/(2n)+2}(1 - S_{\tau_0}^{1/2})^{1/n+1}\left[\frac{6n^3}{(n+1)(3n+1)}S_{\tau_0}^2 + \frac{6n^2}{(3n+1)}S_{\tau_0} + \frac{3n(2n+1)}{(3n+1)}S_{\tau_0}^{1/2} + (2n+1)\right] - hU_p \tag{107}$$

$$\left(\frac{\rho g_x h}{K}\right)^{1/2} - \left(\frac{\tau_0}{K}\right)^{1/2} - \left[\left(\frac{x}{t} + U_p\right)\frac{1}{h}\right]^n \cong 0 \tag{108}$$

$$\frac{\langle h\rangle_x}{h} \cong \left[1 + \left(\frac{K}{\rho g_x}\right)^{1/(2n)}\frac{U_p}{h^{1/(2n)+1}}(1 - S_{\tau_0}^{1/2})^{-1/n} \times [12n^4 S_{\tau_0}^2 + 12n^3 S_{\tau_0}^{3/2} + 6n^2(n+1)S_{\tau_0} + 2n(n+1)(2n+1)S_{\tau_0}^{1/2} + (n+1)(2n+1)^2 (3n+1)]/[(n+1)(2n+1)(3n+1)(4n+1)]\right]^{-1} \tag{109}$$

Table 6. Dimensional Forms of Velocity, Average Velocity, Flow Rate, Local Thickness and Average Thickness for the Ostwald–de Waele Case: $\eta = K|\underline{\underline{\dot\gamma}}|^{n-1}$

$$v_x \cong \frac{n}{(n+1)}\left(\frac{\rho g_x}{K}\right)^{1/n} h^{1/n+1}\left[1 - \left(1 - \frac{y}{h}\right)^{1/n+1}\right] - U_p \tag{110}$$

$$\langle v_x\rangle_y \cong \frac{n}{(2n+1)}\left(\frac{\rho g_x}{K}\right)^{1/n} h^{1/n+1} - U_p \tag{111}$$

$$Q_z \cong \frac{n}{(2n+1)}\left(\frac{\rho g_x}{K}\right)^{1/n} h^{1/n+2} - hU_p \tag{112}$$

$$h \cong \left[\frac{K}{\rho g_x}\left(\frac{x}{t} + U_p\right)^n\right]^{1/n+1} \tag{113}$$

$$\frac{\langle h\rangle_x}{h} \cong \frac{(n+1)}{(2n+1)}\left[1 + \left(\frac{K}{\rho g_x}\right)^{1/n}\frac{U_p}{h^{1/n+1}}\right]^{-1} \tag{114}$$

Table 7. Dimensional Forms of Velocity, Average Velocity, Flow Rate, Local Thickness and Average Thickness for the Bingham Case: $\eta = \tau_0|\underline{\underline{\dot\gamma}}|^{-1} + \eta_\infty$

For $0 \le y \le \delta$:

$$v_x \cong \frac{\rho g_x h^2}{2\eta_\infty}\left[(1 - S_{\tau_0})^2 - \left(1 - S_{\tau_0} - \frac{y}{h}\right)^2\right] - U_p \tag{115}$$

For $y \le \delta$:

$$v_x \cong \frac{\rho g_x h^2}{2\eta_\infty}(1 - S_{\tau_0})^2 - U_p \tag{116}$$

$$\langle v_x\rangle_y \cong \frac{\rho g_x h^2}{3\eta_\infty}\left(\frac{1}{2}S_{\tau_0}^3 - \frac{3}{2}S_{\tau_0} + 1\right) - U_p \tag{117}$$

$$Q_z \cong \frac{\rho g_x h^3}{3\eta_\infty}\left(\frac{1}{2}S_{\tau_0}^3 - \frac{3}{2}S_{\tau_0} + 1\right) - hU_p \tag{118}$$

$$\frac{\rho g_x h}{\eta_\infty} - \frac{\tau_0}{\eta_\infty} - \left(\frac{x}{t} + U_p\right)\frac{1}{h} \cong 0 \tag{119}$$

$$\frac{\langle h\rangle_x}{h} \cong \left[1 + \frac{\eta_\infty U_p}{\rho g_x h^2}(1 - S_{\tau_0})^{-1}\right]^{-1}\left(\frac{1}{6}S_{\tau_0}^2 + \frac{1}{6}S_{\tau_0} + \frac{2}{3}\right) \tag{120}$$

Table 8. Dimensional Forms of Velocity, Average Velocity, Flow Rate, Local Thickness and Average Thickness for the Newtonian Case: $\eta = \mu$

$$v_x \cong \left(\frac{\rho g_x h^2}{2\mu}\right)\left[1 - \left(1 - \frac{y}{h}\right)^2\right] - U_p \tag{121}$$

$$\langle v_x\rangle_y \cong \frac{\rho g_x h^2}{3\mu} - U_p \tag{122}$$

$$Q_z \cong \frac{\rho g_x h^3}{3\mu} - hU_p \tag{123}$$

$$h \cong \left[\frac{\mu}{\rho g_x}\left(\frac{x}{t} + U_p\right)\right]^{1/2} \tag{124}$$

$$\frac{\langle h\rangle_x}{h} \cong \frac{2}{3}\left(1 + \frac{\mu U_p}{\rho g_x h^2}\right)^{-1} \tag{125}$$

It is important to note that, as a first validation step, some few expressions presented in Table 3 and Table 5–Table 8, can be rearranged to reproduce expressions found in the literature for a given rheological model and the stage of a dip-coating process studied (i.e., withdrawal, draining, etc.).[10,14,19,38−40]

Finally, a quantity that could be useful in some studies is the ratio of the average velocity to the velocity in the film–air interface when $U_p = 0$ (i.e., the velocity for $y \geq \delta$, $\tilde{v}_{x,\tilde{y}\geq\tilde{\delta}}$). A list of simplified expressions of this ratio is presented in Table Table 9.

Table 9. Ratio of Average Velocity to the Velocity in the Film–Air Interface: $U_p = 0$

Generalized Herschel–Bulkley

$$\frac{\langle v_x\rangle_y}{v_{x,y\geq\delta}} \cong \frac{{}_2F_1\left(1, 1 - \frac{2}{m}; 2 + \frac{1}{n}; 1 - S_{\tau_0}^m\right)}{{}_2F_1\left(1, 1 - \frac{1}{m}; 2 + \frac{1}{n}; 1 - S_{\tau_0}^m\right)} \tag{126}$$

Heinz–Casson

$$\frac{\langle v_x\rangle_y}{v_{x,y\geq\delta}} \cong \frac{{}_2F_1\left(1, 1 - \frac{2}{m}; 2 + \frac{1}{m}; 1 - S_{\tau_0}^m\right)}{{}_2F_1\left(1, 1 - \frac{1}{m}; 2 + \frac{1}{m}; 1 - S_{\tau_0}^m\right)} \tag{127}$$

Casson

$$\frac{\langle v_x\rangle_y}{v_{x,y\geq\delta}} \cong \frac{S_{\tau_0}^{3/2} + 3S_{\tau_0} + 6S_{\tau_0}^{1/2} + 10}{5S_{\tau_0}^{1/2} + 15} \tag{128}$$

Mizrahi–Berk

$$\frac{\langle v_x\rangle_y}{v_{x,y\geq\delta}} \cong \left\{6n^3\left[S_{\tau_0}^{3/2} + \frac{(n+1)}{n}S_{\tau_0} + \frac{(n+1)(2n+1)}{2n^2} S_{\tau_0}^{1/2} + \frac{(n+1)(2n+1)(3n+1)}{6n^3}\right]\right\} \Big/ \left\{(3n+1)(4n+1)[nS_{\tau_0}^{1/2} + (n+1)]\right\} \tag{129}$$

Herschel–Bulkley

$$\frac{\langle v_x\rangle_y}{v_{x,y\geq\delta}} \cong \frac{n(S_{\tau_0} + 1) + 1}{(2n+1)} \tag{130}$$

Ostwald–de Waele

$$\frac{\langle v_x\rangle_y}{v_{x,y\geq\delta}} \cong \frac{(n+1)}{(2n+1)} \tag{131}$$

Bingham

$$\frac{\langle v_x\rangle_y}{v_{x,y\geq\delta}} \cong \frac{(S_{\tau_0} + 2)}{3} \tag{132}$$

Newtonian

$$\frac{\langle v_x\rangle_y}{v_{x,y\geq\delta}} \cong \frac{2}{3} \tag{133}$$

4. CONCLUSIONS

An analytical and simple mathematical model relating the main parameters in a dip-coating process using a generalized Newtonian fluid was proposed. This model has been obtained based upon rigorous mass and momentum balances applied to a monophasic and non-evaporative system, where the main forces are viscous and gravitational. The phenomena occur far away from the meniscus that is formed at the surface of the fluid–forming reservoir. It is worth mentioning that the work carried out in this study and the generalized nature of the model allowed finding the analytical solutions (*i.e.* mainly film thickness) for dip-coating processes using rheological models such as Heinz–Casson, Casson, Mizrahi–Berk, and partially Herschel–Bulkley, and Bingham. The parameters that can be estimated are velocity profile (eqs 37 and 38), average velocity (eq 47), flow rate (eq 50), local thickness (eq 57), average thickness (eq 62) of the coating film, and the total force required to withdraw the substrate with the film (eq 66). Finally, the sufficient conditions for the model were obtained.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported partially by Universidad Nacional del Litoral (Santa Fe, Argentina), Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina), and Agencia Nacional de Promoción Científica y Tecnológica (Argentina).

NOMENCLATURE

$B[s,a,b]$ = incomplete beta function
C = concentration, kg m^{-3}
Ca = capillary number $(\eta U \sigma^{-1})$
$\underline{e}_i$ = unit vector in the i^{th} direction
e = half thickness of the plate, m
$\underline{F}_e$ = external forces vector, N m^{-3}
F_{film} = force related to the film on the plate, N
F_{plate} = force related to the plate mass, N
F_{total} = total force, N
${}_2F_1[a,b;c;s]$ = Gauss hypergeometric function
Fr = Froude number $(U^2 g_x^{-1} h_L^{-1})$
$\underline{g}$ = gravity acceleration vector, m s^{-2}
g = gravity acceleration component, m s^{-2}
$|g|$ = magnitude of $\underline{g}$ (9.81), m s^{-2}
h = local thickness of the film, m
h_L = h evaluated at L, m
K = consistency index used in eq 22, Pa s$^{n/m}$
L = length of the plate, m
m = second behavior index used in eq 22
n = first behavior index used in eq 22
$\mathbb{N}$ = natural numbers
p = pressure, Pa
Q_z = flow rate per unit width, m^2 s^{-1}
Re = Reynolds number $(\rho U h_L \eta_{\text{ref}}^{-1})$
S_K = ratio of the viscous stress to the maximum stress
S_{τ_0} = ratio of the yield stress to the maximum stress
St = Stokes number $(\rho g_x h_L^2 \eta_{\text{ref}}^{-1} U^{-1})$
s = dummy variable
T = temperature, K
t = time, s
U = reference velocity for the x direction, m s^{-1}
U_p = velocity of the plate, m s^{-1}
V = reference velocity for the y direction, m s^{-1}
$\underline{v}$ = velocity vector, m s^{-1}
v = velocity component, m s^{-1}
W = width of the plate, m
$\underline{x}$ = position vector, m
x,y,z = Cartesian coordinates

Greek Symbols

$\Gamma[s]$ = gamma function
$\underline{\underline{\dot{\gamma}}}$ = rate of deformation tensor, s^{-1}
$|\underline{\underline{\dot{\gamma}}}|$ = magnitude or second invariant of $\underline{\underline{\dot{\gamma}}}$, s^{-1}
δ = position of the viscous to solidlike behavior transition, m
ε = dimensionless ratio $(h_L L^{-1})$
η = apparent viscosity, Pa s
θ = angle between the axis of the plate and the axis of $\underline{g}$, deg
ρ = density, kg m^{-3}
ρ_p = density of the plate, kg m^{-3}
σ = surface tension coefficient, N m^{-1}
$\underline{\underline{\tau}}$ = shear stress tensor, Pa
τ_{ij} = shear stress component acting in jth direction on a plane with a normal vector acting in ith direction, Pa
τ_0 = yield stress coefficient used in eq 22, Pa
ψ = function defined by eq 39

Subscripts

ref = reference state
x = in x direction
y = in y direction
z = in z direction
∞ = at infinite rate of deformation

Special Symbols

$\langle\ \rangle_i$ = averaged quantity in the ith direction
$\tilde{\square}$ = dimensionless quantity
$O()$ = "of the order of"

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