

A semi-empirical power-law model for the dip-coating of a substrate into a particle-containing, non-Newtonian, complex fluid system

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Abstract

The apparent viscosity of a particle suspension of ZrSi_2 particles, polyhydromethylsiloxane (PHMS) preceramic polymer and n-Octane solvent, used to process *polymer-derived ceramic composite coatings*, is shown by viscometric experiments to be shear-thinning. The suspension is dip-coated onto substrates and the measured entrained coating thickness, h_0 , is observed to be a power-law function of U , the substrate extraction speed, as $h_0 = 0.5051U^{0.5}$. The experimentally observed semi-empirical model is directly compared to the results of a variety of theoretically derived Landau-Levich scaling laws and other models that have similar liquids and that include other effects. None of these cases predicts the scaling observed in these experiments. A correction factor is introduced to quantify the difference between the semi-empirical model with existing theoretical models. Possible explanations for the observed scaling behavior are presented.

Keywords

Landau-Levich; non-Newtonian; shear thinning; polymer derived ceramics

1. Introduction

Particle-reinforced ceramic matrix composite (CMC) coatings can be made by a polymer-derived ceramic route [1-5]. CMC coatings show promise in many important applications, such as high-temperature environmental/thermal barrier coatings, because of their attractive thermal and mechanical properties and ease of processing. A representative slurry composition used for making CMC coatings contains sub-micron size particles, a silicon-based preceramic polymer and organic solvent, resulting in a complex fluid system. A typical processing approach is to coat a substrate with this slurry (e.g. by dip-coating or spin-coating), evaporate the solvent, crosslink the polymer and finally convert it to the ceramic composite using high temperature pyrolysis. A previous study [6] involving particle-reinforced CMC coatings has shown the existence of a maximum critical coating thickness, t_c , before pyrolysis, that ensures crack-free coatings after pyrolysis. It has been shown that cracking is due to stresses generated during constrained pyrolysis. t_c depends on the unconstrained shrinkage of the polymer during pyrolysis and increases as the unconstrained shrinkage decreases. The unconstrained shrinkage can be controlled by adding filler particles. The optimal range of filler particle volume fraction (V_f) is 30-40%. Due to the necessity of ensuring that the coating thickness in the polymeric stage remains below t_c , there is a critical need to establish a method that can predict the coating thickness made by dip-coating complex fluids containing suspended particles, whose rheological properties are almost always non-Newtonian.

The ability to well-predict and hence control film thicknesses of dip-coated substrates is of high interest to the engineering research community not only for quality-control of the CMC coatings just described above, but also because there are many other applications of dip-coating involving complex liquids. The classical drag-out (i.e., dip-coating) problem in fluid mechanics

typically involves a flat substrate, vertically withdrawn from an infinitely deep fluid bath at fixed speed, which leads to the formation of a continuous entrained film. Landau and Levich [7] were the first to carry out an analysis, valid to leading order in capillary number $Ca = (\mu U/\sigma)$, where μ is the liquid viscosity and σ is the gas-liquid surface tension, that predicts the film thickness of a *Newtonian* fluid along a plate emerging from the bath at speed U . The thickness prediction of the *Landau-Levich* drag-out problem is:

$$h_0 = \left(\frac{\mu U}{\rho g} \right)^{1/2} f(Ca), \quad (1)$$

where h_0 is the film thickness, ρ is the liquid density, and the function $f(Ca)$ takes the form:

$$f(Ca) = 0.944 \left(\frac{\mu U}{\sigma} \right)^{1/6}, \text{ for capillary number } Ca = \frac{\mu U}{\sigma} \ll 1. \quad (2)$$

Eqn. (2) is valid in the low capillary number regime, in which gravitational forces do not drive liquid film drainage and thus do not regulate the entrained layer thickness. On the other hand, in the large capillary number regime:

$$f(Ca) = 1, \text{ for capillary number } Ca = \frac{\mu U}{\sigma} \gg 1. \quad (3)$$

Eqn. (3) was first obtained by Derjaguin [8] and is valid under conditions in which gravitational drainage dominates. In the intermediate regime, as the capillary number increases from very small values to very large values, gravity plays an increasingly important role. There have been several treatments of the drag-out problem for intermediate Ca . For example, Spiers *et al* [9, 10] predict the film thickness h_0 to be determined by the solution of:

$$(\lambda_c h_0)^{3/2} = 1.78A \{h_0, Ca, \lambda_c\} \left[Ca - (\lambda_c h_0)^2 \right], \quad (4)$$

where $A\{h_0, Ca, \lambda_C\}$ is a numerically determined function of the film thickness, the capillary number and the capillary length $\lambda_C = (\sigma/\rho g)^{1/2}$. (The limit $1.78A\{h_0, Ca, \lambda_C\} = 0.944$ is the result of White and Tallmadge [11].) Eqn. (4) agrees well with experiments involving Newtonian liquids for capillary numbers up to approximately 2. As will be shown, these results do not agree with the experimental results of this work. The theory has been generalized to different geometries, including coatings on cylindrical fibers by Derjaguin [12, 13], to non-vertical plate withdrawal orientations and to include higher order effects by Wilson [14]. Bretherton [15] used asymptotic methods to predict the speed of a wetting gas bubble migrating within a large (small) diameter cylindrical tube with (without) gravitational effects. Park and Homsy [16] validated the matching procedure applied by Landau & Levich and Bretherton, and showed how the curvature of the capillary statics region is determined by matching with the transition layer. The location of the transition region is determined to be near the apparent zero of the outer solution. A high capillary number theory has also been developed by Groenveld [17]. There have been full-scale numerical and experimental efforts [9, 18-20] and treatments of Newtonian liquids that include inertial effects [21].

In practice, knowledge of the viscous behavior of ‘complex’, technologically important polymeric liquids, solutions and suspensions, which are often used as coatings, remains limited [22]. These liquids are typically characterized by shear-thinning or other more complicated *non-Newtonian* behaviors. In the shear-thinning case, the liquids exhibit Newtonian behavior at very low and very high shear-rates, but in the intermediate shear-rate regime often their viscosities are modeled as a power-law function of the shear rate. In general, the original Landau-Levich model and its extensions must be carefully adapted to take non-Newtonian effects into account. Power law, Ellis, Carreau-Yasuda, viscoelastic and even Bingham models have been considered by

different authors [10, 23-26]. These models have all achieved a qualitative level of success, and some experimental results match well with the theoretical predictions. One of the earliest treatments to include viscoelastic effects was by Ro and Homsy [27], who examined the entrained layer thickness as a function of pulling speed by means of an expansion involving both the capillary number and the Weissenberg number. More recently, after concluding that the experimental dip-coating results for various non-Newtonian complex fluid cases cannot be accounted for by considering only the capillary number, Ashmore *et al.* [28] performed an asymptotic analysis to predict the film thickness of non-Newtonian liquids in both shear-thinning and strong elastic limits. Their results give a quantitatively accurate prediction for the film thickness in the polymer solutions studied. Ouremi and Homsy [29] have experimentally studied the effects of adsorbed particles on the drag-out problem, although there are few other studies that have reported modification of the Landau-Levich model for *particle-suspended* non-Newtonian fluid systems. In addition, recently Dixit and Homsy have studied the Landau-Levich problem with elastic [30] and elastocapillary [31] effects. Kretchetnikov and Homsy have examined the drag-out problem with a surfactant-laden liquid resulting in the displacement of stagnation points away from the gas-liquid interface and in film thickening behavior, compared to the case without surfactant. None of the results involving complex fluids cited here provides the same scaling that we have experimentally observed in this work.

This paper provides insight into the drag-out entrainment layer thickness problem for a complex particle suspension by combining practical engineering methodology with mathematical analysis. The semi-empirical model is based on the experimental results presented here and provides a scaling that is in the form of a Landau-Levich model, enabling comparison to other

models and providing insight into the origin of scaling differences due to the complex nature of these experiments.

2. Experiments

2.1 Procedure

The slurry used in this study was prepared following the Greil analysis [32, 33] for the processing of a polymer-derived ceramic composite with low-shrinkage during pyrolysis. A mixture consisting of 30 vol% submicron $ZrSi_2$ particles (Accumet Materials Co., Ossining, NY, USA) and 70 vol% silicon-based polymer precursor polyhydromethylsiloxane (PHMS, HMS-992, Gelest Inc., Morrisville, PA, USA) forms the ‘base slurry’. PHMS, a linear polymer, is liquid at room temperature. To improve the particle distribution uniformity and to enhance particle oxidation during pyrolysis, the $ZrSi_2$ particles were attrition-milled in isopropyl alcohol for 10 hours at room temperature, dried in a convection drying oven ($\sim 100^\circ\text{C}$) and ground back to fine powder using mortar and pestle before mixing with the PHMS. Due to its high volatility, low boiling point (126°C) and low viscosity (~ 1 centiPoise), an organic solvent n-Octane (98+%, Alfa Aesar, Ward Hill, MA, USA) was added into the ‘base slurry’ to further adjust the viscosity. In the present work, the volume ratio of ‘base slurry to n-Octane’ was set at 3:5 to achieve the desired coating thicknesses in the range of withdrawal speeds investigated. Therefore, the volume ratio of ‘ $ZrSi_2$ particles : PHMS : n-Octane’ in the final slurry is 11.25% : 26.25% : 62.5%. The slurry was then ball-milled for 4 hours in a tumbler to remove agglomerates and form a homogeneous particle suspension.

To understand the slurry rheological properties, viscosity measurements were taken using a Haake VT550 rotational viscometer (Thermo Fisher Scientific, Inc., Waltham, MA, USA) with

a SV-2P sensor and a SVP cup, which allows matching of a desirable sample volume (6 ml) and a shear rate range ($4\text{-}390\text{ s}^{-1}$) with the pulling process. Tests were carried out at room temperature ($\sim 20^\circ\text{C}$), with a rotational speed between 10-300 revolutions-per-minute. Different shear-rate testing modes were used: constant, continuously-increasing and stepwise-increasing. The last mode was determined to be the most suitable for this study considering the non-Newtonian nature of the complex fluid.

For coating deposition, the slurry was dip-coated onto stainless steel 304 plate substrates ($30\times 10\times 1.2\text{ mm}$, 600 grit surface finish) using an Instron 4505 (Illinois Tool Works Inc., Norwood, MA, USA) mechanical testing frame to precisely control the withdrawal speed. The investigated withdrawal speeds were between 100 and 1000 mm/min ($1/600$ to $1/60\text{ m/s}$). Coating samples of all thicknesses were dried at room temperature with the substrate/coating in two orientations, one in which the direction of the gravitational force is parallel to the coating-substrate interface (the vertical orientation), and the other in which the gravitational force is perpendicular to the coating-substrate interface (the horizontal orientation). The samples were then crosslinked at 150°C for 2 hours (all processes were carried out in air). Crosslinked thickness data were derived from profilometric measurements (Dektak 6M Stylus Profiler, Veeco Instruments Inc., Plainview, NY, USA) at different locations in each sample and the average thickness was calculated from multiple measurements (a minimum of 8 measurements per coating). Knowing the shrinkage during drying and crosslinking, the wet coating thickness (right after withdrawal from the slurry) is calculated.

2.2 Results

2.2.1 *Apparent Viscosity of the Slurry*

Unlike single-phase liquids, the slurry in the present work is a particle suspension. The submicron ZrSi₂ particles, as well as the PHMS (linear molecules), play an important role in the suspension's rheological properties due to the much higher density (4.88 g/cm³) of ZrSi₂, compared to PHMS (0.99 g/cm³) and n-Octane (0.70 g/cm³).

Viscometric results show that when a constant shear-rate is applied the shear-stress in the slurry reaches steady-state within 10 seconds. Therefore, a stepwise-increasing shear rate mode (as a function of time, 6.2 s⁻¹ per step and 30 seconds per holding) was used to ensure that the measurement of the shear stress was reliable at each shear rate tested (Figure 1.a). This procedure generates one shear stress data point for each applied shear rate every 30 seconds, as shown in Figure 1.b. By re-plotting shear stress as a function of shear rate, the slurry is observed to be shear-thinning (Figure 1.c). This is in contrast with the hypothesis used in the work of Torrey *et al* [34], who assumed that this type of slurry is Newtonian. The data plotted in Figure 1.b show three time ranges over which the shear stress is nearly constant, however, it is hypothesized that these results are due to a lack of adequate viscometric resolution. (The viscometer continuously and automatically samples and records data. Since the measured shear stress fluctuates due to the stepwise-increasing shear rate, time is needed for the readjustment and stabilization of the liquid. Each shear stress data point in Figure 1.b is an averaged number). The measurements are reproducible and the shear-thinning behavior is clear.

The shear-thinning behavior observed in these suspensions is attributed to the breakdown of gel structures in the flocculated suspension caused by the imposed shear [35]. The intensity of the shear determines how many 'flocs' will be destroyed. If the shear rate is high enough, the gel structure will be destroyed so that each particle flows independently in the mixture of preceramic polymer and organic solvent leading to a lower viscosity. Microscopically, the particle

suspension exhibits dynamic equilibrium, which is a balance between the rates of gel breakdown and restoration. In dynamic equilibrium, the suspension exhibits a constant apparent viscosity at any given shear rate. This explains the observation of steady states in our slurry if it is held under a condition of constant shear rate for long enough time.

The red curve in Figure 1.c is the result of fitting the shear stress (τ) versus shear rate ($\dot{\gamma}$) data to the power-law that best characterizes the nature of the quantitative relationship between shear stress and the shear:

$$\tau = K \cdot \dot{\gamma}^n. \quad (5)$$

K is the flow consistency index and n is the power-law exponent. Thus, the apparent viscosity (μ_{app}) for a power-law liquid is given by:

$$\mu_{app} = K \cdot \dot{\gamma}^{n-1}. \quad (6)$$

The fit of the power-law model to the experimental data in Figure 1.c gives $K = 0.11036$ and $n = 0.76729$ so that:

$$\mu_{app} = 0.11 \cdot \dot{\gamma}^{-0.23} \quad (7)$$

Eqn. (7) is plotted in Figure 1.d showing the shear-thinning nature of the liquid.

2.2.2 Experimental Reproducibility

Figure 2 illustrates the reproducibility of the ‘shear stress—shear rate’ measurements just presented. Figure 2 is derived from three ‘shear stress—shear rate’ measurements conducted in the same manner described above. The curves of the three measurements do not entirely overlap (they are close in the low shear rate regime and diverge slightly as shear rate increases) but the key parameters, K and n , still exhibit good reproducibility (Table 1) with standard deviations

being 0.001652 and 0.006621, respectively. The average values of K and n of the three measurements are 0.11 and 0.77 (rounded off at two decimal places), which are the same values of all experiments when rounded off. Note that values taken from measurement 1 were used to construct graphs and to carry out calculations presented here, instead of the average values of K and n . Measurements 1, 2 and 3 were conducted in the same manner as described in section 2.2.1.

Table 1. Experimental reproducibility of the three ‘shear stress—shear rate’ measurements.

	K	n
Measurement 1	0.11036	0.76729
Measurement 2	0.10931	0.76186
Measurement 3	0.10645	0.77781
Average	0.10871	0.76899
Average rounded up to two decimals	0.11	0.77
Standard Deviation	0.001652	0.006621

It is worthwhile to note that Figure 1.c shows the experimentally determined shear stress data diverging from the power law model between 20 s^{-1} and 40 s^{-1} , implying that the slurry—a complex fluid—doesn’t obey the same power law when the shear rate is very low. A possible explanation for this discrepancy is that the inertial effect of the suspended particles is not negligible in this regime. Moreover, there is a nearly linear increase in the shear stress as a function of the shear rate for the first three data points, which is characteristic of Newtonian liquids. However, it will be shown below that the lowest measured shear rates shown in Figure 1.c are of little relevance to the results presented in this work.

2.2.3 Estimation of the Experimental ‘Wet’ Thickness

The entrainment thickness, h_0 , derived in the Landau-Levich model and in our modified results presented below refers to the ‘wet’ thickness of the film as it is being pulled out of the

bath with the same composition of the fluid. However, in the case considered in this work, although the evaporation time varies depending on thickness, most of the n-Octane in a coating evaporates in less than 60 seconds after drawing stops for all investigated withdrawal speeds, i.e., 100-1000 mm/min. Therefore, it is practically infeasible to accurately measure *in-situ* ‘wet’ coating thicknesses and instead we experimentally measure the *crosslinked* thicknesses and utilize the following rationale to indirectly obtain the wet-thickness h_0 from the crosslinked samples. Figure 3 demonstrates the evolution of coating thickness from the ‘wet’ to the ‘dry’ and finally to the ‘crosslinked’ stage.

Upon deposition onto the substrate, the ‘wet’ coating is longitudinally constrained by the substrate. Thus, the shrinkage due to evaporation and crosslinking occurs predominantly in the transverse thin film direction. A coating sample in the wet stage keeps its original composition and thickness, h_0 . Since the volume ratio between the base slurry ($\text{ZrSi}_2 + \text{PHMS}$) and n-Octane is 3:5, the coating thickness in the dry stage will shrink to 3/8 (37.5%) of its wet thickness upon the evaporation of n-Octane, leaving only a ‘dense’ coating made of the base slurry. Subsequently, the temperature is raised to 150°C to crosslink the polymer. During crosslinking, pure PHMS polymer coating thicknesses shrink approximately 5% [34]. The filler particles take up 30% of the volume fraction of the base slurry so that the coating thickness reduction is 3.5% from the dry stage to the crosslinked stage as shown here:

$$\Delta h_{dry \rightarrow crosslinked} = \frac{[h \cdot 0.3 + h \cdot 0.7 \cdot 0.95]_{crosslinked} - [h]_{dry}}{[h]_{dry}} = 0.965 - 1 = -0.035 . \quad (8)$$

The coating thickness after PHMS crosslinking at 150°C, h_{CL} , can be experimentally measured using either a profilometer or the SEM, since the crosslinked coating is sufficiently rigid.

Consequently, the following equation is obtained to correlate the crosslinked thickness with the wet thickness:

$$h_{CL} = h_0(\text{exp}) \cdot 37.5\% \cdot 96.5\% = 0.362 \cdot h_0(\text{exp}), \quad (9)$$

in which $h_0(\text{exp})$ is the experimental wet coating thickness derived from the measurement of the crosslinked coating samples.

Experimental results (measured h_{CL} thicknesses) are presented by the solid red and solid black lines in Figure 4. The reason that two lines are presented is the finite length of the plate (substrate) used in the experimental process. Since the substrate has finite length, then, after it is withdrawn from the liquid bath, the speed of the moving plate very quickly reduces to zero, resulting in a loss of upward momentum in the liquid film. This promotes excess liquid drainage after the plate has been withdrawn from the bath because gravity becomes important as illustrated by the noticeable difference in the thickness of the films dried in the ‘vertical’ (solid black line) vs the ‘horizontal’ (solid red line) mode shown in Figure 4. It is observed that for samples dried in the vertical orientation after dip-coating, excess slurry drains to the bottom of the plate and either a meniscus or droplets form that pinch off from the sample depending on the plate withdrawal speed. By comparison, under conditions identical to the vertical drying case, samples flipped to a horizontal drying position after extraction from the slurry exhibit negligible drainage. It is due to the continued drainage in the vertical drying mode that its measured coating thickness is always lower than that of samples dried in the horizontal drying configuration. The only exception is at the lower end of withdrawal speeds, e.g., $U = 100$ mm/min, in which case both ‘vertical’ and ‘horizontal’ samples match well with the predicted thickness, possibly because in this regime the coating is so thin that gravitational forces are limited *even after*

drawing has stopped. The model results reported in this work apply to the *horizontal* drying mode.

The experimental data shown in Figure 4, ' $h_0(\text{exp})$, horizontal' in particular, can be fitted by the scaling law of the coating thickness (h'_0) as a function of the withdrawal speed (U) as follows (Figure 5):

$$h'_0 = 0.0006315 \cdot U^{0.50}. \quad (10)$$

The results are summarized in Table 2. In subsequent sections we compare this result to other models and then provide a rationale for the result by development of the semi-empirical scaling model for this process.

Table 2. Actual and predicted coating thicknesses derived from different models.

U (mm/min)	100	300	700	1000
U (m/s)	0.0017	0.005	0.012	0.017
h_{CL} (exp, vertical) [μm]	10.3 \pm 0.3	14.6 \pm 0.1	19.1 \pm 0.3	22.4 \pm 0.5
h_0 (exp, vertical) [μm] (Eqn. 9)	28.5 \pm 0.8	40.3 \pm 0.3	52.8 \pm 0.8	61.9 \pm 1.4
h'_{CL} (exp, horizontal) [μm]	9.4 \pm 0.4	15.8 \pm 0.2	24.8 \pm 0.1	29.7 \pm 0.6
h_0 (exp, horizontal) [μm] (Eqn. 9)	26.0 \pm 1.1	43.6 \pm 0.6	68.5 \pm 0.3	82.1 \pm 1.7
h_0 [μm] (Eqn. 19)	26.4	51.0	84.8	105.1
h_0 (Ashmore) [μm] (Eqn. 15)	30.9	59.7	99.3	123
t (Eqn. 21)	0.985	0.854	0.807	0.781
h'_0 [μm] (Eqn. 10)	25.7	44.5	68.0	81.3

2.2.4 Comparison of the Experimental Semi-Empirical Coating Thickness Model with other Models

Comparisons are made between the measured thicknesses given by Eqn. (10) in Figures 4 and 5 and other models that predict entrained film thickness involving complex liquids. Ashmore *et al* used the Criminale-Ericksen-Filbey constitutive equation [36] and tested their theory on a weakly viscoelastic liquid consisting of 0.06 wt% polyacrylamide (PAA) in a 1:1 mixture (by weight) of water and glycerol, and demonstrated a good fit between experimental and calculated coating thicknesses. The 0.06 wt% PAA solution slurry has properties (such as shear-thinning behavior) very similar to those of the slurry examined in the present work. Specifically, some rheological and physical properties from the two cases are compared in Table 3. Note that the two liquid systems are different in their polymer molecular weight and constituency, however, they both show shear-thinning behavior, which is believed to originate from the similar linear-chain structure of PAA and PHMS. Moreover, solvents like water, glycerol and n-Octane are all small molecules, thus should not be able to contribute to the shear-thinning effect, although the filler particles used in the present study noticeably thicken the slurry. Defining κ_m to be the curvature of the static meniscus, the film thickness proposed by Ashmore *et al* [28] takes the form,

$$\frac{h_0}{\kappa_m^{-1}} = \left[9f(n)^3 \left(\frac{KU^n}{\sigma\kappa_m^{1-n}} \right)^2 \right]^{1/(2n+1)} \quad (11)$$

for a vertical film, in which

$$\kappa_m = \sqrt{\frac{2\rho g}{\sigma}}, \quad (12)$$

$$f(n) = \frac{\ell^2 \kappa_m}{h_0}, \quad (13)$$

and

$$\ell = \left(\frac{\sigma h_0^{n+2}}{3KU^n} \right)^{1/3}. \quad (14)$$

Substituting the approximation $f(n) = 0.646-0.76 \log(n)$ [28] and the properties of the slurry given from Table 3 into Eqn. (11) leads to the following relationship between the film thickness and the substrate withdrawal speed:

$$h_0 = 0.001435 \cdot U^{0.60}. \quad (15)$$

It is apparent that the Ashmore model does not capture the dependence of the experimental entrained thickness on pulling speed of coating layers processed from the slurry used in the experiments reported in this work.

Table 3. Comparison of properties of the 0.06 wt% PAA solution in [28] and the slurry in the present work.

	0.06 wt% PAA solution [28]	ZrSi ₂ -filled PHMS in n-Octane
Density ρ [g/cm ³]	1.08	1.59
Polymer molecular weight [g/mol]	2.2×10^6	$1.8-2.1 \times 10^3$
Surface tension σ [mN/m]	61	35
Flow consistency index K	0.10	0.11
Power law exponent n	0.71	0.77
Zero shear rate viscosity η_0 [Pa.s]	0.067	< 0.1
$f(n)$	0.90	~0.83
κ_m [m ⁻¹]	-	943.6

Finally, we compare the generalized Newtonian models of Afanasiev *et al* [23] with our experimental results. For the value of $n = 0.76729$ valid in this work (at the Ca number applicable here), the prediction of the film thickness from the matched asymptotic analysis of Afanasiev *et al* for a power-law liquid depends on the withdrawal speed to the power of 0.6055, which is *not* in agreement with the experimental results presented above. In addition, in comparing a particular case, it is seen that their matched asymptotic analysis gives a value of film thickness $\sim 31 \mu\text{m}$ at a withdrawal speed of 700 mm/min (see the Appendix), which is less than the experimental coating thickness of approximately 50 μm reported (vertical, Figure 4). Numerical integration of the lubrication model of Afanasiev *et al* [23] for this case gives an even more inaccurate value of film thickness than their matched asymptotic analysis.

In summary, the Ashmore model is shown to agree closely with the experiments in films made from PAA solutions, however, it overestimates the film thickness for the non-Newtonian particle suspensions presented in this work. The Afanasiev model underestimates the film thicknesses presented here. Since no models correctly predict the scaling of the thickness with the withdrawal speed (under conditions for which the gravitational influence on draining is minimal), the conclusion is that the exponent determined experimentally is not simply due to the shear thinning (non-Newtonian) nature of the fluid being drawn and, instead, is attributable to other physical effects.

A physical rationale for the experimental power-law scaling presented in Eqn. (10) is sought. Our approach is to start with the classical Landau-Levich model and using systematically applied modifications eventually derive the result given in Eqn. (10). In this way a discussion of the physical effects that may contribute to the final form of entrainment coating thickness result is facilitated. The effectiveness of Eqn. (10) in predicting film thickness is given in Figure 5,

where good agreement between the predicted and the actual thicknesses can be found throughout the entire order of magnitude range of withdrawal speeds considered.

3. Semi-empirical Modeling

3.1 Relevance of the Landau-Levich Model

The experimentally determined scaling law given by Eqn. (10), offers no physical insight into the origin of the power law exponent or the coefficient. The purpose of this discussion is to *provide insight* into different physical effects on entrainment scaling and to relate them to the case presented in this paper.

The starting point of the discussion is the Landau-Levich model. Since the conditions for its applicability are known, modifications can be made to this model to account for the differences in the complex liquid system and in the experimental setup used here, such as the finite sample length. For a Landau-Levich model to apply, three of the multiphase system intrinsic properties: the liquid viscosity, the liquid density and the gas-liquid surface tension are required. The latter two properties are readily available regardless of the fluid rheological nature. Our slurry viscosity is shear-rate dependent as presented in Figure 1. Figure 1.d shows that the maximum apparent viscosity of our slurry is below 0.1 Pa.s at the lowest shear rates. The largest withdrawal speed used is 1000 mm/min (0.017 m/s), and the surface tension of the slurry is measured to be 35 mN/m using a pendant drop method [37] so that *maximum* estimated value of Ca is 0.05, or $Ca^{1/3} = 0.368$. The capillary number dictates whether Eqn. (2), (3) or some other formulation should be used as a starting point for the description of a drag-out process.

In order that the effect of gravity may be neglected in the Landau-Levich drag-out analysis, $Ca^{1/3} \ll 1$ [21]. Therefore, we can assume that although gravitational drainage can play

a very minor role on entrainment thickness, it is dominant only in the regime of much larger Ca and so even though the scaling given by Eqn. (3) agrees with the result presented, it is not physically relevant to the current experimental observation, and so we begin the discussion with Eqn. (2) (and Eqn. (1)) as the starting point.

A review of the dip-coating process is depicted in Figure 6. The plate substrate is vertically withdrawn from the bath at a constant speed, U , in the positive x-axis direction. The direction normal to the plane of the substrate is parallel to the y-axis. As is well known, the liquid region may be subdivided into an entrainment region, where the liquid is directly entrained by the motion of the plate to form an adhering film and the static meniscus (or capillary-static) region in the bath away from the film, where the interface shape is minimally distorted by the motion of the plate. In general, in the entrainment region, viscous forces are more important than capillary forces and the liquid is set into motion adjacent to the moving plate due to the transfer of momentum from the plate to the viscous liquid. In the static meniscus, capillary forces are more important than viscous forces. Separating the entrainment and the meniscus regions is a relatively short transition region (or dynamic meniscus), where the capillary and viscous forces are comparable. To determine the resulting entrained film thickness using a Landau-Levich approach requires knowledge of the solutions for the flow and interface shape in the capillary-static and transition regions.

3.2 Shear Rate at the Stagnation Point Thickness

The effect of the non-uniform liquid viscosity is examined by incorporating our experimentally determined values into the model. The behavior of the complex fluids considered

in this work is accounted for by determining an apparent viscosity, accomplished by combining withdrawal speed and film geometry into a shear rate.

Figure 7 illustrates the Landau-Levich transition region in which there will be a stagnation point at the gas-liquid interface where the flow speed of the liquid vanishes. It divides the movement of the liquid at the interface into an area above, where liquid moves upward accelerating as it approaches the lamellar region until reaching the speed of the moving plate, and an area below, where liquid accelerates as it moves away from the substrate and then slows down at a distance further into the bath. In the transition region, the fluid closest to the liquid-plate interface moves with the same speed as the plate surface due to the no-slip condition, but slows down nearer to the gas-liquid free surface (in the y -direction). Far downstream from the transition region, a.k.a. in the entrainment region, if there is no gravitational effect ($Ca^{1/3} \ll 1$) then the flow is plug-type, and since the influence of gravity is anticipated to be small compared to viscous forces the flow speed is very nearly uniform throughout the entrained film thickness.

A *horizontal* dashed line in Figure 7, the stagnation point thickness line (SL), is drawn from the stagnation point at the gas-liquid interface to the plate surface in a direction parallel to the y -axis, i.e. normal to the substrate surface. To advance a physical description of the semi-empirical modeling result, it is assumed that the lateral slurry flow speed decreases along the SL *linearly* from its maximum value at the liquid-plate interface to zero at the gas-liquid interface. Thus, a single shear rate is applicable along the shear line. Similarly, during actual viscosity measurements, the slurry fills the gap between a viscometer rotor and a cup, and a virtual SL can also be considered to exist along the radial direction of the cylindrical rotor-cup viscometer, with maximum speed at the rotor-liquid interface and zero speed at the liquid-cup interface. Therefore, the form of the slurry velocity gradient in the viscometer setup is very close to the

profile assumed along the SL during the dip-coating process. As a consequence, shear rates in the slurry during the drag-out process can be directly correlated with those obtained in viscosity measurements. Once the liquid's shear rate on the SL is known, the apparent liquid viscosity value for a given withdrawal speed can be calculated by making use of Eqn. (6), the form of which was experimentally determined using the same slurry. (It is noted that the *theoretically* predicted lateral flow speed at small Ca , along the SL, which is in the transition region, is quadratic in the y -coordinate, but the linear approximation of the flow speed is not anticipated to be a significant source of error in the analysis, because the curvature of the flow speed along the SL is not large.)

The slurry at the plate is assumed to obey a no-slip condition and, therefore, it translates at the same speed as the plate withdrawal speed U . The thickness of the entrained slurry at the SL is defined as mh_0 with $m > 1$ due to the meniscus shape, where h_0 is the uniform entrained film thickness. Applying these conditions, the shear rate along the shear line and the apparent viscosity can be approximated as:

$$\dot{\gamma} = \frac{\partial v_x}{\partial y} = \frac{U}{m \cdot h_0} \quad (16)$$

and

$$\mu_{app} = K \cdot \left(\frac{U}{m \cdot h_0} \right)^{n-1}, \text{ respectively.} \quad (17)$$

3.3 Empirical Correction

Substituting Eqn. (17) into (1) and (2), leads to the following modification of the Landau-Levich model:

$$h_0^{(2n+1)/3} = 0.944 \cdot K^{2/3} \cdot m^{2(1-n)/3} \cdot U^{2n/3} \cdot \sigma^{-1/6} \cdot (\rho g)^{-1/2}. \quad (18)$$

The slurry, a particle suspension, has been assumed to be homogeneous and the evaporation of n-Octane has been neglected.

In an approach similar to the one presented here, Groenveld [17] used $m = 3$, but for Newtonian liquids at higher Ca . Based on this work, it is assumed that the value of the numerical factor m relevant in this study falls between 1 and 3 due to the low Ca . For simplicity, we set $m = 2$ in the following calculation. The slurry density (ρ) is determined to be 1.59 g/cm^3 using the rule of mixtures [37] and the magnitude of the gravitational acceleration is 9.8 m/s^2 . The exponent of U , $2n/3$, is a function of ‘ n ’ characterizing the power-law nature of the slurry. Including the shear-thinning slurry rheology and all of the other conditions assumed above leads to the following power law scaling:

$$h_0 = 0.001226 \cdot U^{0.60}. \quad (19)$$

Comparing Eqn. (19) with Eqn. (1) and (2) reveals that the exponent of U in (19) is slightly smaller than the Newtonian value of $2/3$ given in (1), i.e. $0.60 < 0.67$. Our conclusion is that this difference in the exponent is directly related to the non-Newtonian behavior of the liquid. It is interesting to note that although the approaches used are different, Eqn. (19) and (15) (the Ashmore model applied to this case) and the Afanasiev model all have the same power law withdrawal speed exponent 0.60 , although the coefficients multiplying $U^{0.60}$ are different. As is clear from Figure 4, both our Eqn. (19) and the Ashmore model *overestimate* coating thicknesses over a wide range of withdrawal speeds except in the slowest withdrawal speed regime. At the speed $U = 1000 \text{ mm/min}$, the value predicted by the Ashmore model is 17% higher than our current prediction given in Eqn. (19) and is approximately 50% higher than the experimental

coating thickness for the case of horizontal drying. In general, despite the agreement of the scaling exponent with these other models, neither our modifications nor other theoretical models reproduce the experimental results. This calls for further research in this area.

The lack of agreement of the experimental results, presented in this work with the modified entrainment law (Eqn. 19) and with other models previously described, is quantified by means of an empirical adjustment, denoted as $t(U)$, which maps the modified Landau-Levich scaling law given by Eqn. (19) to the observed experimental results:

$$h'_0 = h_0 \cdot t = 0.001226 \cdot U^{0.60} \cdot t(U), \quad (20)$$

i.e., it maps the predicted coating thickness (h_0) to the measured coating thickness (h'_0) in the horizontal configuration. The form of the power law correction $t(U)$ required to fit the experimental results reported earlier (Figure 8) is:

$$t(U) = 0.5151 \cdot U^{-0.1001}. \quad (21)$$

It provides Eqn. (10), written again here:

$$h'_0 = 0.0006315 \cdot U^{0.50}. \quad (10)$$

The results are summarized in Table 2. The Ca number in this work is sufficiently small that gravity is not a major drainage influence during drag-out, as shown in treatments of the drag-out problem involving Ca numbers of unity and higher values [9-11, 21]. Therefore, the value of our approach has revealed how various physical effects may or may not account for the actual scaling law exponent of 0.50 that is measured in our experiments and quantified through the correction factor.

4. Discussion

Due to the low Ca number 0.05 derived in the present work, it is reasonable to assume that, in the drag-out stage, gravity has a minor influence [20]. However, the results reported in this paper predict that the thickness of the film dip-coated on a substrate scales as the square root of the withdrawal speed U , a non-standard Landau-Levich low capillary number thin coating film result. A list of other effects have been included by researchers to modify to the Landau-Levich scaling law such as a variety of rheological liquid behaviors, treating higher order capillary number effects in the asymptotic analyses and inertial effects. No results provide the same scaling as observed in the model presented here.

Other effects unique to this study that need explanation. In this application, the work is focused on the coating of rigid substrates of *finite length*, and the *arrest* of sample drag-out occurs prior to thickness measurements made in vertical or horizontal orientations. As shown above, using a different orientation of the sample lead to different results. The drag-out configuration of finite sample length is different from the ‘infinite’ substrate configuration on which virtually all other theories are based. In a vertical orientation, sample arrest results in additional observed physical phenomena. First, the liquid film undergoes thinning and then there is the rupture of the liquid film that disrupts the dynamic meniscus (transition region), the region within which the entrainment layer thickness is fixed during the drag-out stage. The deformation of the film and the rupture process (that involves surface tension and possibly disjoining forces) may induce changes in the entrained film geometry before measurement. We have calculated whether or not there will be significant film thinning in ‘horizontal’ samples during drag-out, using the approach of de Ryck and Quéré [21], and they have shown not. Therefore, our semi-

empirical modeling approach has only been applied to the case of measurements made in the horizontal configuration avoiding unnecessary complications.

Finally, *the viscosity of the suspension* has been measured as a function of the shear rate revealing power-law behavior as reported earlier. However, in a suspension, there is an additional complication arising from the explicit dependence of the viscosity on the volume fraction of particles. The Einstein law [38] and the Krieger-Dougherty law [39] are examples of particle volume fraction dependent viscosities. During substrate extraction, flow may give rise to variable particle speeds leading to non-uniform particle distributions throughout the liquid during experiments. This would cause variations in the viscosity not captured in the experimental viscometric measurements and thus not described by shear-thinning representations.

Other effects that deserve consideration in future studies include: interaction of particles with the gas-liquid interface that generate additional forces in the liquid, and the evaporation of solvent during entrainment. *The solvent, n-octane, has a low vapor pressure and evaporates easily. which may lead to thickness variations and compositional differences that would impact properties such as the viscosity. The total evaporation time of n-octane is nearly proportional to the coating thickness and pulling speed. For the experiments reported, the evaporation times were on the order of a minute (60s) or less. Using a representative coating experiment, at a withdrawal speed of 500 mm/min = 0.833 cm/s, the wet film thickness shown in Figure 7 under these conditions is approximately 15 microns. The dry thickness is therefore 5.625 microns (see Section 2.2.3). The substrate coating length is approximately 3 cm, so the total time required to extract the substrate from the bath is 3 cm/.833 cm/s = 3.6 seconds. Approximately 5 percent of the solvent evaporation takes place during extraction and 95 percent of the evaporation occurs after extraction has completed. Using a time scale based on the extraction and the static*

evaporation times, an estimate of the rate of thickness change is approximately -.147 microns per second.

Marangoni effects are driven by constitutionally generated gradients in the surface tension and affect the film thicknesses in dip-coating experiments because the only resistance to surface tension gradients is the (tangential) viscous force in the fluid at the interface. Flow rates are affected in the dynamic meniscus and also in the film if the evaporation leaves a non-uniform composition along the film interface. Previous work has shown that for continuous, steady state drawing, if the capillary number is *greater* than approximately 10^{-3} , the film thickness will be different than for the clean case[40, 41]. In our experiments the film appears to have evaporated nearly uniformly during the longer static part of the process, and so the details of the origin of the concentration gradients and thus the tangential Marangoni forces in this case is not entirely clear but still could be important. This is an area that needs further modeling.

Also, the segregation of polymer molecules in the liquid may result from an affinity to the moving plate, influencing the entrainment thickness. Further details related to crosslinking and particle inertia can influence the rheology of the liquid in different, unknown ways.

5. Summary

Two new, important experimental results are reported in this work. The first is the measurement of the apparent fluid viscosity of a complex, particle-suspended non-Newtonian liquid as a function of the shear rate. The apparent fluid viscosity behaves as a power-law liquid for the shear rates considered, with $\mu_{app} = 0.11 \cdot \dot{\gamma}^{-0.23}$ and a power-law exponent of $n = 0.76729$.

The second result is the measurement and discovery of a semi-empirical scaling law for the liquid film thicknesses: $h=0.0006315 \cdot U^{0.50}$ of entrained particle-suspended non-Newtonian complex fluid layers deposited on substrates by dip-coating. The semi-empirical scaling law is accurate over a large range of withdrawal speeds.

Insight into the scaling behavior is achieved by using a Landau-Levich modeling approach that includes systematically applying modifications that allow for additional physics, for example, incorporation of the experimentally determined apparent viscosity of the non-Newtonian slurry as a function of the shear rate. A linear approximation to the flow speed along a virtual line (orthogonal to the liquid-plate interface and terminating at the ‘stagnation point’ on the gas-liquid interface) provides a single shear rate, so that that the viscosity in the original Landau-Levich model can be replaced by a function of withdrawal speed. However, although the scaling relation determined by consideration of the shear-rate dependence of the viscosity finds $h_0 \sim U^{0.60}$, which agrees with other theories in the literature, this scaling does not match the experimental results. Thus, a correction factor $t(U)=0.5151U^{-1.001}$ is identified that accounts for the overestimation of the previous theories and that matches the experimental results for this fluid system. The general applicability of this scaling law for other complex liquid systems remains to be investigated calling for fundamental experimental and theoretical research in this important materials processing area.

Acknowledgements

R.K.B. would like to acknowledge partial support for this research from US Department of Energy, Office of Nuclear Energy (DoE-NEUP) Grant through Idaho National Laboratory (Grant #10-918) and US Department of Energy, National Energy Technology Lab (Grant #DE-

FE0023142).

Notes

The authors declare no competing financial interest.

Appendix: Calculation of the film thickness following Afanasiev, Munch and Wagner [23].

The film thickness represented by the power law:

$$h_{\infty}^{PL} = \tilde{A}(n)\varepsilon^{3/(4n+2)},$$

by fitting the data on page 9 to a quadratic function of n (5.19a) instead of solving the partial differential Eqn. 5.3 and/or 5.4.

n	0.5	1.0	2.0
$\tilde{A}(n)$	1.488	0.9458	0.6826

The result is:

$$\tilde{A}_{fit}(n) = 0.5475n^2 - 1.9056n + 2.3039.$$

Using the value $n = 0.76729$, gives $\tilde{A}(0.76729) = 1.1641$. Also note that $\varepsilon = Ca^{1/3}$, therefore $\varepsilon = 0.368$ when $Ca = 0.05$ in this work. The matched asymptotic analysis in AMW begins to deviate from the numerical integration of the lubrication theory for $\varepsilon > 0.1$ approximately; more so for larger n . It over-estimates the value of the film thickness compared to the numerical integrated value, the latter is believed to be more accurate in this regime.

Here h_{∞}^{PL} (dimensionless) has been defined by scaling the dimensional thickness $\overline{h_{\infty}^{PL}}$ by

H , where

$$H = \left(\frac{KU^n}{\rho g \cos \alpha} \right)^{1/(n+1)} = \left(\frac{KU^n}{\rho g} \right)^{1/(n+1)} \quad \text{when } \alpha = 0. \quad (3.4)$$

$$\text{Thus, } \overline{h_{\infty}^{PL}} = H\tilde{A}(n)\varepsilon^{3/(4n+2)} = \left(\frac{KU^n}{\rho g} \right)^{1/(n+1)} \tilde{A}(n)\varepsilon^{3/(4n+2)}.$$

To calculate the value of $\overline{h_{\infty}^{PL}}$ at a certain withdrawal speed, e.g., $U = 700$ mm/min, we

use

$K = 0.11$, $U = 700 \text{ mm/min} = 1.167 \text{ cm/s}$, $\rho = 1.59 \text{ g/cm}^3$, $e = 980 \text{ cm/s}^2$, $n = 0.76729$,
 $\tilde{A}(0.76729) = 1.1641$, $\varepsilon = 0.368$, $\frac{1}{n+1} = 0.5658$, $\frac{n}{n+1} = 0.4342$ and $\frac{3}{4n+2} = 0.5918$. Lastly, the
result is $\overline{h_{\infty}^{PL}} \approx 31 \text{ }\mu\text{m}$.

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Figure 1. Viscometric measurements of the ZrSi_2 -filled PHMS slurry. (a) shear rate as a function of time; (b) corresponding shear stress as a function of time; (c) a plot of shear stress vs. shear rate with a power law curve superimposed (Eqn. 5); (d) calculated apparent viscosity as a function of shear rate (Eqn. 7).

Figure 2. Calculated apparent viscosity of the slurry as a function of shear rate.

Figure 3. Schematic of coating thickness evolution during dip coating. The ‘wet’ coating thickness, h_0 is the thickness immediately after dip coating and the ‘crosslinked’ thickness, h_{CL} is the experimentally measured thickness taken after crosslinking of the polymer.

Figure 4. Comparison of wet coating thicknesses for ‘vertical’ ($h_0(\text{exp})$, vertical) and ‘horizontal’ ($h_0(\text{exp})$, horizontal) drying with predicted values from Ashmore’s analysis [28] (h_0 (Ashmore), Eqn. (15)) and from a modification of the Landau-Levich model presented as Eqn. (19) in the present work (h_0). The experimental wet thicknesses are calculated, using Eqn. (9) from the measured crosslinked thicknesses (h_{CL} , vertical and h_{CL} , horizontal) which are also plotted here.

Figure 5. The experimental coating thickness, ‘ $h_0(\text{exp})$, horizontal’, fitted by the scaling law of the coating thickness (h'_0) as a function of the withdrawal speed (U), namely Eqn. (10).

Figure 6. Diagram of the dip-coating process. The liquid area is subdivided into ‘entrainment region’ and ‘static-meniscus region’ (‘capillary-static region’) separated by a ‘transition region’ (‘dynamic meniscus region’). h_0 is the constant film entrainment thickness and m is a numerical factor.

Figure 7. Flow pattern during the drag-out process. The stagnation point thickness is the value of film thickness at the location x where the flow speed is zero at the gas-liquid interface.

Figure 8. The empirical correction factor $t(U)$. The best-fit curve is a power law function.