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Mastering the Coating Thickness Obtained Using Liquids with a Yield-Stress

Bertil Trottet[a], Marco Marconati[a], Joseph L.Keddie[b], Marco Ramaioli[a,*]

[a]Department of Chemical and Process Engineering, University of Surrey, United Kingdom GU2 7XH
[b]Department of Physics, University of Surrey, United Kingdom GU2 7XH
marco.ramaioli@surrey.ac.uk

Dip coating is a very common process in food manufacturing. Controlling the thickness of the coating is key to deliver the desired sensorial properties and to be compliant with the product's nutritional claims. Whilst dip coating with Newtonian liquids is physically well understood, coating food products almost invariably involve liquids with more complex rheology. This makes the process more difficult to design and control and reduces the coating homogeneity. Developing novel food products with improved nutritional attributes often calls for reducing the coating thickness and non-homogeneity should be avoided to guarantee the quality of the final product. In this study, we focused on the coating of a flat surface using Carbopol solutions and a commercial ketchup, following a Herschel-Bulkley rheological model. The final average coating thickness was always significantly lower than the critical thickness that can be estimated from liquid density and yield stress. Liquids with a yield stress in the range 4-56 Pa were considered in this study and the steady withdrawal speed from the bath was varied in the range 0.1-20 mm/s. The resulting average coating thickness and its uniformity are discussed. The results are interpreted in the context of an existing theory for dip coating with liquids with a yield stress. This study paves the way toward an integrated design of the coating process and the liquid rheology of foods, such as chocolate or ketchup. This can enable the development of new food products allying improved nutrition, a consumer preferred sensory profile and cost.

1. Introduction

Surface coating is an effective way to modify the surface of food products and improve their organoleptic properties (e.g. chocolate flavoured coatings), while decoupling the surface composition from the composition of the bulk of the product, conditioning strongly the overall nutritional value. Sometimes coatings are also used to introduce a moisture barrier and preserve moisture gradients in a heterogeneous product, such as ice cream cones (Talbot, 2009).

Dip coating is a common process in food manufacturing, owing to its simplicity. It is also widely used during food consumption, for instance when seasoning using dips.

Dip coating a plate with Newtonian liquids is physically well understood and the effect of the liquid viscosity and the withdrawal speed on the coating thickness was described successfully in the classical theory by Landau and Levich. More recently, it was shown that the contact angle of the liquid with the plate is an important physical quantity that can strongly influence the coating thickness (Snoeijer et al, 2008).

However, coating food products almost invariably involves liquids with non-Newtonian rheology. Chocolate coatings and seasoning dips, such as ketchup or mayonnaise are the most common examples.

The non-Newtonian rheology makes the process more difficult to design and control and can result in non-homogeneous coatings. The presence of a yield stress can for instance lead to the coexistence of solid and liquid regions (Coussot et al, 2006, Coussot et al, 2009, Cochard and Ancey, 2009, Coussot, 2014).

The dip coating of a plate by non-Newtonian liquids, including yield stress liquids was also considered in the literature (Ashmore et al, 2007, Maillard et al, 2014 and Maillard et al. 2015).

In this study we consider the impact of different rheological properties, immersion depth and withdrawal speed on the resulting coating thickness to facilitate the development of novel food products with thin and homogeneous coatings.

2. Materials and Methods

This study considered the following yield-stress liquids: solutions of Carbopol Ultrez 21 (supplier Noveon Inc, USA) with polymer concentration ranging from 0.1% and 0.25% and a commercial ketchup sauce (Independent Ketchup, UK). The complexity inherent to characterising the rheology of yield stress liquids has been discussed in several studies (Isla et al, 2004.) In this study, the rheology of the yield stress liquids was characterised at 22°C using a plate plate geometry (d = 50 mm) on a rheometer type Physica USD 200 (Paar Physica, Germany). A yield stress ramp and a creep test were used to characterise the shear rheology and to identify accurately the material yield stress.

The dip coating process was studied by dipping a thin flat plate (T x W x L = 2.5 x 90 x 120 mm) in a yield stress liquid at 22°C. The plate was coated to avoid wall slip. The dip coating was performed using a texture analyser model TA.XT plus (Stable Micro Systems, UK, Figure 1), imposing a controlled dipping and withdrawal speed, whilst measuring the force applied to the plate using a 2 kg load cell. The dimensions of the liquid container were 80 x 120 x 155 mm (Wc x Lc x Hc). The steady withdrawal speed of the plate from the bath was varied in the range 0.1-20 mm/s. The immersion depth was varied in the range 20-90 mm. Lateral images were taken using a Basler camera (acA1929-155µm), as shown in Figure 2. After careful alignment of the plate and the camera, the thickness of the plate can be used as reference distance to measure the average coating thickness and the thickness distribution along the plate from the lateral images.

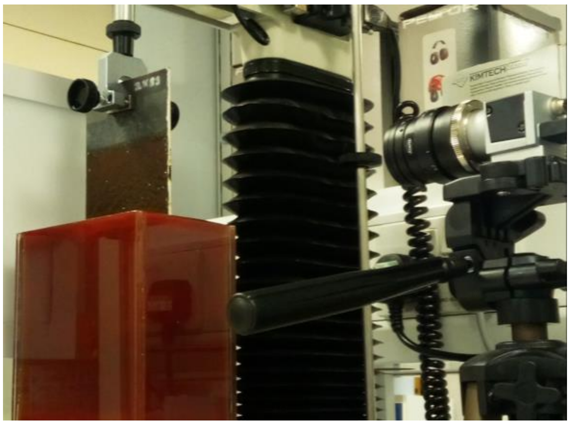

Figure 1: Experimental set-up comprising a dipping apparatus and a flat plate. In this image, the plate is coated with a thin ketchup layer.

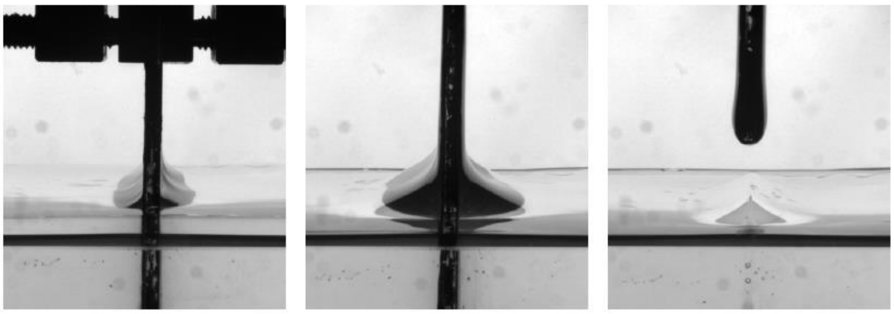

Figure 2: Typical side views of the plate withdrawal phase of a dipping experiment using a Carbopol solution. Left: beginning of the withdrawal phase, Center: intermediate snapshot showing the coated plate above a fully developed liquid meniscus, Right: Complete withdrawal of the plate from the bath. The coating thickness at the bottom of the plate is higher than the average as a result of the meniscus break-up.

3. Results

3.1 Rheology

A rheological characterization of the materials was conducted to support the interpretation of the dip coating experiments. The yield stress of the different solutions used in the study was determined with creep tests and shear ramps from 5 10^{-3} to 10^{2} reciprocal seconds were used to fit the remaining parameters of the Herschel-Bulkley rheological model:

$$\tau < \tau_c \Rightarrow \dot{\gamma} = 0 \text{ (solid regime)} \qquad (1)$$
$$\tau > \tau_c \Rightarrow \tau = \tau_c + k\dot{\gamma}^n \text{ (liquid regime)}$$

Figure 3 shows typical profiles obtained from the rheometric tests with yield stress liquids, including a shear ramp (left) and a creep test (right). In these figures, the 0.2% solution of Carbopol Ultrez 21 presents a yield stress of 56 Pa.

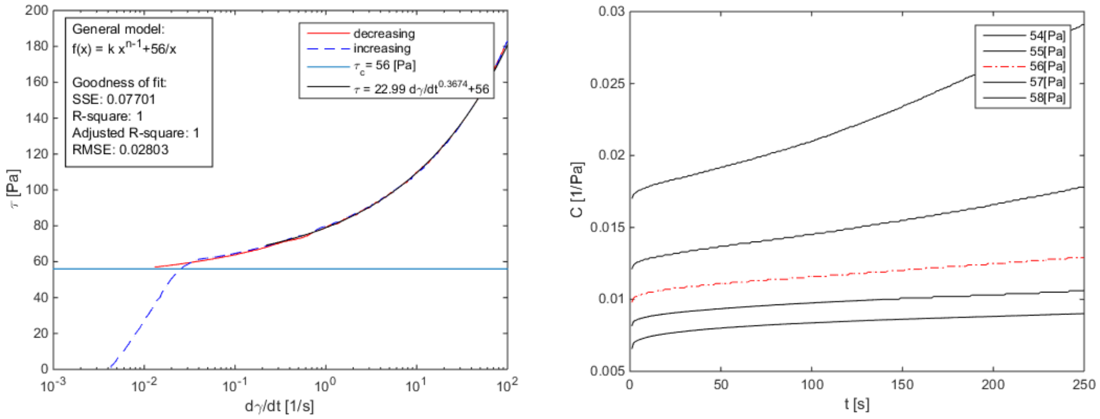

Figure 3: Typical rheometrical results obtained during a shear ramp (left) and a creep test (right) with Yield stress liquids. In this example, the 0.2% solution of Carbopol Ultrez 21 presents a yield stress of 56 Pa.

The Herschel-Bulkely model describes well the rheological results obtained for diluted carbopol solutions (0.1-0.2 %) and the commercial ketchup considered in this study. The parameters of the rheological model are schematically given in Table 1. The Carbopol parameters are consistent with those obtained by Maillard et al, 2016.

Table 1: Herschel-Bulkley parameters obtained for the yield stress liquids considered in this study.

	τ_c (Pa)	K (Pa s^n)	n (-)
Acqueous Carbopol Solutions	4-56	0.4-0.5	~0.35
Ketchup	12	22	0.28

3.2 Evolution of the force applied to the plate during dipping and withdrawal

During the dipping experiments, the plate was immersed in the liquid bath and then withdrawn. The plate velocity was maintained constant during the experiments and only the direction was varied. A layer of the material close to the plate yielded and was dragged out of the bath forming a thin coating, with no measurable drainage occurring.

The force applied to the plate during both phases of the experiment are shown in Figure 4. The force sensor was tared when the plate was above the liquid. After covering the initial distance of the plate bottom from the bath (10 mm), an upward (positive) force was recorded, upon deformation of the interface to create a stable liquid meniscus. An upward force was then measured, increasing linearly with the immersion depth. This force results from the sum of the buoyancy and the viscous dissipation during the downward movement of the plate. Upon reversal of the plate velocity direction, a sudden inversion of the force was recorded. The downwards withdrawal force is dominated by the downwards viscous force, stronger than the upward buoyancy. A downwards force is recorded during the breakage of the meniscus between the bath and plate, followed by a constant force corresponding to the residual weight of the coating on the plate.

Various immersion depths (20 to 90 mm) were considered. The similarity of the resulting force patterns can be appreciated in Figure 4. The mass of coating per unit width of the plate varied linearly with the coated length (L_{eff}), as shown in the inset of Figure 4.

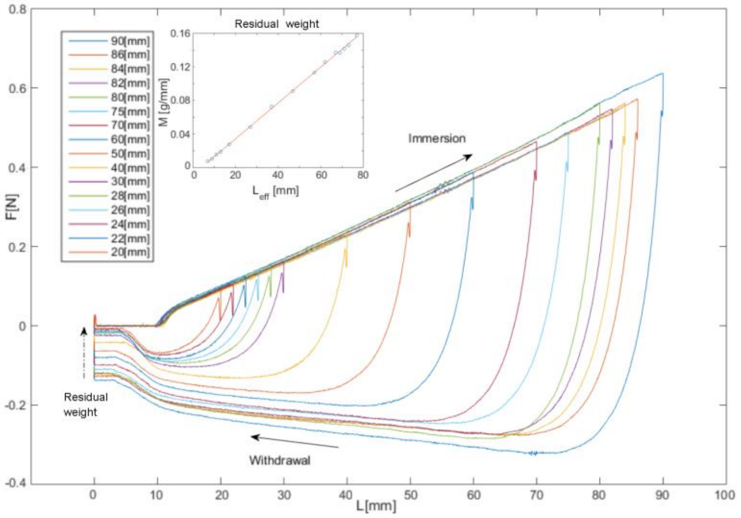

Figure 4: Force history for several length of displacement observed during the process of coating. The linear behaviour of the residual mass in function of the effective coated length (figure inset) is noticeable. For this case, the material yield stress is 22 Pa and the plate velocity is 5 mm/s.

3.3 Average thickness of the coating and thickness distribution

The residual average thickness of the coating was computed from the residual force measured on the plate after withdrawal. The dipping experiments were performed using different concentrations. The effect of varying the plate velocity in the range 0.1 mm/s to 20 mm/s was also investigated. The effect of both parameters on the final coating thickness is illustrated in Figure 5, for experiments during which the plates were immersed in the bath over a depth of 90mm.

Increasing the dipping and withdrawal velocity has a weak effect on the coating thickness, except at very low yield stress. Conversely, increasing the yield stress of the liquid, increased significantly the coating thickness..

The theoretical thickness of coating ($h_c = \tau_c / 3 \rho g$) expected at low speed based on previous studies (Maillard et al, 2014) is also indicated in Figure 5, for different material yield stress. This low speed limit compares positively with our results.

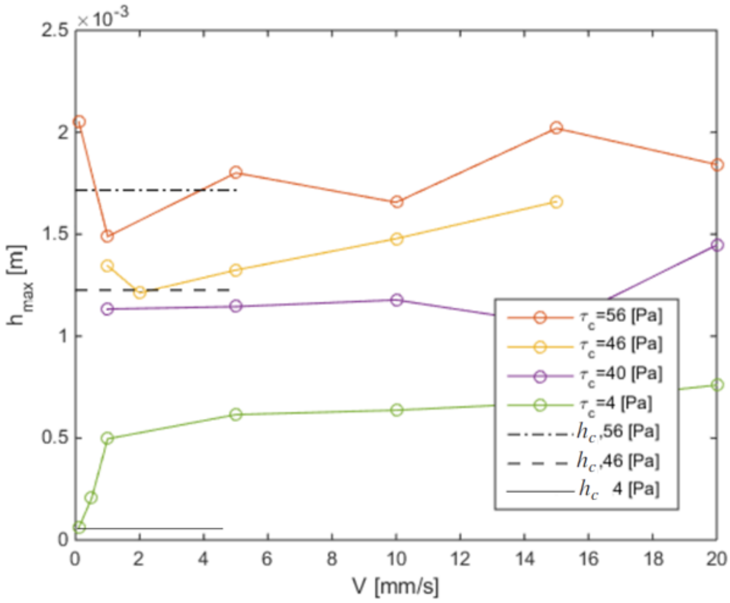

Figure 5: Effect of the dipping and withdrawal velocity on the coated thickness, using liquids with different yield stress. The theoretical coating thickness expected at low velocity ($h_c = 0.3\ \tau_c / \rho\ g$) is included for comparison.

A higher variability was observed with the solutions with higher yield stress. Experiments involving multiple dip coatings were successfully performed to reduce variability.

The homogeneity of the coating thickness was measured quantitatively from side images, similar to the images shown in Figure 2. The thickness was observed to vary typically by more than 25% along the vertical position on the plate. A higher thickness is systematically present at the bottom of the coating because of the breakage of the meniscus between the film and the liquid in the bath.

The measured average coating thickness obtained using different liquids and different plate withdrawal speeds can be interpreted based on the theory presented by Maillard et al, 2014.

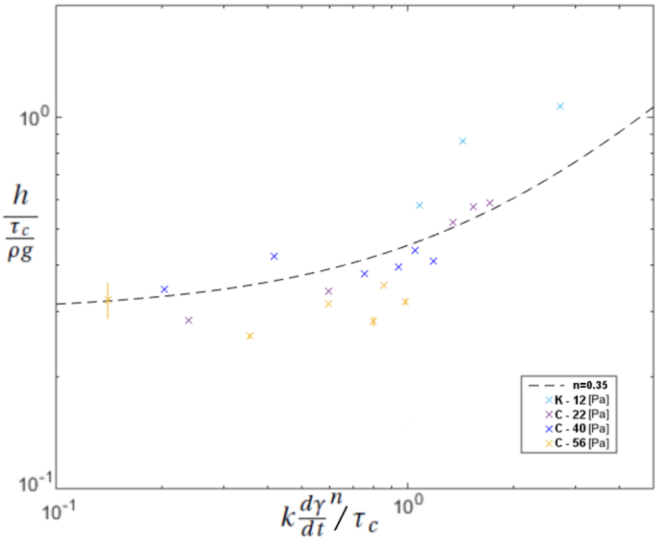

Figure 6: Dimensionless coating thickness h / (τ_c /ρ g) plotted against the inverse of the dimensionless Bingham number. The points K-12 were obtained using the ketchup sauce, while the others were obtained using the Carbopol solutions. For all liquids, the number indicates the yield stress. The dashed line shows the prediction of the theory described in eq. 4. (Maillard et al. 2014)

Dimensional analysis can be used to define a master curve and reduce the number of variables down to one dimensionless number. A dimensionless coating thickness can be obtained by dividing the coating thickness (h) by the maximum thickness that can withstand its own weight without yielding ($\tau_c / \rho g$):

$$G = \frac{h}{\frac{\tau_c}{\rho g}} \tag{2}$$

The dip coating process can be characterized by the inverse of the dimensionless Bingham number, comparing the shear stress in the liquid at the wall with the yield stress of the material:

$$Bi^{-1} = \frac{k\left(\frac{d\gamma}{dt}\right)^n}{\tau_c} \tag{3}$$

The experimental results are summarized in non-dimensional form in Figure 6, which shows a fair agreement with the theory presented by Maillard et al. 2014, according to which:

$$G = 2\alpha(1 + (\alpha^n Bi^{-1})) \tag{4}$$

where α is the ratio of the coated thickness over the thickness of the liquid layer inside the bath, that was measured experimentally (α= 1/6.7).

Only two data points are presented for the commercial ketchup sauce, because the low yield stress obliges to use very low withdrawal velocities (0.1 – 0.5 mm/s) to maintain the inverse of the Bingham number lower than one and hence obtain a coating thickness approaching the minimum ($h_c = 0.3 \tau_c / \rho g$). Such lower limit is impractical in most applications.

This study paves the way toward an integrated design of the withdrawal speed used during the coating process and the rheology of liquid used to coat. Indeed, it allows identifying the best compromise between speed and coating thickness and more specifically the conditions below which reducing the process speed does not lead to a significant reduction in coating thickness. This can enable the development of novel coated food products that are the best compromise between improved nutrition, a consumer preferred sensory profile and cost.

4. Conclusions

Dip coating with food and non-food yield stress liquids was studied by withdrawing plates from different depth and using different speeds. The coating weight increases linearly with the dipping depth, although the coating thickness was observed to vary along the plate. The coating thickness depends strongly on the yield stress of the liquid and weakly on the withdrawal speed. For liquid with very low yield stress - such as the 12 Pa commercial ketchup sauce considered in this study - impractically low withdrawal speeds (lower than 0.1 mm/s) should be used to obtain the lowest possible coating thickness. This study paves the way toward an integrated design of the coating process conditions and the rheology of the material used to coat. This can enable the development of new food products allying improved nutrition, a consumer preferred sensory profile and cost.

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