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On measuring wettability in infiltration processing

Véronique Michaud[a,*] and Andreas Mortensen[b]

[a]Laboratory for Polymer and Composite Technology (LTC), Ecole Polytechnique Fédérale de Lausanne (EPFL), Station 12, CH-1015 Lausanne, Switzerland

[b]Laboratory for Mechanical Metallurgy, Ecole Polytechnique Fédérale de Lausanne (EPFL), Station 12, CH-1015 Lausanne, Switzerland

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Capillary pressures encountered in composite processing are often evaluated by measuring infiltration rates as a function of applied pressure. Such data are generally interpreted assuming slug-flow. Using the Brooks–Corey correlations we relax this assumption, to indicate possible pitfalls of the slug-flow approach and to show how such data can nonetheless be used to derive meaningful capillary parameters.

Keywords: Infiltration; Composites; Capillary phenomena; Wetting; Threshold pressure

Many composite materials are produced by infiltration. This process is largely governed by capillarity, which acts to drive or oppose motion of the infiltrating fluid into the porous solid preform to be infiltrated. Quantifying capillary forces, by analysis or measurement, is of obvious importance in understanding the process.

In the absence of interfacial reactions (which are important in some systems but complicate the problem immensely), the relevant thermodynamic parameter is the work of immersion W_i [1,2]. According to Young's equation [3]:

$$W_i = \sigma_{lv}\cos(\theta) = \sigma_{sv} - \sigma_{sl} \quad (1)$$

where σ_{lv} is the surface tension of the liquid infiltrant, θ $\iota\sigma$ its wetting angle on a flat solid substrate, and σ_{sv} and σ_{sl} are the solid/atmosphere and solid/liquid interfacial energy, respectively.

Both σ_{lv} and θ, and hence W_i, are measurable directly using the sessile drop technique [3]; however, this technique is often not usable for systems of relevance to composite processing. Reinforcement materials are generally not available as flat and large substrates. Also, wetting in infiltration is dynamic, which can influence θ [3–5]. Direct methods are therefore often used to measure capillary forces in infiltration; these come in two classes.

The first relies on the slug-flow assumption [1,2,4,6,7]. In slug-flow, infiltration takes place with a fully saturated infiltration front, across which there is a single pressure difference, ΔP_γ, caused by curved menisci of the liquid surface – as with a liquid in a straight capillary tube.

The second approach is based on methods that were developed in soil science and reservoir engineering. Here, capillary forces are quantified, not with a single pressure difference but with curves plotting the capillary pressure vs. the fraction of filled void space (or "saturation"), called drainage or imbibition curves, respectively, when the infiltrating fluid does not wet, or wets, the solid [1,2,8–13]. This approach is more complex and also somewhat more cumbersome experimentally, hence it is more rarely adopted in the study of composite processing. However, it is fundamentally more correct.

The point of this note is to examine the former approach in light of theory underlying the second.

Consider the first method. It rests on Darcy's law written for fully saturated flow, which states that the rate of flow of a Newtonian and incompressible fluid through a solid at sufficiently low Reynolds number (typical of infiltration processing) is proportional to the local gradient of pressure P within the fluid:

$$v_o = -\frac{K}{\eta}\nabla P \quad (2)$$

* Corresponding author. Tel.: +41 21 693 49 23; fax: +41 21 693 58 80; e-mail: veronique.michaud@epfl.ch

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where the fluid "superficial velocity" v_o is the volume of fluid passing through a unit surface cut across the porous medium per unit time, K is the permeability of the porous medium (in the most general case a tensor and of units m^2) and η is the viscosity of the fluid (in Pa s).

Practically, to measure ΔP_γ one produces an experimental set-up such that infiltration of a homogeneous and non-deforming preform takes place along a single direction parallel to a principal direction (Ox) of K. In slug-flow continuity dictates that v_o be constant everywhere along the infiltrated preform. When the total pressure differential ΔP_T driving the motion of the fluid is kept constant, then the position of the infiltration front, at $x = L$, is:

$$L^2 = \frac{2Kt}{\eta(1 - V_s)}(\Delta P_T - \Delta P_\gamma) \tag{3}$$

where $x = 0$ is the preform entrance, ΔP_γ is the capillary pressure, counted positive when it opposes infiltration, and V_s is the volume fraction of solid phase in the preform. Plotting L^2/t (or, when the front position is not dynamically tracked, L^2 for a fixed infiltration time t) vs. ΔP_T then yields a straight line that intersects the abscissa axis at $\Delta P_T = \Delta P_\gamma$.

Measurements of capillary pressure drop values conducted in this manner have been published by many authors, for both polymer and metal composite systems [4,6,14–30]; an extensive review of the subject is given in Refs. [20,31]. Methods vary, but reproducible values that obey expectations are often obtained (e.g. ΔP_γ is inversely proportional to the average preform pore diameter) [20,31]. The method, however, assumes slug-flow while in many such experiments there is clear evidence that flow is not fully saturated (e.g. [23,27]).

We now consider the same experiment, namely the infiltration along a single direction (x) of a non-deforming preform driven by a constant pressure, ΔP_T, but assume unsaturated flow. Infiltration thus proceeds gradually, over a range of pressures described by the drainage–imbibition curve [1,2,10–13,32]. Mass conservation dictates:

$$\frac{\partial v_o}{\partial x} = -\frac{\partial V_l}{\partial t} \tag{4}$$

where V_l is the local volume fraction liquid in the preform. The permeability K is now a function of V_l, and V_l itself varies between 0 and $(1 - V_s)$ as the local pressure in the liquid, P, increases.

As is well known, for unidirectional infiltration driven by a constant pressure the problem can be solved using the Boltzman transformation [8,33,34]. We define:

$$\varphi = \frac{x}{\sqrt{t}} \tag{5}$$

and, after substitution of Eqs. (4) and (2) into Eq. (3), the governing equation becomes:

$$\varphi = \frac{\mathrm{d}\left[-2\frac{K}{\eta}\frac{\mathrm{d}P}{\mathrm{d}V_l}\frac{\mathrm{d}V_l}{\mathrm{d}\varphi}\right]}{\mathrm{d}V_l} \tag{6}$$

to be solved with boundary conditions:

$$\varphi = 0 \text{ (i.e. } x = 0 \text{ and } t > 0), \quad V_l = V_l(\Delta P_T) \tag{7}$$

and

$$\varphi = \varphi_{\text{front}}, \quad V_l = 0 \tag{8}$$

where $V_l(\Delta P_T)$ is the fraction liquid in the preform for $P = \Delta P_T$ and φ_{front} is the value of φ at the tip of the liquid front advancing into the preform. Solving the problem requires knowledge of the two functions $K(V_l)$ and $V_l(P)$; these are known in the form of semi-empirical correlations. We use hereafter the correlations of Brooks and Corey, which are well established in soil science, and have been successfully confronted with experimental data [32,35–37], including in composite material processing [8,9,38–40].

When $\theta > (\pi/2)$, which is generally the case in composite processing, the Brooks and Corey correlation reads:

$$S_l = \frac{V_l}{1 - V_s} = 1 - \left(\frac{P_b}{P}\right)^\lambda \tag{9}$$

and

$$K = K_{\text{sat}} S_l^2 \left[1 - (1 - S_l)^{\frac{(2+\lambda)}{\lambda}}\right] \tag{10}$$

Here, the liquid saturation S_l depends on P via (i) the "bubbling pressure" P_b, which is the first pressure at which the liquid penetrates the preform, and (ii) a "pore size distribution index" λ that measures the spread in effective pore diameter within the preform (the greater the spread, the smaller is λ). P_b is inversely proportional to the average pore diameter, all else being constant. K_{sat} is the permeability of the fully saturated preform.

Substituting Eqs. (9) and (10) in Eq. (6) and integrating once subject to Eq. (8) yields:

$$\frac{\mathrm{d}\varphi}{\mathrm{d}S_l}\int_0^{S_l}\varphi_{(s)}\mathrm{d}s = -2\frac{K_{\text{sat}}P_b}{(1 - V_s)\eta}\frac{(1 - S_l)^{\frac{-(\lambda+1)}{\lambda}}}{\lambda} \times S_l^2[1 - (1 - S_l)^{(2+\lambda)/\lambda}] \tag{11}$$

This non-linear integro-differential equation is solved numerically for the function $\varphi(S_l)$ subject to Eq. (7) using Mathematica™ (Wolfram Research Inc., Champaign, IL). The infiltration front position, $\varphi_{\text{front}}\sqrt{t}$, is predicted; this, of course, is the measured quantity L in slug-flow infiltration experiments (Eq. (3)).

The results of this calculation are plotted in Figure 1 in adimensional form, defining the infiltration front position as

$$F = (\varphi_{\text{front}})^2 \frac{(1 - V_s)\eta}{2K_{\text{sat}}P_b} \tag{12}$$

while dimensionless applied pressure is defined as

$$p = \frac{P}{P_b} \tag{13}$$

This adimensionalization of pressure and infiltration velocity is such that infiltration under slug-flow will give a straight line of slope 1, intersecting the horizontal axis at $p = 1$. Indeed, in this case $\Delta P_\gamma = P_b$, λ tends towards infinity since the preform structure tends towards one of perfectly uniform pores (e.g. a bundle of straight capillaries) and Eq. (3) applies. As seen, as p increases, all curves gradually become straight lines of slope unity.