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THE EFFECT OF PERMEANT ON THE MEASURED PERMEABILITY OF A REINFORCEMENT

John Summerscales

Advanced Composites Manufacturing Centre
School of Engineering, Reynolds Building
University of Plymouth
Plymouth, Devon, PL4 8AA, United Kingdom.

SUMMARY: Darcy's Law did not initially contain a term for the viscosity as the value for water could be taken as one. Further the equation does not include a term for contact angle as the model assumes flow in wetted media. In order to model Liquid Composite Moulding processes, it was necessary to add a viscosity term to account for the range of fluids used. For unsaturated (wetting) flow, the conditions at the flow front will be different to the wetted flow behind the flow front. The wetting flow permeability may vary with the fluid. Steenkamer *et al* (1995) concluded that "fabrics should be characterised with the actual liquid moulding resin selected for a given application". This paper will review the literature and discuss the need to introduce a further term to Darcy's Law to account for the different surface energies/contact angles at the flow front in the determination of reinforcement permeabilities using model fluids.

KEYWORDS: permeability, permeant, test fluid.

INTRODUCTION

The manufacture of continuous fibre-reinforced thermosetting matrix composites in closed moulds often employs the techniques usually referred to by the generic names Liquid Moulding Technologies (LMT) or Liquid Composite Moulding (LCM), and more specifically known as Resin Transfer Moulding (RTM) [1-6]. For larger structures, Resin Infusion under Flexible Tooling (RIFT) [7-9] is becoming increasingly important. A variety of other acronyms have been used for these processes [10].

RTM and RIFT processes are normally modelled using Darcy's equation [11]. The one-dimensional form of this equation relates volumetric flow rate (Q) to the process parameters:

$$Q = \frac{KA.\Delta P}{\mu L} \tag{1}$$

where K is a constant of proportionality known as the permeability, A is the cross sectional area of the porous medium normal to the flow direction, $\Delta P/L$ is the pressure gradient driving the flow and μ is the fluid viscosity. For simulation of the process, modelling should use the tensor form of Darcy's equation.

Kozeny [12] and Carman [13] developed an expression to relate the volumetric flow rate of fluid to the microstructural features of the porous bed:

$$Q = \frac{\varepsilon A m^2 \Delta P}{k \mu L} \tag{2}$$

where ε is the porosity (one minus volume fraction of fibres), m is the hydraulic radius, and k is the Kozeny constant. Blake [14] defined the hydraulic radius as the volume in which fluid actually flows, εV (where $V = AL$), divided by the wetted surface area (S). Substituting $m = \varepsilon V/S$ into equation 2 yields:

$$Q = \frac{\varepsilon^3 A V^2 \Delta P}{k \mu S^2 L} \tag{3}$$

The measurement of the permeability of the laminate stack is clearly a function of a number of parameters as indicated above. Darcy's equation, as originally proposed to model the flow of water in the aquifers at Dijon, did not include a viscosity term as water has a notionally constant viscosity over the temperature range considered (1.792 mPas at 0°C; 0.8902 mPas at 25°C). A viscosity term has now been introduced into the equation which permits modelling of a variety of resin systems. The equation as originally proposed was for saturated (*i.e.* fully wetted porous medium) flow. It is now generally accepted that the equation can be used for unsaturated (wetting) flow and hence it finds application in modelling the processes under consideration here. However, there is evidence that the measured permeability is a function of the test fluid used.

Griffin *et al* [15, 16] reported permeability (units x 10^{-12} m^2) variation in radial flow experiments between 165-208 for glycerol and 1288 for polyester resin for the impregnation of the same twill weave carbon fibre fabric.

Steenkamer *et al* [17] reported experiments to compare motor oil, diluted corn syrup and vinyl ester resin, and state that "the motor oil showed little affinity for the fibreglass reinforcements, while the vinyl ester resin and the diluted corn syrup wet out the fibre quite well". In a more complete report of this work [18] they claimed that "fabric permeability is dependent on the type of test fluid used". They also stated that "surface tension and contact angle measurements indicate that interactions at the microscopic level between the fibre and the test fluid account for these differences in permeability". They noted that "since sizings/binders are usually soluble in the resin, the chemical composition of the resin may … change during infusion, in addition to gel-induced changes". They conducted unsaturated radial flow in-plane permeability experiments at a constant flow rate of 16.2 $cm^3 s^{-1}$. The mould was 250 mm square with a 3.175 mm cavity between two 25.4 mm acrylic face sheets. The tests were conducted on two fabrics each at two volume fractions using three fluids under identical experimental conditions. The summary results are presented in Table 1.

Table 1: Mean values of permeability for three fluids and two fabrics under identical conditions (data derived from Steenkamer et al, references 17/18)

	A_f (gsm) V_f (%)	Diluted corn syrup/ deionised water	Motor oil SAE 10W-30	Vinyl ester resin Derakane 411-C50
Certain Teed 816 continuous strand mat	450 16.9	$K_{11} = 5.5 \times 10^{-9}$ m^2 $K_{22} = 6.1 \times 10^{-9}$ m^2	$K_{11} = 10.0 \times 10^{-9}$ m^2 $K_{22} = 10.5 \times 10^{-9}$ m^2	$K_{11} = 7.3 \times 10^{-9}$ m^2 $K_{22} = 8.2 \times 10^{-9}$ m^2
Certain Teed 816 continuous strand mat	450 22.6	$K_{11} = 3.2 \times 10^{-9}$ m^2 $K_{22} = 3.6 \times 10^{-9}$ m^2	$K_{11} = 7.1 \times 10^{-9}$ m^2 $K_{22} = 7.2 \times 10^{-9}$ m^2	$K_{11} = 5.7 \times 10^{-9}$ m^2 $K_{22} = 6.4 \times 10^{-9}$ m^2
Hexcel DB170 biaxial ±45° knit	595 43.9	$K_{11} = 0.93 \times 10^{-9}$ m^2 $K_{22} = 0.77 \times 10^{-9}$ m^2	$K_{11} = 2.52 \times 10^{-9}$ m^2 $K_{22} = 1.50 \times 10^{-9}$ m^2	$K_{11} = 1.55 \times 10^{-9}$ m^2 $K_{22} = 1.22 \times 10^{-9}$ m^2
Hexcel DB170 biaxial ±45° knit	595 58.6	$K_{11} = 0.70 \times 10^{-9}$ m^2 $K_{22} = 0.56 \times 10^{-9}$ m^2	$K_{11} = 1.74 \times 10^{-9}$ m^2 $K_{22} = 1.32 \times 10^{-9}$ m^2	$K_{11} = 1.23 \times 10^{-9}$ m^2 $K_{22} = 0.87 \times 10^{-9}$ m^2
Viscosity:		190 mPa s	155 mPa s	135 mPa s
Work of adhesion:		1125 μN cm^{-1}	658 μN cm^{-1}	634 μN cm^{-1}
Work of spreading:		-189 μN cm^{-1}	16 μN cm^{-1}	-74 μN cm^{-1}
Contact angle:		44.6°	spreads	37.7°

These data show the highest value of permeability when the flow fluid is motor oil and the lowest value of permeability when the flow fluid is corn syrup. The viscosities of the fluids increase in the sequence resin, oil then corn syrup. Micro-Wilhemy dynamic contact angle measurements were performed on single fibres extracted from the continuous strand mat with three test liquids (deionised water, glycerol and formamide analyser, each with contact angles greater than zero). This was used to inform the calculation of the work of adhesion, work of spreading and contact angles (Table 1). Both the principal in-plane permeabilities and the work of spreading increased as the test fluid was changed from diluted corn syrup to vinyl ester to motor oil. The work of spreading is negative for the first two of these liquids indicating that pressure must be applied to achieve wetting of the fibre surfaces. They conclude that "until a more complete understanding of fluid-fibre interactions is developed, it appears that fabrics should be characterized with the actual [liquid moulding] resin selected for a given application, since permeability measurements made with other idealized fluids yield only apparent permeabilities".

Karbhari and Palmese [19] investigated four different sizings on S2-glass fibres used in preforms for resin transfer moulding (Table 2). They state that "fibre-sizing-resin interactions occurring during the infusion stage affect wet out and local flow behaviour through the development of stoichiometric imbalances in local regions.

Table 2: Surface free energies (SFE), flow rates and capillary pressures for different surface coatings on S2-glass fibres wetted with vinyl ester resin (data derived from Karbhari and Palmese, reference 19)

Materials	**Sized for**	**polar SFE** **dyne cm^{-2}**	**dispersive SFE** **dyne cm^{-2}**	**total SFE** **dyne cm^{-2}**	**transient flow** **g min^{-1}**	**steady flow** **g min^{-1}**	**capillary pressure** **x 10^4 dyne cm^{-2}**
449 sizing	Epoxy	10.88±2.51	44.44±4.52	55.33±5.17	20.1	0.4	99.6
463 sizing	Epoxy	6.94±1.40	45.07±2.80	52.00±3.13	14.1	1.1	97.8
933 sizing	BMI/PEEK	12.60±3.02	32.50±3.95	45.10±4.97	21.6	0.5	78.1
365 sizing	UPE/VE	8.6±1.18	33.09±1.0	41.69±2.25	20.9	1.9	76.6
Note that the fibre diameters were 13 μm for 365 sized fibre and 9 μm for the other three							
411-C50 VE		1.2±1.0	34.2±1.0	35.4±0.7	-	-	-

In the context of a European-funded project (BE5477), the permeability was measured for a series of reinforcement fabrics. The Plymouth data from wetting radial flow experiments was used to inform an isothermal VIp/SEPRAN simulation of rectilinear experiments where race-tracking had been eliminated conducted by Brochier in France. For Brochier E3795 (290 gsm 5-harness satin weave with flow enhancing tows) Injectex 6K carbon fibre fabric, the simulation modelled the experimental curves well. For Brochier E3833 (290 gsm 5-harness satin weave with no flow enhancing tows) 6K carbon fibre fabric, the results were more variable. The permeability reported by another partner, measured in saturated rectilinear flow using a glycerol/water mixture was consistently higher than permeabilities measured at Plymouth [20] and hence over-predicted the flow distance at any time during the simulated experiment [21].

Fell *et al* [12] conducted wetting radial flow experiments on 13 layers of 7781 satin-weave glass fibre fabric with the warp fibres aligned using LY564-1 epoxy resin in a 3 mm mould cavity (notional fibre volume fraction of 51%). The variable process parameters are given in Table 3. The driving pressure was 1.70×10^5 Pa in all experiments.

Table 3: Permeability experiments on 7781 satin weave glass fabric.

Expt	T (°C)	μ (Pa s)	V_f (%)	Hole (mm)	K_1 (x 10^{-12} m^2)	K_2 (x 10^{-12} m^2)
1	30	0.437	48.6	0	8.75	9.22
2	35	0.296	48.3	0	8.54	8.39
3	30	0.437	49.2	8	10.31	9.25

Parallel experiments on the same batch of reinforcement were conducted at two other laboratories using wetted uniaxial flow in a rectilinear mould with a glycerol/water mixture as the permeant and using a multiple cavity rectilinear experiment with corn syrup. The reported permeabilities were in the approximate ratio 1:2:3 for resin:glycerol:corn syrup experiments.

Bréard [23] measured permeabilities in one-dimensional flows and found ratios ranging from 0.4 for unidirectional reinforcements to 0.8 for fibre mats between unsaturated and saturated preforms. Bréard *et al* [24] have compared unsaturated and saturated dynamic flows through porous media and propose to introduce the degree of saturation into the equations that govern the flow in order to increase the accuracy of numerical predictions. They state that, "except at very low injection velocity for which capillary effects may come into play, there is more resistance to the flow in a dry preform than when the fabric or mat has already been wetted and has become saturated". For three types of reinforcement (random, bidirectional and unidirectional) they clearly showed that the permeability in unsaturated flow (i.e. before the flow front has moved to fill the cavity) is lower than for saturated flow. After the apparent mould fill, the permeability rose from the unsaturated to the saturated flow value with a small delay attributed to the time required for complete saturation of the tow.

CONCLUSION

There is a growing body of evidence to indicate that the measured permeability in unsaturated (wetting) flow differs from that in saturated (wetted) flow. This may be a function of contact angles and/or surface energies. It would be useful if this situation could be resolved so that permeabilities could be translated between fluids in order to permit quantitative modelling of Liquid Composite Moulding processes using permeabilities measured with non-curing Newtonian fluids.

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