FLOW AND FILTRATION MODELLING OF CARBON NANOPARTICLE LOADED THERMOSETS IN LIQUID MOULDING

E. Reia da Costa, A. A. Skordos and I. K. Partridge

Composites Centre, Cranfield University, MK43 0AL, UK: e.f.r.costa@cranfield.ac.uk

ABSTRACT: Different carbon nanoparticles were dispersed in an epoxy resin at 0.25 wt.% loading for subsequent liquid moulding (RTM). Carbon and glass fabrics were infused in a rectangular mould which allows visual assessment of the flow front position. Nanoparticle retention was inspected by means of Scanning Electron Microscopy (SEM) imaging and visual observations. A filling modelling methodology that incorporates filtration effects was adapted and developed. This combines a conventional Darcy's solution with a set of equations representing the flow and filtration of suspended carbon nanoparticles. An analytical solution for the case of 1-D flow was derived and a finite differences solution methodology was developed. This methodology accounts for an initial prescribed flow rate boundary condition followed by a pressure driven flow until complete filling of the porous medium. The theoretical filtration coefficient necessary for subsequent finite element base simulation of the process was determined.

KEYWORDS: Carbon Nanoparticles, filtration, Resin Transfer Moulding (RTM), Darcy's law, Finite Differences Method (FDM)

INTRODUCTION

Flow of particulate suspensions in porous media is a phenomenon which occurs in a variety of industrial and natural processes such as wastewater treatment, oil extraction and contaminated groundwater flow. Particle filtration by a porous media in the context of composite manufacturing can occur when carbon nanoparticle filled resins are used to infuse a fibrous preform. Carbon nanoparticles can offer significant improvement in the electrical properties of the final composite. The efficiency of the enhancement is highly dependent on the successful distribution of nanoparticles within the composite. Therefore, the capability to predict the influence of flow processes on the final distribution of nanoparticle concentration can become very useful in the context of process design. Furthermore, the effect of the presence of nanoparticles and associated filtration on the flow at the macroscopic level can be critical.

The subject of modelling flow of particle filled resins in fibrous porous media has received limited attention up to date. A control volume based approach has been developed by Elgafy et al. [1, 2] in order to predict the trajectories of spherical carbon nanoparticles in a resin suspension during liquid moulding processing. A methodology incorporating a 2-D Darcy's flow solution has been proposed by Erdal et al. [3] and subsequently enhanced by Lefevre et al. [4, 5]. A stochastic approach has been

proposed to simulate liquid filtration processes of spherical particles through fibrous materials including re-suspension [6]. A model of the filtration phenomenon using Darcy's law and accounting for the permeability drop due to particle filtration was developed in [7].
In this work the flow behaviour of carbon nanoparticle filled epoxy in carbon and glass performs was investigated experimentally in a resin transfer moulding set up and a filling modelling methodology incorporating filtration was developed. An analytical solution for linear flow was derived and a finite differences filling methodology appropriate for the non-linear case was implemented.

MATERIALS AND METHODS

A two component thermoset epoxy resin (Araldite LY564) with an amine hardener (Aradur 2954) filled with various types of carbon nanoparticles was used to infuse a uni-weave carbon (280 g/m^2) and glass fabrics (480 g/m^2), supplied by Hexcel and Marineware respectively. Commercially available multiwalled carbon nanotubes C100 and P940 were supplied by CNT Co and Thomas Swan, respectively, in dry form. Surface modified MWCNTs supplied by Zyvex and carbon nanofibres (CNF) by Pyrograf® Products, Inc. were used to modify the resin at 0.25wt.% loading. Dispersion of nanoparticles in the resin was carried out using high shear mixing of CNF, a combination of triple roll milling and ultrasonication for C100, ultrasonication for P940 and triple roll milling for surface activated CNTs. Subsequent moulding was carried out using a piston driven Isojet RTM setup and a 340 × 340 mm mould cavity under 2 bar pressure. The injection temperature varied between 65 and 75 ºC and cure at 80 ºC for 90 min was followed by free standing post cure at 140 ºC for 8h.

RESULTS AND DISCUSSION

Resin Flow

The solution of the 1-D Darcy's problem for constant viscosity η, permeability K and porosity ε with prescribed pressures at the inlet P_0 and outlet P_∞ predicts linear dependence of the flow front position on square root of time [8]. Fig. 1 illustrates the resin flow front profiles during filling versus the square root of time alongside a linear fit using the 1-D Darcy's law result. Significant deviation from the linear behaviour is observed in the case of dry CNT and CNF filled systems. In contrast, the control and modified CNT filled materials follow the linear fit closely. Deviation from the square root dependence can be attributed to the retention of nanoparticles by the reinforcement which modifies both the local permeability of the fabric and the resin viscosity.
At the beginning of filling, resin flows relatively fast as the pores of the reinforcement are not restricted by retained nanoparticles. As the pores start to be clogged at later stages of filling the overall porosity of the reinforcement drops and the permeability of the fabric decreases. Consequently the flow of resin becomes slower and deviations from a square root dependence of flow front position on time such as those observed in Fig. 1 occur.

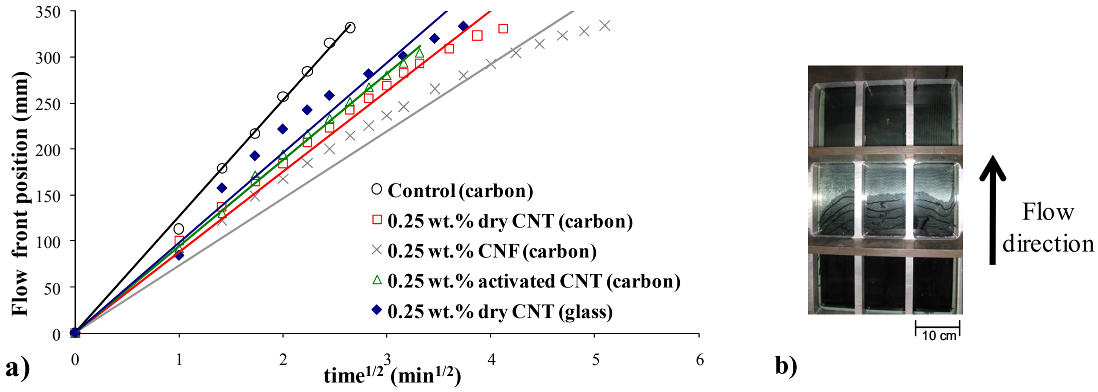

Fig. 1 a) Flow front profiles during filling; **b)** top view through glass of the resin flow in RTM.

Analytical Model for Linear Flow

The proposed method for modelling filtration and flow utilises Darcy's law which relates the fluid velocity U to the pressure gradient P, by a proportionality coefficient described by the ratio between the fabric permeability K with the product of porosity ε and viscosity η. This is then combined with a set of equations representing the flow of retention and suspension of carbon nanoparticles. A mass balance (1) connects the concentration of particles $C(x, t)$, with the amount of particles retained by the fabric $\sigma(x, t)$ as follows:

$$\frac{\partial(\sigma + \varepsilon C)}{\partial t} + \vec{U}.\nabla C = 0 \tag{1}$$

The kinetics of filtration are incorporated in the model using the following law:

$$\frac{\partial \sigma}{\partial t} = k_0 UC - k_r \sigma UC \tag{2}$$

Eq. (2) assumes that both the retention and the re-suspension rates are proportional to the amount of nanoparticles passing through or retained respectively, with k_0 and k_r the corresponding proportionality coefficients. Assuming that re-suspension of retained nanoparticles is very low the second term in the RHS of Eq. (2) can be neglected. In this case retention only depends on the velocity U and concentration of nanoparticles C. An analytical solution for the dependence of nanoparticle concentration on the distance from the inlet x and on time t considering prescribed pressures at the flow front (P_∞) and resin inlet (P_o) and zero retention at the flow front is derived as follows:

$$\sigma + C = C_o \left[1 + \varepsilon k_o \sqrt{\frac{2K(P_o - P_\infty)}{\varepsilon\eta}} \cdot \sqrt{t - \frac{x^2 \varepsilon\eta}{2K(P_o - P_\infty)}} \right] \cdot e^{-k_o x} \tag{3}$$

Evaluation of the Filtration Coefficient

Eq. (3) was utilised to determine the filtration coefficient k_0 for the three systems where significant filtration occurred. This was carried out by combining experimental measurements of the gradient of nanoparticle concentration with the model solution.

Evaluation of the location at which the concentration of nanoparticles becomes negligible ($0.0001 g/cm^3$ for the purposes of this analysis) was determined by analysis of SEM images of the delamination fracture surface of carbon reinforced composite samples and by visual inspection of the glass reinforced panels. These results were then coupled with the model using the generalised reduced gradient nonlinear optimisation technique [9] implemented in Excel to estimate k_0. The results of the estimation are summarized in Table 1. Higher k_0 values were obtained for the CNF filled resin when compared to dry MWCNT dispersions. This is due to the larger dimensions of carbon nanofibre particles. The average content of carbon nanoparticles in the volume of the composite within which the concentration is not negligible was determined and reported in Table 1. The results are in good agreement with the values for the total concentration of particles determined by the model. The model solutions for the P940, C100 and CNF filled composites are illustrated in Fig. 2. Fig. 2 shows a very rapid decreasing trend on the concentration of particles. The CNF filled composite has the highest particle content at the inlet (x=0 m) which is due to the nature of the carbon nanoparticles themselves and the aggregates size in suspension, which are both larger than those present in dry carbon nanoparticles filled suspensions.

Table 1 Theoretical k_0 and average concentration values for dry carbon nanoparticles

	P940 (carbon fabric)	**CNF (carbon fabric)**	**C100 (glass fabric)**
k_0 **[cm^{-1}]**	0.66	0.89	0.74
Average C [kg/m^3]	12.7	9.73	10.3

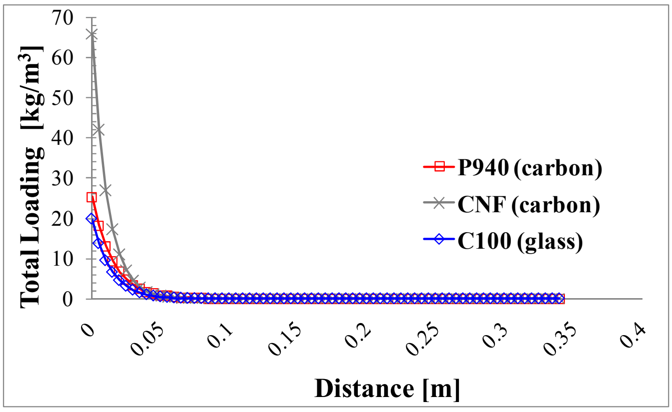

Fig. 2 Estimated total ($C + \sigma$) concentration of dry carbon nanoparticles along the composite.

Finite Differences Model

A finite differences (FD) solution of the non-linear in terms of material behaviour 1-D flow and filtration problem was developed. This is appropriate for both the simulation of 1-D in plane flow in an RTM scenario and through the thickness flow in an infusion scenario. The movement of the flow front is described by a moving grid dimension whilst prescribed flow rate and prescribed pressure boundary conditions are combined at the inlet via a maximum pressure constraint. Changes in permeability, viscosity and porosity are addressed within the FD solution by constantly updating these properties as a function of retained and suspended nanoparticle concentrations. Then both the pressure profile and the total concentration of particles are solved, until the grid size corresponds to the length of the actual composite panel.

CONCLUSIONS

Macroscopic filtration occurs during the RTM injection of resins containing unmodified carbon nanoparticles. This is confirmed by the deviation of experimental observations from the linear Darcy's behaviour. No filtration issues are identified macroscopically in systems with modified MWCNTs.
An analytical model describing the linear flow and filtration of particles in liquid moulding was developed and utilised to calculate the filtration coefficient k_0 and the total loading distribution of particles in the final composite. A finite differences solution of the Darcy's flow particle filtration problem in 1-D was developed and implemented. Extension of this work to two dimensions is currently under development based on non linear finite element analysis.

ACKNOWLEDGEMENTS

The work reported here was funded by the Engineering and Physical Sciences Research Council via the Innovative Manufacturing Research Centre at Cranfield University (GR/R68139/01).

REFERENCES

1. Elgafy, A., Khalid, L., *Engineering Solution in Monitoring Nanoparticle-Fluid Flow During Nanocomposites Processing.* Journal of Nanoparticle Research, 2007. **9**(3): p. 441-454.
2. Elgafy, A., Khalid, L., *Carbon nanoparticle-filled polymer flow in the fabrication of novel fiber composites.* Carbon, 2006. **44**(9): p. 1682-1689.
3. Erdal, M., Güçeri, S., Danforth, S. C., *Impregnation Molding of Particle-Filled Preceramic Polymers: Process Modeling.* Journal of the American Ceramic Society, 1999. **82**(8): p. 2017-2028.
4. Lefevre, D., Comas-Cardona, S., Binetruy, C., Krawczak, P., *Coupling filtration and flow during liquid composite molding: Experimental investigation and simulation.* Composites Science and Technology, 2009. **69**(13): p. 2127-2134.
5. Lefevre, D., Comas-Cardona, S., Binetruy, C., Krawczak, P., *Modelling the flow of particle-filled resin through a fibrous preform in liquid composite molding technologies.* Composites Part A: Applied Science and Manufacturing, 2007. **38**(10): p. 2154-2163.
6. Destephen, J. A., Choi, K. J., *Modelling of filtration processes of fibrous filter media.* Separations Technology, 1996. **6**(1): p. 55-67.
7. Chohra, M., Advani, S. G., Gokce, A., Yarlagadda, S., *Modeling of filtration through multiple layers of dual scale fibrous porous media.* Polymer Composites, 2006. **27**(5): p. 570-581.
8. Gebart, B. R., *Permeability of Unidirectional Reinforcements for RTM.* Journal of Composite Materials, 1992. **26**(8): p. 1100-1133.
9. Fylstra, D., Lasdon, L., Watson, J., Waren, A., *Design and Use of the Microsoft Excel Solver.* INTERFACES, 1998. **28**(5): p. 29-55.