

FLOW OF CARBON NANOPARTICLE LOADED EPOXY RESIN IN LIQUID MOULDING

E.F. Reia da Costa^{1*}, A.A. Skordos¹, I. K. Partridge¹ and A. Rezaei²

¹ Composites Centre, Cranfield University
MK43 0AL, UK

² BAE Systems, Advanced Technology Centre
BS34 7QW, UK

*e.f.r.costa@cranfield.ac.uk

SUMMARY

The Resin Transfer Moulding of carbon and glass epoxy composites containing various types of carbon nanoparticles is investigated. The work focuses on the influence of nanoparticles on flow, the filtration of the nanofiller, and the potential of incorporating these effects in process models.

Keywords: resin transfer moulding (RTM), nanoparticles, dispersion, filtration, flow

INTRODUCTION

The introduction of nanometric scale particles in polymeric matrices led to the development of nanocomposites. Carbon nanotubes (CNTs) have received immediate and growing attention since their discovery by Iijima [1] due to their high electrical conductivity, combined with an attractive mechanical and thermal properties and a very high aspect ratio. The transfer of these unique properties to the polymer nanocomposites remains a challenge. A homogeneous and stable dispersion of carbon nanotubes in the polymer medium is necessary in order to achieve adequate transfer of their advantageous properties to the nanocomposite. Nanotubes tend to form aggregated structures due to their high surface area, which reaches values higher than 1000 m²/g [2]. Both physical and chemical dispersion methods have been used to obtain satisfactory and stable suspensions. Some of the most common physical dispersion methods are ultrasonication, shear mixing and triple roll milling. In terms of chemical dispersion techniques, CNT surface functionalisation, polymer wrapping and surfactant assistance promote the chemical bonding of nanotubes to the polymer [3].

The use of nanocomposites as part of high performance components in the aerospace industry necessitates the incorporation of nanoparticles within continuous fibre, usually carbon, composites. Current research on the subject focuses on the production of nanoparticle loaded fibre reinforced composites employing and adapting existing manufacturing processes. Resin Transfer Moulding (RTM) and Vacuum Assisted Resin Transfer Moulding (VARTM) have been used for the production of composite coupons and relatively larger scale structural elements [4-7]. In order to make the processing feasible the content of nanotubes was limited below 0.3 wt.% Although the use of effective dispersion methods of nanoparticles in the polymer matrix can lead to stable

suspensions, increased nanoparticle concentrations lead to very high resin viscosities and render the application of liquid moulding technologies very difficult [8]. Other composites manufacturing processes such as hand layup [9, 10] and growth of aligned CNT forests [11], offer potential solutions for the manufacture of composites with higher concentrations of nanoparticles.

In addition to issues related to the high viscosity of resins filled with nanoparticles, filtration can also lead to inadequate component quality. It can cause clogging of the channels due to accumulation of nanoparticles which can consequently slow down the progress of the filling process. This effect is accompanied by gradients in the concentration of nanoparticles.

In the present work different types of carbon nanoparticles (0.25 wt.%) are used to modify an epoxy matrix appropriate for liquid moulding. Carbon and glass fabrics are infused in a mould that allows visual observation of the flow front position. Filtration is characterised by means of Scanning Electron Microscopy (SEM) and electrical conductivity measurements and its effect on flow profiles is evaluated. The first steps towards a filling modelling methodology that incorporates filtration effects are established.

MATERIALS AND EXPERIMENTAL PROCEDURE

Materials

The resin system used in this work was a two-component thermoset epoxy resin (Araldite LY564) with an amine hardener (Aradur 2954). This is a low viscosity resin system (900 mPas) suitable for RTM applications. The epoxy to hardener ratio is 100/35. Multiwalled carbon nanotubes (MWCNT) and carbon nanofibres (CNF) were used to modify the resin. Dry MWCNT nanoparticles P940 and C100 were supplied by Thomas Swan and CNT Co. respectively, and surface modified MWCNT by Zyvex. CNF nanoparticles were supplied by Pyrograf® Products, Inc. The loading was 0.25 wt.% for all formulations. A uniweave carbon fabric (280 g/m²) supplied by Hexcel and a uniweave glass fabric (480 g/m²) supplied by Marineware were utilised.

Dispersion methods

CNF nanoparticles were added to the resin and the suspension was mixed in a DISPERMAT® CN F2 high shear mixer. Dry nanotubes C100 were dispersed in the epoxy using triple roll milling (TRM Torrey Hills Technologies) and ultrasonication using a Branson S-450D horn whilst P940 were just ultrasonicated. Surface activated nanotubes were dispersed in the resin by triple roll milling.

Resin Transfer Moulding

Moulding was carried out using an Isojet RTM setup. The resin was degassed and placed inside a piston chamber at 30 °C. Filling was performed under a pressure of 2 bar into the mould cavity. The mould used for the infusion is an aluminium tool with a glass top cover, allowing monitoring of the flow front position during injection. The mould temperature at injection was 65 °C for all systems except the control and the dry CNT (P940) filled composite panels for which a mould temperature of 75°C was utilised. The cure cycle for was 1h 30min at 80 °C (1bar). Post cure was carried out in an oven at 140 °C for 8h. The produced panel dimensions were 340 × 340 mm.

Electrical Conductivity

Electrical measurements were carried out on rectangular specimens with dimensions of 30 × 30 × 3.2 mm for carbon composites and 30 × 30 × 3.7 mm for glass composites. The surfaces of interest were painted with a suspension of silver in methyl isobutyl ketone (Acheson Electrodag 1415M).

DC electrical resistivity of the carbon composite samples was measured using a DC precision current source (Keithley model 6220) and a nanovoltmeter (Keithley model 2182A) via the three-point delta current reversal technique. The electrical conductivity of the samples was measured using 100 μA current in three directions: through thickness, transverse and longitudinal.

Through thickness electrical conductivity of the glass composite samples was measured via AC impedance spectroscopy using a Solartron SI 1260 frequency response analyser. Twenty nine frequencies from 1 Hz to 1MHz were swept on a logarithmic scale. The electrical resistance of the samples was determined from the peak value of the imaginary impedance spectrum.

RESULTS AND DISCUSSION

Filtration

Filtration of the nanoparticles by the reinforcement was evident during the filling of dry CNT and CNF nano-filled composites. In contrast, surface modified CNTs did not show macroscopic evidence of filtration during the process. SEM was used to analyse the distribution of nanoparticles in the inlet and outlet regions and in the composite. Fig.1.a illustrates CNT agglomerates with an approximate size of 50 μm in the inlet region in the case of dry P940 CNTs. The composite delamination surface for the same material contains CNT aggregates concentrated in resin rich pockets as observed in Fig.1.b and 1.c. The occurrence of these aggregates becomes less frequent as we move away from the resin inlet due to filtration, whilst the resin located at the outlet contains virtually no CNT agglomerates.

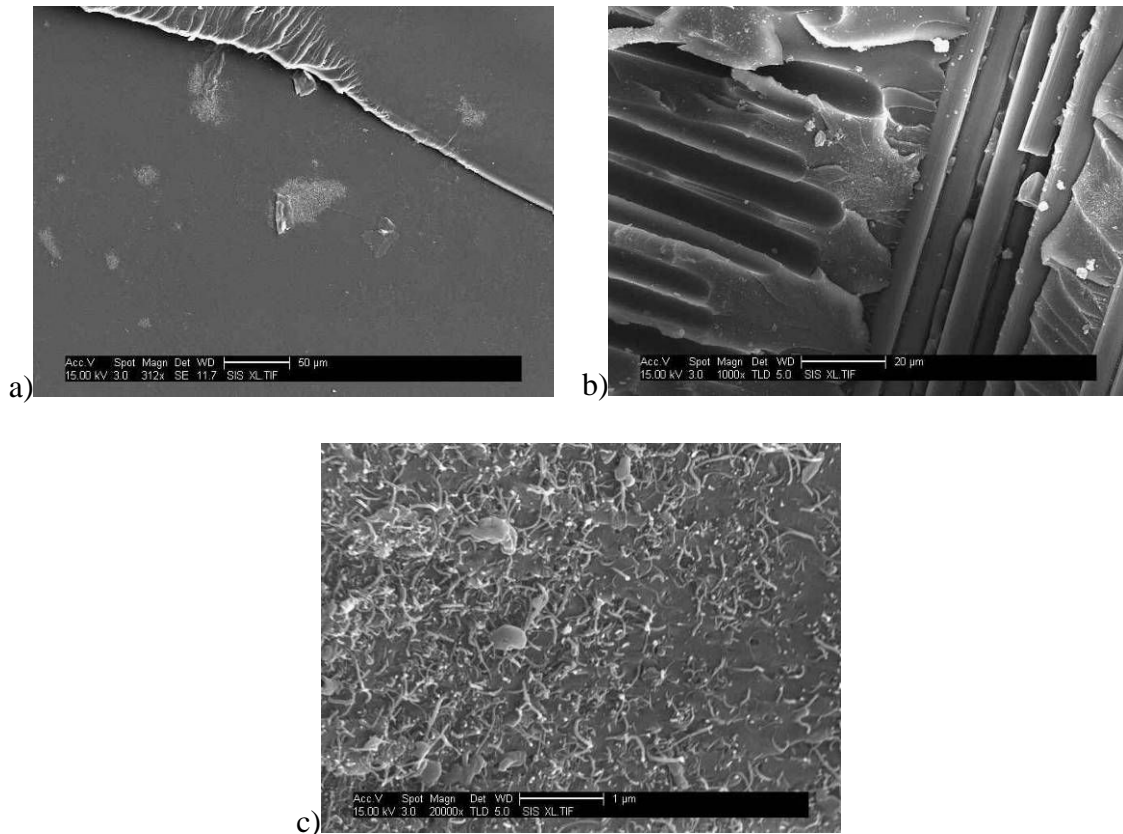


Fig.1. a) 0.25 wt.% dry CNTs (P940) at the inlet gate; b) delamination surface of carbon composite filled with 0.25 wt.% dry CNT; c) detail of nanotube agglomerates present in b).

Similar effects are observed in the case of the 0.25 wt.% CNF filled resin. Fig.2.a shows an aggregate of CNF nanoparticles with a size greater than 10 µm at the inlet. These aggregates are retained by the fabric and diminish the occurrence of nanoparticles at the outlet (Fig.2.b).

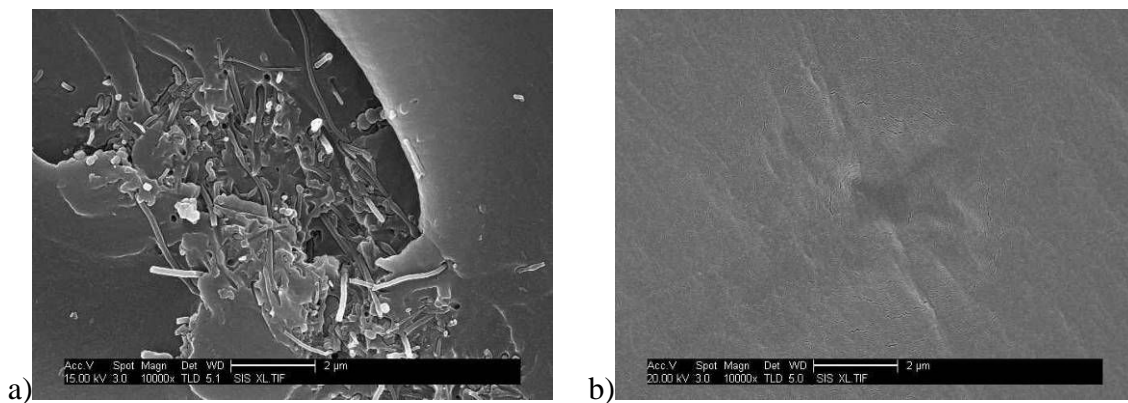


Fig.2. 0.25 wt.% CNF filled resin at the a) inlet and b) outlet.

Resin Flow

Darcy's problem accepts the following solution for a material of constant viscosity η , and a porous medium of constant effective permeability K in an one dimensional situation with prescribed pressures at the inlet and outlet.

$$h(t) = \sqrt{\frac{2K}{\varepsilon\eta}(p_o - p_\infty)t} \quad (1)$$

Here $h(t)$ denotes the flow front position at time t , ε the porosity of the fabric and p_o , p_∞ are the prescribed pressures at the inlet and outlet of the mould respectively. This solution implies a linear dependence of flow front position on square root of time.

Fig.3 illustrates the resin flow front profiles during RTM infusion versus the square root of time alongside a linear fit using Eq. (1). 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 material 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.

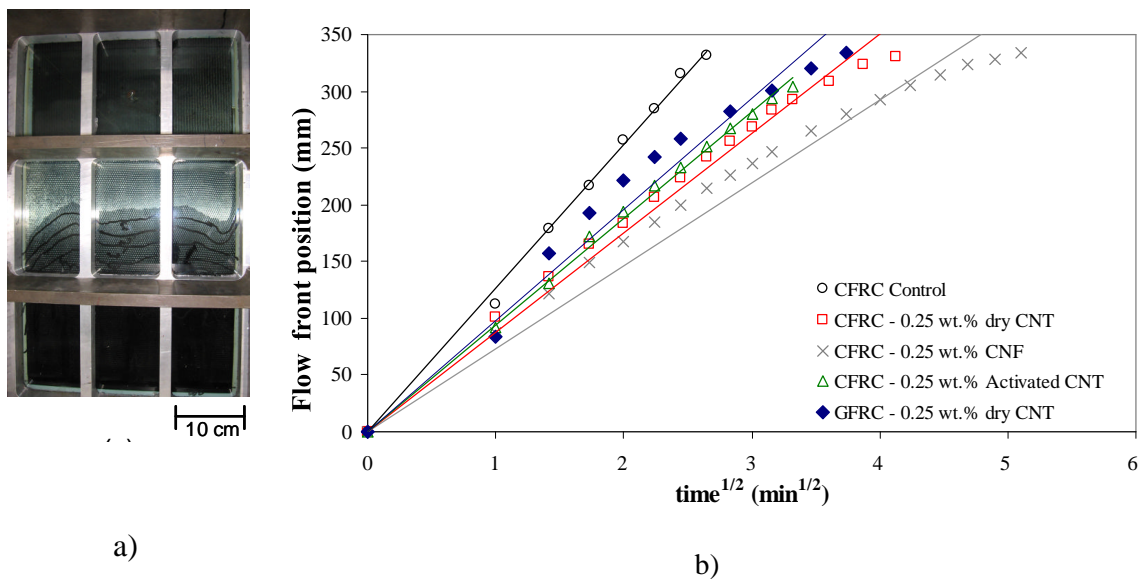


Fig.3. a) Top view through glass of the resin flow in RTM; b) resin flow front profiles during RTM injection.

A modification of the governing equations is necessary in order to incorporate the effect of filtration in filling analysis. Darcy's law (2) relates the fluid velocity U to the gradient of pressure p via a proportionality coefficient expressed as the ratio of permeability to viscosity:

$$U = -\frac{k}{\eta} \cdot \left(\frac{\partial P}{\partial x} \right) \quad (2)$$

This needs to be accompanied by a continuity relation that connects the concentration of particles in the resin C , with the amount of particles retained by the fabric σ as follows:

$$\frac{\partial(\sigma + \varepsilon C)}{\partial t} + U \frac{\partial C}{\partial x} = 0 \quad (3)$$

The kinetics of filtration can then be incorporated in the model by a constitutive law which in its simplest form [14] can be expressed as:

$$\frac{\partial \sigma}{\partial t} = k_0 UC - k_r \sigma UC \quad (4)$$

This form of the kinetics equation 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. (4) can be neglected. Then retention only depends on the velocity U and concentration of nanoparticles C .

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 following Eq. (3) 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 as those observed in Fig.3.b occur.

Electrical properties

The electrical conductivity results of carbon specimens indicate highly anisotropic electrical behaviour of the composite. The electrical conductivity along the fibre direction and the transverse direction is three and one orders of magnitude higher respectively, than the conductivity in the through thickness direction. This is attributed to the influence of the carbon fibres, which govern the electrical behaviour of the material. Through thickness conductivity results illustrated in Fig.4 were used to establish a correlation between the occurrence of filtration effects and spatial variations of the electrical behaviour. It can be observed that carbon nanoparticles induce a slight increase of the electrical conductivity of the composite whilst the conductivity tends to

decrease as we move away for the inlet. This phenomenon occurs even in the system with surface modified nanotubes indicating filtration at the microscopic level.

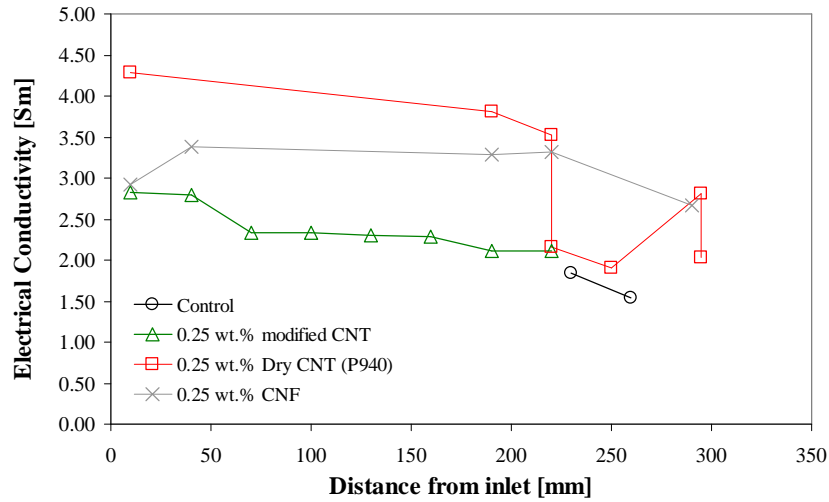


Fig.4. Through thickness electrical conductivity of the nanoparticle filled carbon composites as a function of the distance to the inlet gate.

Through thickness conductivity results for the glass composite are presented in Fig.5. The conductivity values obtained are in the order of 10^{-9} S/m for the composite with 0.25 wt.% dry CNT (C100), a value 2-3 orders of magnitude higher than that of the control glass composite. Filtration is also evident from the drop of conductivity towards a plateau value at a distance of about 70 mm from the inlet.

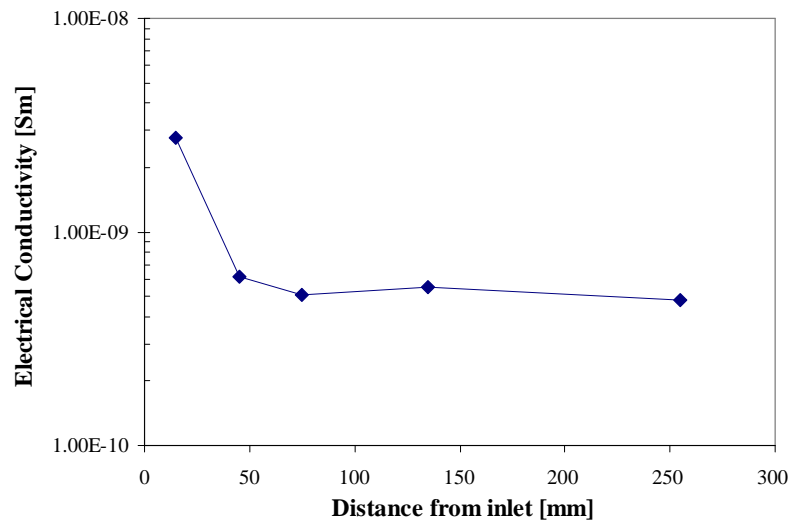


Fig.5. Through thickness electrical conductivity of 0.25 wt.% dry CNT (C100) filled glass composites as a function of the distance to the inlet gate.

CONCLUSIONS

Macroscopic filtration occurs during the RTM injection of resins containing unmodified carbon nanoparticles. In these systems aggregates of carbon nanoparticles were found in resin rich-pockets closer to the inlet side of the mould, while very few nanoparticles are present in the outlet side of the composite. This result is confirmed by a decreasing trend in electrical conductivity as a function of the distance from the inlet of the injection. The conductivity of carbon composites is governed by the fibres, with the addition of nanoparticles having a marginal effect. In contrast, the conductivity of glass composites increases significantly with addition of carbon nanoparticles. No filtration issues were identified macroscopically in systems with modified CNTs. However, conductivity measurements indicated a decreasing trend as a function of distance from the outlet, which points to a potential effect of deep filtration of well dispersed CNTs.

The square root dependence of flow front position on time expected from one dimensional Darcys' law is not followed in fillings of systems prone to filtration. An extension of impregnation modelling to incorporate particle retention and re-suspension and local variations of viscosity and permeability as a function of the local concentration of nanoparticles is currently under investigation.

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