WETTING MECHANISMS OF VERTICALLY ALIGNED CARBON NANOTUBE (VACNT) COMPOSITE STRUCTURES IN READINESS FOR ADDITIVE LAYER MANUFACTURE

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Abstract
It is proposed that by embedding as grown Vertically Aligned Carbon nanotube (VACNT) 'forests' in polymer layers both uniform distribution and controlled alignment can be maintained throughout a bulk composite. In order to attain quasi-continuous reinforcement of the matrix it will be necessary to overlap such reinforcements between individual layers in the structure. By producing such a composite it is expected that a high level of intra and interlayer reinforcement can be achieved. It is thought that overlapping can be achieved by the partial embedment of VACNTs within individual polymer layers. We apply the simple Lucas –Washburn model on the nanoscale dimensions of the CNT forest and observe discrepancies between expected processes and experimental results. Further investigations are conducted through the partial embedding of CNT in thermoplastic layers followed by micros CT analysis of the wetting process. We observe peaks of polymer flow at the CNT-EVA interface and suggest that such features indicate a complicated wetting mechanism unlike that proposed in the Lucas –Washburn model.

1 Introduction

1.1 Aligned and dispersed multi layer CNT composite structures

The outstanding mechanical, electrical, and thermal properties of individual CNT have been well documented in the two decades that have passed since the discovery of these new carbon allotropes [1]. Despite such properties providing speculation of the large range of applications for CNTs, processing difficulties have meant that few CNT based technologies and products have emerged regardless of the extensive research into the field. In the area of composite materials many of the measured properties of CNT make them attractive for use as fillers in 'nano' or 'multi-scale' composites which can utilise such characteristics on a macro scale. The immense conductive properties of CNT, both thermal and electrical, make them an ideal choice for conductive composites particularly in polymer matrices where the matrix material is an insulator. Conversely the majority of research has focused on mechanical reinforcement of a polymer matrix as the Tensile Strength and Young Modulus of CNT exceed any known material to date [1].

Current attempts at creating CNT composite materials by blending or mixing CNT into a polymer matrix have often resulted in considerably lower levels of reinforcement than those predicted by traditional rule of mixtures models [2]. Such observations are often attributed to several key processing difficulties including dispersion, owing to the tendency of CNT to agglomerate, adhesion of the matrix and CNT and even damage of the CNT during processing [3]. As a result many research groups have begun to experiment with new methods of CNT composite manufacture, several of which use as produced aligned CNT in an attempt to solve the current problem of CNT dispersion whilst also introducing alignment to the composite structure. Wardle et al. [4] report the complete wetting of CNT 'forests' through capillary effects using RTM6 resin, a low viscosity thermoset resin, and achieve considerable reinforcement using only low (~1 vol %) density CNT forests. Furthermore the production of similar samples using higher density CNT forests created by mechanical bi-axial compression after production can further increase the modulus of such composites by approximately 200%. Another group [5] focused on producing 'bucky paper' from aligned CNT forests and in doing so also mechanically increased the density of as grown forests prior to composite production. Their results show an even greater percentage increase in mdoulus. Despite this the values of reinforcement still fall short of theoretical models that most researchers now attribute to the waviness of the as grown CNT when compared to the perfect fibres used in modelling [6].

These composite production methods illustrate that effective reinforcement of a polymer matrix is possible but further work is necessary if such results are to be extended beyond a single as grown CNT forest. Unless vast improvements in CNT forest production are achieved it is likely that the axial length, or height, of CNT forests will be limited to the self termination that occurs usually at heights below 5 mm [7]. In theory large area forest growth is possible and could be done in a continuous process as CNT have already been grown on a moving substrate [8], but in order to achieve bulk structures coupling between separate CNT forests within the bulk will still be pivotal. Such factors instigate the need for a multi-layer CNT composite production process in an additive layer manufacture fashion and several methods have been proposed [9]. The success of any such method will rely on the CNTs effectively providing efficient interlayer reinforcement and allowing successful transfer of load between separate forests contained throughout the bulk material. In order to achieve such a process the microstructure of the system is critical and to achieve quality interlayer reinforcement a combination of forest patterning and controlled partial embedding of CNT is required. Current research [10] shows that CNT forest structures wet readily with low viscosity resins through capillary effect and forests of millimetre height wet fully in times of less than a single second. These observations make partial embedding of CNT in resins difficult and indicate that a firm understanding of the wetting process in CNT forests will be required if a multi layer composite structure is to be realised.

1.2 Modelling of Dynamic capillary rise

Capillary rise is a highly complex phenomenon even for a simple capillary tube and many important factors govern the momentum balance of the fluid including viscous losses, local acceleration of the fluid, entrance effects, the capillary pressure and the hydrostatic pressure. Including all of the prior terms allows calculation of the full linear momentum balance but proves to be highly complex and as a result can only be solved numerically. Consequently several terms are often neglected according to the specific situation in order to simplify the equations in an effective but accurate manner. The best example of such simplification and what could be described as the foundation of dynamic capillary rise is the works of Lucas [11]

and Washburn [12] in which a relationship were the height of liquid rise in a capillary is found to be proportional to the square root of the time that has passed. Such a result is obtained by simply balancing capillary pressure effects that occur due to the surface interactions between the three phases at the liquid capillary boundary against the viscous pressure loss as the fluid is drawn into the tube as defined by the Hagen-Poiseuille equation. The resulting Lucas-Washburn equation (1) has been used to describe capillary flow dynamically in many situations but is most accurate in the early and intermediate stages of capillary rise as it ignores entrance effects as well as retardation of capillary rise due to gravity and is depicted as follows;

$$h^2 = \frac{\sigma R \cos(\theta)}{2\mu} t \tag{1}$$

where h is the height of capillary rise, σ is the fluid surface tension, R is the inner radius of the capillary, θ is the contact angle, μ is the fluid viscosity and t is the time since $h=0$. As the equation ignores the influence of gravity it is most appropriate in the early stage of capillary rise and is sometimes called the short term asymptotic solution of the Lucas-Washburn equation.

As well as the traditional Lucas-Washburn equation two further simple analytical models can be used to improve the accuracy of predictions in different time domains. The first is to include the influence of gravity when investigating longer timescales, known as the implicit form of the Washburn equation (2),

$$t(h) = -\frac{8\mu}{\rho g R^2} h - \frac{16\mu\sigma^2 \cos(\theta)}{\rho^2 g^2 R^3} \ln\left(1 - \frac{\rho g R}{2\sigma \cos(\theta)} h\right) \tag{2}$$

where ρ is the fluid density and g is the acceleration due to gravity. This result was given in Washburns early work, but is often overshadowed owing to its implicit form and the effectiveness of the short term solution. Finally Zhmud et al. [13] proposed a long term asymptotic solution (3) to the Washburn momentum balance by considering the turbulent nature of the developed flow of fluid in the capillary.

$$h = \frac{2\sigma \cos(\theta)}{\rho g R}\left[1 - e^{\left(-\frac{\rho^2 g^2 R^3}{16\mu\sigma\cos(\theta)} t\right)}\right] \tag{3}$$

This result provides a long time frame solution that is useful in well developed capillary rise scenarios.

A comparison of these solutions is shown in Figure. 1, where data has been calculated to illustrate the capillary rise of water in a glass capillary of radius of 100 μm. It is suggested that the experimentally observed capillary driven wetting of aligned CNT forests can be fitted to such a model thus allowing a degree of control over the process leading to partial embedment of CNT in a polymer layer. As a rough approximation a CNT forest can be modelled as a bundle of capillary tubes as suggested by Washburn when addressing capillary flows in porous media. More complete models of capillary rise in porous media have also been used by applying the Darcy law, and have shown good agreement with experimental data [14]. Considering the complex structure of the as grown CNT it is like they will behave

more like porous media than bundles of capillaries however both porous model and Washburn's models involve the same relationship between height of capillary rise and elapsed time with constants relating to the properties of the capillary tube or porous structure respectively. Often the use of porous models involves experimental measurement of certain values such as the final capillary rise height, which is not possible for CNT forest and consequently Washburn's simplistic approach will be used as an approximation in this case.

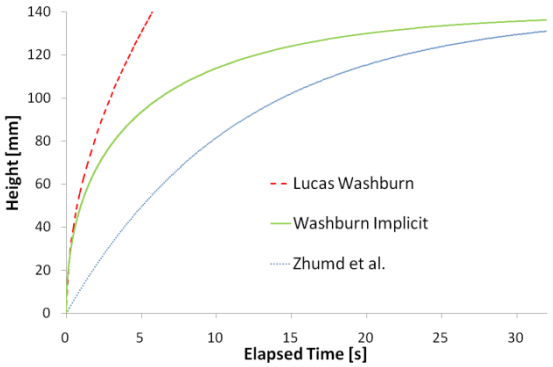

Figure 1. A plot of the dynamic capillary rise models for water in a glass capillary of radius 100μm illustrating the implicit model as well as the two asymptotic solutions

1.3 Dynamic capillary rise in 'as grown' CNT forest structures

When considering the penetration of fluids into a CNT forest a capillary driven process is observed, however the polymer does not penetrate inside of the individual CNT but rather into the porous regions that exist between the CNT in the overall structure. The as grown CNT forest is characterised as having a certain density, which describes the ratio of the volume of such porous regions to that of the CNT and can be calculated either through the use of electron microscopy, or by accurately weighing and measuring of the as grown structures [4]. In a CVD process CNT are grown from a thin film of metal catalyst, typically iron, which forms small 'islands' when annealed that each initiate the growth of a single CNT. The dimensions and distribution of such islands are critical in achieving vertical self alignment of the CNT which allows the growth of forests to millimetre heights. As a result CNT produced using CVD, such as the ones used in this study, have typical densities, or porosities, of 1 % volume fraction [15]. Consequently it is possible to calculate an average inter CNT spacing which can be used to calculate an approximate values for an average capillary radius to be used in the Dynamic capillary rise models. The values of the CNT radius R_{CNT} and the spacing between individual CNT d are important in different aspects of the momentum balance. The interaction between the CNT and the fluid are the driving force behind the capillary pressure thus using a larger radius than that of the CNT will increase this pressure and also effect viscous losses calculated at the tube walls. Using the CNT radius will have other implications though and will mean that gravitational effects are reduced as the volume of liquid being drawn into the structure will be far more than that considered by the model. Considering such details an approximation will be made using a radius of 4 nm and 40 nm to cover the range of scenarios remembering that each term will have a varying effect with development of the capillary flow.

2 Dynamic capillary rise models, materials and testing methods

2.1 Application of dynamic capillary rise models to CNT structures

It is possible to estimate expected capillary rise in CNT forests by inputting data to the models described previously and plotting the expected height against elapsed time. Models were investigated using approximate values for Hexcel RTM6 resin, often used in aerospace composite production, at a processing temperature of 100ºC. The fluid properties of the RTM6 were taken as detailed in Table 1. Measurement of the contact angle between CNT and fluids has been achieved [16] but is a challenging process, and in this case we assume a contact angle of 30º as it is observed experimentally that the resin readily wets the CNT forest.

Fluid	Viscosity[Pa.s]	Density[kgm^{-3}]	Surface Tension[Nm^{-1}]
RTM6 (@100ºC)	0.050	1110	0.032

Table 1. Fluid parameters used for modelling the wetting of CNT forests with RTM6 resin [17]

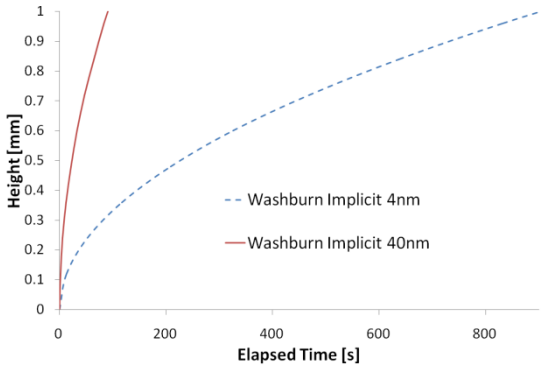

Figure 2. A plot of the implicit Washburn model using parameters of RTM6 resin and different values of the capillary radius

Figure 2 shows the outcomes of the models up to a capillary rise height of ~1 mm which is the area of interest when considering the CNT forests used in this case. Both short-term and implicit models provide the same result over the area considered which is in the early stages of the capillary rise process and the long time model provides an inaccurate result as expected and hence is not plotted. The data for capillary radii of both 4 nm and 40 nm shows that the expected time for the resin to rise 1mm inside of the forest is several orders of magnitude larger than the experimentally observed result of less than a second [10]. Such a result indicates that the Lucas-Washburn approach to dynamic capillary rise may be inaccurate at nanoscale dimensions. Possible explanations include molecular interactions that may occur as the size of the pores in the structure approach that of the molecules in the fluid, inaccuracies due to assumption in the simplistic model or even complex wetting mechanisms within the CNT structure.

2.2 Materials

We use CVD CNT forests of areas up to 1 cm^2 and heights of around 1 mm that are produced in house using a 50.8 mm diameter quartz furnace similarly to Hart et al. [15]. The thermoplastic used in the wetting experiments was the co-polymer Ethylene Vinyl Acetate (EVA) with a 40 wt% vinyl acetate composition and a molecular weight of around 22,000 supplied by Sigma Aldrich.

2.3 Investigation of CNT forest wetting mechanisms

In order to investigate wetting mechanisms of CNT forests it is of interest to observe the movement of the fluid inside of the structure. Experiments were conducted to allow the investigation of the capillary wetting of CNT forests with molten EVA co-polymer. This thermoplastic was chosen as it has a relatively low molecular weight and a fairly high viscosity, approximately 400 Pa.s at 180ºC, which can be varied with temperature when the polymer is molten. As described in the previous models it is expected that at heights below 1 mm the capillary rise process will be in the early stages and consequently it follows that the viscous resistance to flow will provide the greatest retardation to the capillary process. Using a specially constructed rig CNT forests were precisely dipped into a molten reservoir of EVA heated to 180ºC using a hot plate. The CNT forest was left in contact with the EVA for a total of 5 min then the whole system was left to cool. After cooling the CNT are embedded into the EVA and the growth substrate can be removed, as illustrate in Figure. 3 , simply by using a pair of tweezers.

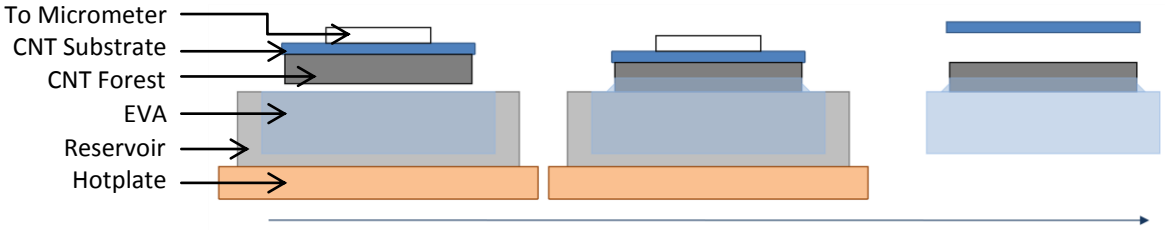

Figure 3. A Schematic of the EVA-CNT composite production process

The embedded CNT structures were then analysed using a Hitachi S-3200N scanning electron microscope (SEM) and Micro-CT scans were performed using an X-tek Benchtop CT 160Xi system with 80 kV voltage and 80 µA current. A Varian 1313 flat panel detector with 1000 x 1000 pixels and pixel size of 127x127 μm^2 was used. The isotropic voxel size of the reconstructed images was 3.4 μm^3, analysis was performed using VGStudio Max software.

3 Results and discussion

3.1 SEM and µ-CT analysis

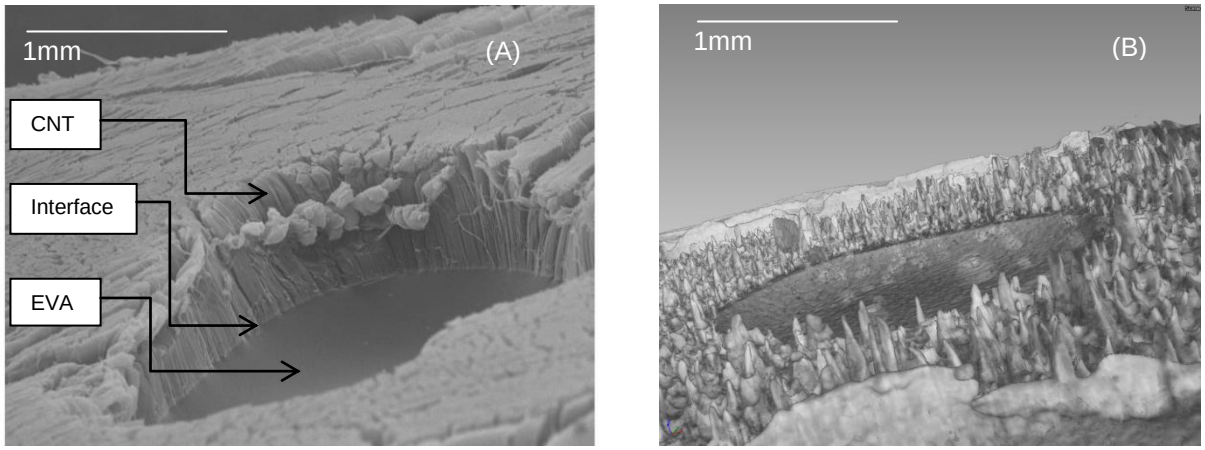

Figure 4. Example images of SEM (A) and µ-CT (B) images of EVA-CNT forest interactions

Figure 4. shows a comparison of an SEM image and a µ-CT scan model of the same partially embedded CNT forest in an EVA layer. It can be seen that a circular gap was present in the centre of this particular CNT forest owing to contamination of the catalyst during the CVD

process; however such a sample provides a helpful comparison site when comparing images and also reveals the CNT-EVA interface. Optical microscopy provides little help when trying to understand the degree of wetting in such samples, despite their millimetre scale, as the CNTs absorb almost all visible radiation [18] thus characterisation of the forest is difficult. Consequently SEM is often used when investigating forest structures and in this case wetting and provides a topographic image of the composite structure. SEM analysis allows confirmation of the CNT forest alignment after embedding, as well as a view of the CNT-EVA interface. Using SEM, detailed observation of the micro structure and wetting process is difficult as observations are only possible at the surface of the sample. In an attempt to understand the wetting process in more detail μ-CT was used to investigate capillary processes inside the forest structure. Looking at several samples produced in a similar fashion we consistently see the same result as shown in Figure 5. To assist in understanding these results, scans were also performed on as grown CNT forests and it was found that the forest could not be detected using the μ-CT process used in this study. This could be due to the low density of CNT inside the forest structure, 1 vol%, causing little effect on the attenuation of the incident x-rays when compared to the surrounding atmosphere. Thus it is proposed that the CT model represents the capillary driven wetting mechanism as the molten EVA enters the CNT forest. The models show a spiky surface where the CNT and EVA interact, and it appears that the EVA is being drawn into the forest in channels. As the scanner was unable to detect pure CNT it is not possible to know the exact location of the CNT within the structure, but comparisons with SEM images indicate that from the outside the structure of the forest appears unaffected. Using the VGStudio package it is possible to look at individual slices from the 3-D model thus allowing further investigation of the observed peaks. It appears that the peaks are fairly uniform in terms of cross sectional area although though some larger peaks and ridges are also present. By comparing data from several samples we observe that the average peak diameter is of the order of ~ 120 ± 60 μm, as calculated from multiple individual slices.

3.2 Discussion

Micro CT analysis of partially wetted CNT forests using EVA has illustrated that the capillary driven wetting process in CNT forests is a complex procedure. It appears that the polymer forms ‘channels’ of movement into the forest structure during capillary wetting. The difficulty in identifying the location of the CNTs within the structure hinders a full understanding of the process. Speculatively it is possible that the CNT are agglomerating as the polymer wicks into the structure although no evidence of such a mechanism can be seen from the SEM analysis and the outer surfaces of the forest appear uniform. Alternatively it may be that the axial nature of the structure may favour wetting in the vertical direction as opposed to isotropic porous structures where wetting spreads uniformly in all direction. As a result the polymer maybe inhibited from entering some areas of the forest due to defects that may have formed in the outer ‘crust’ edge of the forest structure [18] and spread slower in the horizontal direction leaving the forest structure mainly unaffected. Furthermore the effect may be a result of the high molecular weight of the EVA molecules or possible molecular effects that occur between individual molecules and the CNTs.

4 Conclusions

Investigations were undertaken into wetting mechanisms of CNT forests with polymers. We apply a simple dynamic wetting model based on the Lucas-Washburn equation and the nano dimensions of as grown CNT forest structures. Results show that wetting in CNT forest

structures should be very slow owing to the viscous drag created by the nanoscale of the structure. Contrastingly experimental observations have seen the total wetting of CNT forests of around 1 mm in height in times of less than 1 second through capillary action using low viscosity resins. Practical investigations of CNT forest wetting on the micro scale were conducted through μ-CT analysis of CNT forests that were partially embedded in EVA layers through capillary driven wetting. Observations show the formation of peaks of polymer being drawn into the forest structure that have diameters of the order of 120 μm and similar cross sectional areas although with irregular perimeters. The wetting mechanisms occurring in CNT forests is clearly a complicated process and it is proposed that the formation of these peak like structures aids the wetting process and begins to explain the unexpected high speed of capillary driven wetting observed in CNT forests. Such results are important in the development of multi layer CNT composite structures where accurate control of forest wetting is desirable to make large bulk structures with micro structured nano reinforcement, where alignment and dispersion are retained.

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