

MEASUREMENT OF NANOPARTICLE DISTRIBUTION IN COMPOSITE LAMINATES PRODUCED BY RESIN TRANSFER MOLDING

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Abstract

Particle fillers are often added to a polymer composite matrix to enhance or to add additional properties to the matrix. For example, hard inorganic particles can be added to aid in fracture toughness improvements. Other properties such as the enhancement of mechanical, thermal, electrical and fire resistivity properties of the matrix can also be achieved with the addition of particle fillers. Popular liquid composite molding (LCM) composite manufacturing processes such as resin transfer molding (RTM), are inherently sensitive to particle filtration from the reinforcement fibers and can lead to an inhomogeneous particle distribution.

In this study, composite laminates with a nanoparticle loaded matrix were produced by RTM and their particle distribution was measured, allowing the effect of process parameters to be evaluated. In general, a non-homogenous particle distribution was observed. A high particle concentration was found near the resin inlet and decreased non-linearly with increasing distance from the inlet. The particle concentration retained within the laminate was found to increase with the resin flow time. With sufficient flow time, the injected resin particle concentration was achieved everywhere within the cured laminate.

1. Introduction

Particle fillers are often added to a composite polymer matrix to enhance or give additional properties to the matrix. For example, hard inorganic particles such as alumina or silica can be added to aid in fracture toughness improvements. Other properties, such as the enhancement of mechanical, thermal, electrical and fire resistivity properties of the matrix can also be achieved with particle addition.

In LCM processes, liquid resin is injected into a textile, where afterwards, the resin is cured. An injection of particle filled resin systems into textiles is inherently sensitive to particle filtration. For particle filled resin systems flowing through fiber reinforcement, three possible filtration cases exist:

- 1) **No retention:** Particles flow freely through the fiber reinforcement. Even particle distribution is possible.

- 2) **Deep filtration:** Particles are non-evenly distributed inside the fiber reinforcement. A higher concentration is found at the inlet, and concentration decreases with higher filtration length.
- 3) **Cake filtering:** Particles are hindered and cannot enter the fiber reinforcement. A cake of particles form outside of the preform entry.

Obtaining even particle distribution is important to obtain consistent properties provided by the particle fillers across the laminate. Examination of particle distribution is important to understand if 1) a particular process is suitable, and 2) if process parameters have an influence on how particles are distributed.

Several experimental techniques exist to characterize particle distribution in a composite. Optical techniques are the most commonly employed. Examples include optical microscopy and scanning electron microscopy. The information provided by optical techniques is predominantly at the micro-scale allowing the determination of local particle distribution. i.e., information whether the particles are being retained within fiber tows, outside the fiber tows, or both. However, local particle deposition information can only be obtained from one cross section. In order to provide reliable information about particle distributions, image analysis has to be performed at many locations. Additionally, for small particles such as nanoparticles, their presence can only be identified as a “cloudy” region in an image, giving only qualitative information as to whether or not particles are present at a given location.

Basic SEM examination is done by Reia da Costa et al. for carbon nanofiber (CNF) and carbon nanotube (CNT) loaded epoxy resin flow in composite infusion [1]. Teh et al. use SEM for local examination of micron-sized silica particle fillers in the fracture of epoxy [2]. Extending the optical SEM approach, but providing quantitative analysis of particle distribution is done by Yum et al. [3]. Particle concentration (at local locations) is quantified using an electron probe microanalyzer (EPMA). Elements are mapped with electron beam bombardment and analyzed by superimposing the elemental mapping over top of an optical image. The area fractions of specific elements are then used to determine the concentration of particles. Analysis is performed outside and within fiber tows allowing particle distribution to be quantified. However, as this technique is based on an optical approach, it is subject to aforementioned “local concentration” limitations.

Another approach to gain insight into particle distribution behavior in the fiber reinforcement is to study the physics of deposition by means of particle flow simulations. Hwang et al. examine micro-scale particle deposition in a fiber preform by means of computer simulation [4]. Recent work by Reia da Costa and Skordos involve modeling of carbon nanofiber (CNF) and carbon nanotube (CNT) filled epoxy resin flow during a composite infusion process. Their model is validated by 1-D fluid flow analytical solutions [5]. However, proper insight using simulation approaches requires sufficient simulation validation and therefore, accurate experimental characterization of particle distribution.

Applying an ignition mass loss, or burn off technique, removing the polymer matrix and reinforcement fiber from a composite allows the particle filler concentration to be characterized across the entire laminate length. Lefevre et al. performed such a burn out technique to characterize micro-scale glass beads in PET fiber mat / polyester matrix composites [6].

In this paper, resin transfer molding (RTM) experiments are performed using nanoparticle filled epoxy matrix. After curing, the local distribution is determined by an adapted burn out method characterizing the particle filtration. Using this procedure, the process parameters of

resin flow time and the particle concentration in the matrix resin infused were examined to determine their impact on final particle distribution.

2. Experiments

2.1. Al_2O_3 -epoxy / aramid fiber RTM produced laminates

The produced laminates consisted of layers of 140g/m² twill weave Kevlar 49 fibers. The epoxy resin was Dow D.E.R. 330 resin cured with a cycloaliphatic/aromatic amine hardener (Air products Ancamine 2167). Nanoalumina particles (nominally 20nm) were added to the epoxy matrix by blending together neat resin with a particle filled (40wt%) masterbatch consisting of nanoalumina particles dispersed in the same neat resin. Mixing of the master batch particle dispersion and pure D.E.R. 330 resin was done by using a SpeedMixerTM (SpeedMixer DAC 150.1 FV) at 2500 rpm. For curing, the appropriate stoichiometric amount of the amine hardener (Air Products Ancamine 2167) at 53 g/eq was added using epoxy equivalent weight (EEW) of the various resin blends. Particle concentration in the resin was verified by performing thermal gravimetric analysis (TGA) from resin samples at the injection inlet.

Laminates consisted of 14 layers of the aramid fabric. As the nominal cavity height of the heated RTM tool (Figure 1) used to produce the laminates was 3.3mm, the resulting fiber volume fraction was 41%.



Figure 1. Heated injection test rig used to produce RTM laminates used in this paper.

The heated injection tool was produced by Surface Generation Ltd. (SG) (Lyndon, Oakham, United Kingdom) and consisted of 15 individual sub-surface heaters running on a proportional-integral-derivative (PID) control loop. The total test area provided by the tool injection cavity is 33cm x 55cm. To produce the samples in this paper, the injection area was subdivided into three sections nominally 8cm x 30cm using neoprene “frames” allowing three 8cm x 20cm laminate samples to be produced simultaneously.

Resin infusion into the aramid fibers was carried out at 50°C, with 3bar of injection pressure. After the resin injection was complete, the aramid laminates were cured according to the recommended cure cycle of the epoxy hardener; a first cure was performed in the mold at 80°C for 2 hours, followed by demolding and curing a further 3 hours at 150°C in a forced convection oven.

2.2. Particle burnout procedure

The burn off technique is an adaptation of a conventional matrix burn off usually used to measure the volume fraction of fibers for glass or carbon fiber / epoxy matrix composites (e.g. ASTM D2584 [7]). In this study, the burn off temperature was raised to 1000°C, allowing for the full thermal decomposition of the aramid reinforcement fibers in addition to the epoxy matrix. When inorganic particle fillers are used, the only constituent remaining after the burn off process are the deposited particles. We have found with thermal gravimetric analysis (TGA) that in an oxygen environment, the onset of the epoxy decomposition begins at approximately 300°C. The aramid fiber decomposition begins at around 470°C. With increasing temperature and time, the calcination product of the decomposed epoxy and aramid are completely removed. For sample sizes of nominally 0.3cm x 1cm x 2cm subjected at 1000°C, 3 hours was found to be sufficient to burn away the epoxy matrix and aramid fiber. In addition to the suitability for aramid/epoxy composites, this temperature and method was also found to be sufficient for application to carbon fibers. Although in this study, only the ignition loss of aramid fiber composites is shown.

Sectioning a cured laminate at discrete known locations and then applying the burn off methodology allowed the distribution of particles that result from the manufacturing process to be determined. The sectioned samples were placed in porcelain crucibles with resin and fiber burn out carried out in a high temperature muffle oven (Heraeus Laboratory Muffle oven M 110). Particle content was determined by weighing the samples prior to the burn out process (fibers, matrix, and particles) and after the burn out process (only particles remaining). The sectioned samples were measured using a caliper to a precision of 0.05mm. Sample masses were weighed using a high precision scale (Mettler DeltaRange AE 166) to a precision of 0.0001 grams. To determine the average mass of particles at a given laminate position along the flow direction, a minimum of three side-by-side samples were cut at each length position along the laminate length. By measuring the samples prior to the burn out process, the sample volume could be calculated. The mass % of particles ($\%m_{particles}$) with respect to the resin mass could be calculated from Equation (1).

$$\%m_{particles} = \frac{m_{particles}}{m_{particles} + m_{matrix}} \quad (1)$$

The proportion of the resin weight (particles and matrix) is determined by removing the fiber contribution to the overall sample mass (Equation (2)), assuming that the laminates were void-free:

$$m_{particles} + m_{matrix} = m_{sample} - (V_{fiber} \cdot V_{sample} \cdot \rho_{fibers}) \quad (2)$$

The ratio of remaining particles to the resin mass in the composite can then be calculated from the overall sample mass and the overall sample volume by combining Equation (1) and Equation (2); where $m_{particles}$, m_{matrix} , m_{sample} are the mass of the particles, matrix and the overall composite sample respectively, V_{sample} is the overall volume of the sample being burned out, V_{fiber} is the volume fraction of fiber (calculated from sample volume, fiber area weight, and fiber density), and ρ_{fibers} is the density of the fibers.

Particle concentrations in the epoxy resin at the injection inlet was determined by performing TGA on resin samples entering the laminate.

3. Results and Discussion

The burn out procedure was performed on the produced laminates to evaluate the effect of following parameters on the final particle distribution:

- Saturated flow time, i.e. the change of particle distribution with time
- Particle concentration (loading) in resin

3.1. Effect of resin flow time / volume

Characterization of particle distribution changes with injection time is an important consideration for part size scale-up; i.e. relevant in the production of large composite structures that could be meters in length. To demonstrate the effect of the resin flow time (or the overall volume of resin that is passed through a laminate) on the particle retention, a series of laminates were produced varying the total amount of volumes of resin flow. Applying the same injection pressure, this was achieved by varying the resin infusion time.

Each laminate was fully infused, with the amount of excess resin passing out of the laminate until the resin outlet ports were blocked off prior to curing being varied. The amount of resin overflows examined were approximately 5, 30, and 50% of the available porous space within the laminate samples. For the 20cm long, 8cm wide, nominally 3.3mm thick laminates this equated to about 2, 10, and 20g of resin overflow respectively. The aramid laminates were impregnated with 6.5wt% nanoalumina loaded resin (verified with TGA analysis of inlet resin).

As shown in Figure 2, a non-uniform particle distribution was observed, with the highest particle retention occurring near the resin inlet and decreasing with increasing distance from the inlet. So long as the resin continues to flow with the same conditions, with increasing resin infusion time, it was observed that the local particle concentration in the laminate increased. Examining the samples from positions near the outlet, in the tests with 5 and 30% overflow, it was observed that the particle concentration are below that of the inlet resin concentration (measured by TGA). However, as the retention of particles increased with time, in the sample with 50% overflow the minimum concentration is higher than the particle concentration of the injected resin. Therefore, although particle filtration was present, a desired minimum amount of particle fillers was achieved across the entire length of a laminate

in our setup; although the amount of resin volume (and the excess resin waste) required to do so must be considered.

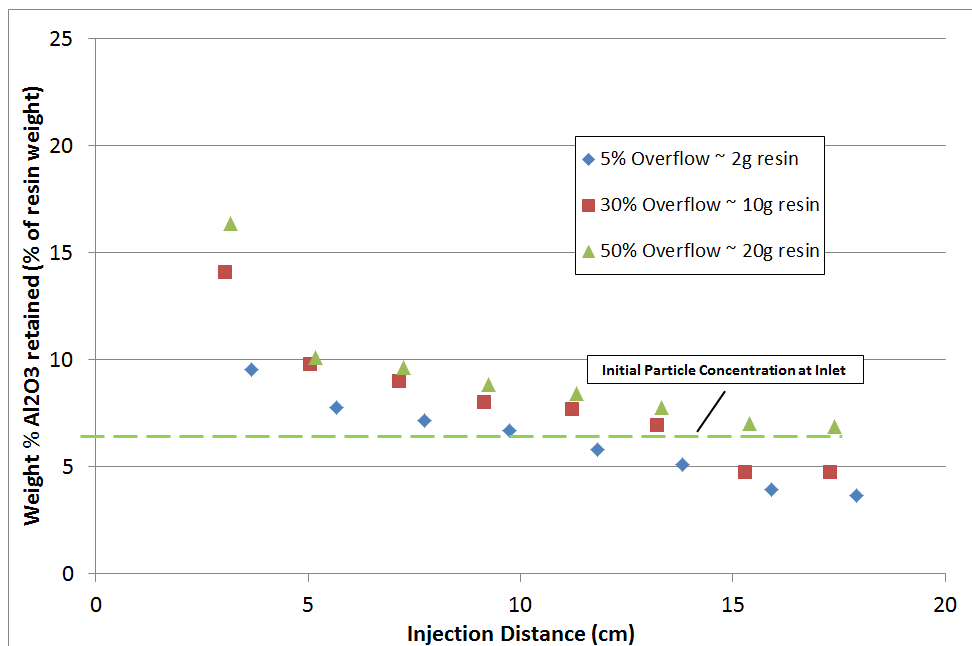


Figure 2. Particle distribution in RTM produced nanoalumina-epoxy / aramid laminates. All samples were injected at the same temperature and resin pressure. The resin volume passed through each sample was altered by controlling the resin flow time. Excess resin is represented as overflow.

3.2. Effect of particle concentration in resin

To evaluate the effect of particle loading (concentration), laminates of the same fiber volume content, and therefore porosity, were infused with resins of different particle loadings. The aim was to evaluate whether a lower particle concentration in the resin is less sensitive to particle clogging and filtration; thus to see if the deep filtration case observed in Figure 3 could be improved. To test this, the laminates were infused with 6.5wt% and 3.1wt% (slightly less than $\frac{1}{2}$ the concentration) nanoalumina addition. The filtration effects are shown in Figure 3. The infusions were repeated in each case, and showed similar results.

All laminates were infused with the same volume of resin by restricting the laminates to the same overflow conditions (50% excess resin overflow, or ~ 20g of resin). With the controlled conditions, reducing the particle concentration from 6.5wt% to 3.1wt% nanoalumina still resulted in a similar deep filtration effect. Examining the mass retained along the laminate length, as indicated in Figure 3, it can be seen that reducing the particle concentration resulted in approximately almost one half the mass of particles retained, which is appropriate considering the mass balance (volume and particle concentration). This result, combined with similar filtration curves observed between the two particle concentration conditions, indicate that in this case (under these specific conditions of fiber textile, fiber volume, etc.), lower particle concentration did not reduce particle clogging within the preform. Therefore, it appears that at dilute particle resin concentrations, the clogging/filtering mechanisms are independent of particle concentration in the infused resin.

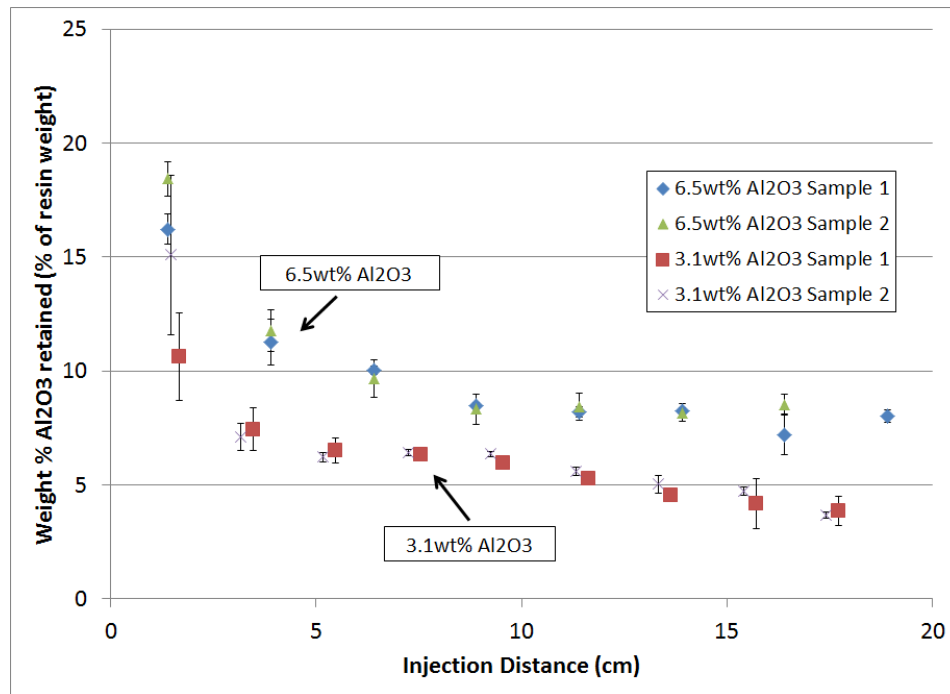


Figure 3. Particle distribution in RTM produced nanoalumina-epoxy / aramid laminates. All samples were injected at the same temperature and resin pressure. The resin concentration injected into the laminates differed at 3.1% and 6.5%

4. Conclusions

For the characterization of the RTM process shown in this paper, particle distribution of infused nanoalumina particles into twill weave aramid fibers was found to be non-uniform along the laminate length. In general, the concentration of alumina particles was observed to decrease across the laminate length in a non-linear manner.

Concerning our experimental setup, the RTM process variables examined and the textiles investigated, the following conclusions can be made:

- The concentration of particles retained in the laminate increased with resin flow time (more mass flow), with sufficient flow time of excess resin, an overall concentration could be achieved which is higher than the concentration of particles of the injected resin
- A reduction of particle concentration in the injected matrix resin did not improve filtration sensitivity

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