

EXPERIMENTAL ANALYSIS OF THE FILTRATION OF PARTICLES DURING THE LIQUID COMPOSITE MOLDING PROCESS USING AN ELECTRON PROBE MICRO ANALYZER

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Abstract

Advanced composite materials developed by adding filler particles to fiber-reinforced composite materials, filtration phenomena can occur between the fiber strands during impregnation stage. In order to investigate the mechanisms of filtration, a microscopic means of measuring the particle content in a cured composite part using an electron probe micro analyzer (EPMA) is proposed in this study. The concentrations of nano-sized and micro-sized particles of a spherical shape and of high aspect ratios were measured in the intra-tow region and the inter-tow region of fibrous media separately. The distributions of filler particles in cured composite parts showed different aspects according to the sizes or shapes of particles and process conditions.

1 Introduction

Advanced composite materials developed by the addition of filler particles into the matrix of composite materials have been expected to be improved in mechanical or conductive properties. And some functional particles are applied to conventional composite materials in order to introduce new functions such as self-healing [1] or photovoltaic effect [2]. Carbon nanotubes (CNTs) have received wide attention as filler particles due to their remarkable mechanical properties [3], thermal conductivity and electrical conductivity [4, 5]. And the improvements in the properties in CNT-reinforced composite materials have been reported by many investigators [6, 7].

When the filler particles are added to a fiber-reinforced composite material, the filtration phenomenon can occur during the impregnation stage in the liquid composite molding (LCM) process such as the resin transfer molding (RTM) process. The particles are filtered between the fiber tow by physical capturing, electrostatic force or the Van der Waals' force between the particles and the fiber walls. The filtered particles may cause the problems such as decrease in permeability, increase in mold filling time, void formation and the non-uniform distribution of the material properties or of the new functions. Therefore, it is important to understand the mechanisms of filtration phenomena and the critical parameters affecting

filtration aspects. To do this, a proper method for measuring the concentrations of filler particles in the composite product is essential.

Experimental investigations on the filtration of the particle-suspended resin in fibrous media during the manufacturing of composite materials have been reported. Chohra et al. [8] proposed a filtration model considering sieve mechanism in multiple fabric layers. In the experimental study to validate the model, they used microparticles and dual-scale woven fiber mats and suspension was injected along the thickness direction of fiber mats. The particle amount filtrated on each layer was measured by rinsing each mat and collecting the particles. Nordlund et al. [9] investigated the filtration phenomena using microscopic imaging and micro-particle image velocimetry (micro-PIV). They used a colorless glycerol/water mixture and fluorescent micron-scale particles to enable the measurements. In above studies, liquid suspensions rather than cured parts were analyzed, and some limitations on the material of fluid or the size of particles existed.

In the experimental research of Lefevre et al. [10, 11], in order to measure the particle distributions in cured final parts, they used burn-off test. Samples were cut from the cured part and the matrix and fibers of each sample were eliminated by sample calcinations, so the mass of remained particles could be measured. They used synthetic PET fibers as reinforcements, because they could be eliminated completely by calcinations. Glass micro beads were used as filler particles and collected to be measured at the end of this process. However the nanoparticles are difficult to be collected and measured by this method and some limitations on the materials likewise.

In the present research, a new method to measure the particle concentration in final cured composite parts using an electron probe micro analyzer (EPMA) is proposed. The measurements were done for nanoparticles as well as microparticles, both in the intra-tow region and in the inter-tow region separately. Few limitations were put on choosing the materials of matrix and fibers.

It is difficult to measure the CNTs concentrations in polymer-based composite materials because carbon element composes polymer material mostly. Hence, CNTs cannot be collected or detected from the final product. We introduced CNT-silver particles in which silver nanoparticles are chemically bonded on the walls of CNTs. The silver nanoparticles served as tracers to detect the CNTs using an EPMA device.

2 Experimental details

2.1 Materials

The epoxy system consisted of bisphenol-A-type resin and an amine-type hardener (KFR-130/KFH-140, Kukdo Chemical, Korea) and the viscosity of their mixture was 300cps at room temperature. Spherical titanium dioxide particles of nano and micro scale (Alfa Aesar, USA) are used as spherical particles, and CNT-silver particles were used as the filler particles of high aspect ratio. The CNT-silver particles consist of multi-walled CNTs of the diameters from 10 to 15nm and of the lengths from 10 to 20 μ m. Silver nanoparticles have the diameters of 30nm in average and they are chemically bonded to the CNTs (Bioneer HQ, Korea). The mass ratio of CNT to silver is 30:70. The filler particles are shown in Fig. 1, and their features are listed in Table 1.

As fiber reinforcement, dual-scale mats of glass fiber of unidirection orientation (Han Kuk Fiber, Korea & Owens Corning, USA) were arranged in the mold to be parallel or normal to suspension flow. The flow channels of the fibrous media are classified into two categories: the inter-tow region and the intra-tow region. The channels of the inter-tow region have hundreds of micron scale and those of the intra-tow region do the scale of several micron.

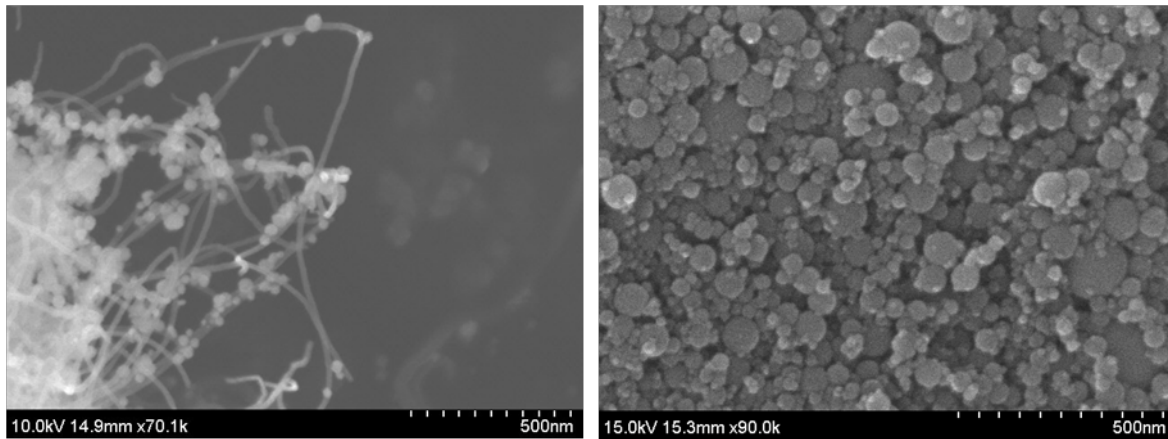


Figure 1. FE-SEM images of (a) CNT-silver particles and (b) TiO₂ particles of 32nm diameter in average.

Filler Particle	Composition	Form	Diameter	Length
Titanium dioxide	TiO ₂	Sphere	32nm	
Titanium dioxide	TiO ₂	Sphere	1μm	
CNT-silver	C	Nanotube	10~15nm	10~20μm
	Ag	Sphere	30nm	

Table 1. Features of filler particles

2.2 Dispersion process

Dispersion of filler particles in liquid resin was conducted by solvent method. Acetone for TiO₂ particles and IPA for CNT-silver particles were used to dilute the epoxy resin. Then the filler particles were dispersed in the resin using a tip-type ultrasonicator device (CV 505 power supply and a CV 33 convertor, Sonics & Materials, Inc., USA). The solvent in the suspension was then evaporated by heating in a bath-type ultrasonicator (SD-D300H SeongDong, Korea) to maintain the dispersion state. Finally convection oven and were used to eliminate the solvent completely.

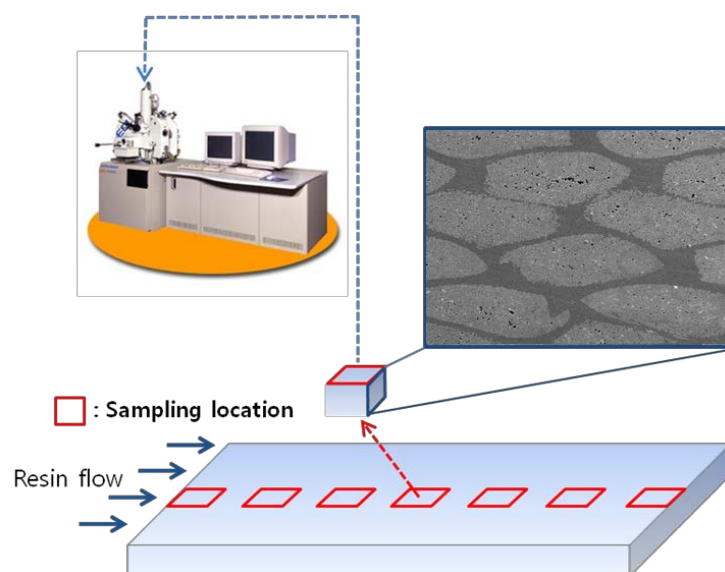


Figure 2. Scheme for measuring the particle concentrations on the cross-section of the composite parts using the EPMA device.

2.3 Resin transfer molding process

The particle-suspended resin was mixed with hardener and put into a vacuum chamber for 20 minutes to eliminate air voids. The suspension was injected into a mold filled with the glass fiber under a constant pressure. After filling was completed, the mold was put in a convection oven for resin polymerization.

2.4 Measurement by an electron probe micro analyzer

Seven samples were cut along the direction of resin injection. The samples were then mounted inside transparent epoxy. Grinding and polishing were done successively by SiC papers of 800 to 4000 grit and diamond pastes of 3 μ m and 1 μ m (Struers, Denmark) for measurement by the EPMA. Quantitative analyses were conducted using an electron beam ranging from 1 μ m to 300 μ m on the cross-sections of the samples (Fig. 2).

3 Results and discussions

3.1 Distributions of the TiO₂ particles in the cured parts

The distributions of the filler particles in the fiber-reinforced composite materials were found and investigated. The first point in the figure represents the initial concentration of filler particles at the entrance of the fibrous media. The value was smaller than the actual content of the filler particles. It resulted from the incomplete dispersion of filler particles in the polymer matrix; in other words, agglomerated particles existed sparsely among the materials and were not accounted for by the EPMA measurements.

When TiO₂ particles of 32nm in diameter were used as filler particles, concentration values of seven locations along the resin flow and of two different fibrous regions were plotted as shown in Fig. 3. The concentration values showed nearly the same in every location and in both regions. It is expected that very little physical capturing could happen because the scale of the filler particles was much smaller than that of the flow channels between fiber strands. Electrostatic or chemical attraction forces might affect the filtration phenomena but the hydrodynamic drag force of resin flow on particles was dominant in the condition of this study.

When TiO₂ particles of 1 μ m in diameter were used, the results were shown in Fig. 4. The particle concentrations in the inter-tow region were nearly identical through the whole composite part like the case of nanoparticles. The concentrations in the intra-tow region showed some variations and were slightly higher than those in the inter-tow region. This attributes to the filtration of the microparticles inside the fiber tow.

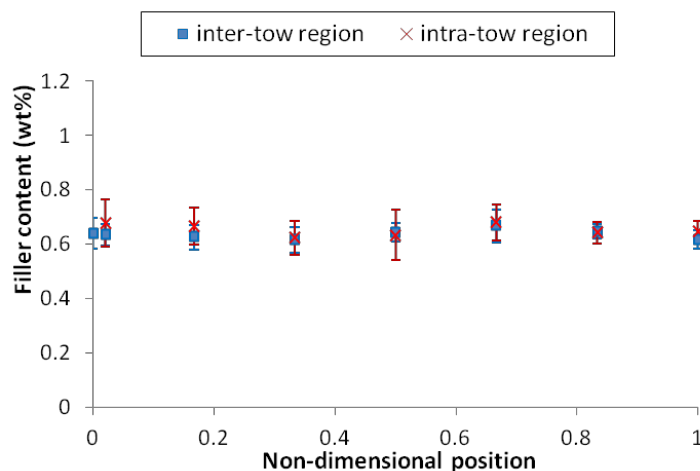


Figure 3. The concentrations of TiO₂ particles of 32nm in diameter with initial concentration of 1wt%, fiber volume fraction of 0.3, injection pressure of 1atm.

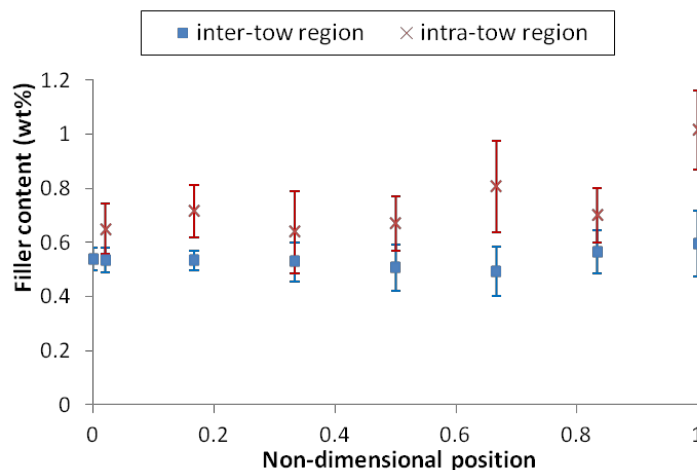


Figure 4. The concentrations of TiO₂ particles of 1 μ m in diameter with initial concentration of 1wt%, fiber volume fraction of 0.3, injection pressure of 1atm.

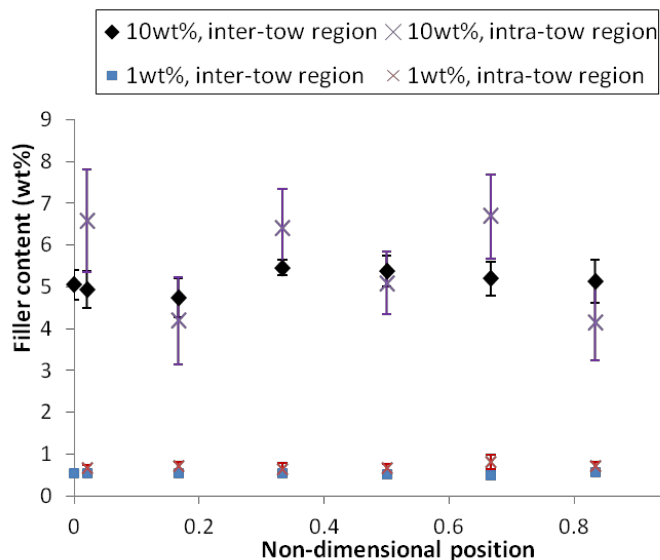


Figure 5. The concentrations of TiO₂ particles of 1 μ m in diameter with initial concentration of 10wt% and 1wt% respectively, fiber volume fraction of 0.3, injection pressure of 1atm.

Fig. 5 compares the results of different initial concentration. The values in the intra-tow region when the initial concentration was 10wt% had considerable variation up and down due to active filtration of many particles. The concentrations in the inter-tow region were uniform like previous cases.

3.2 Distributions of CNT-silver particles in the cured parts

The results when CNT-silver particles were used as filler particles in Fig. 6-8. When the dispersion time was 7 hours, the concentrations in the inter-tow region increased along the resin flow direction and those in the intra-tow region showed quite lower values as shown in Fig. 6. It is because the agglomerate particles could not readily penetrate into the fiber tow and they joined the resin flow in the inter-tow region to contribute to the increase in the concentrations in that region.

In the composite parts produced by 20 hours of dispersion process, on the other hand, the number of well-dispersed particles increased, so the concentrations in the intra-tow region also increased compared to those in the case of 7 hours dispersion (Fig. 7).

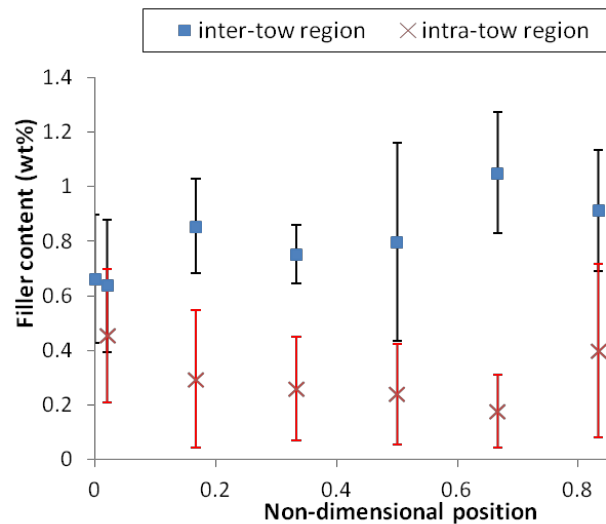


Figure 6. The concentrations of CNT-silver particles with initial concentration of 1wt%, fiber volume fraction of 0.3, injection pressure of 1 atm, dispersion process of 7 hours.

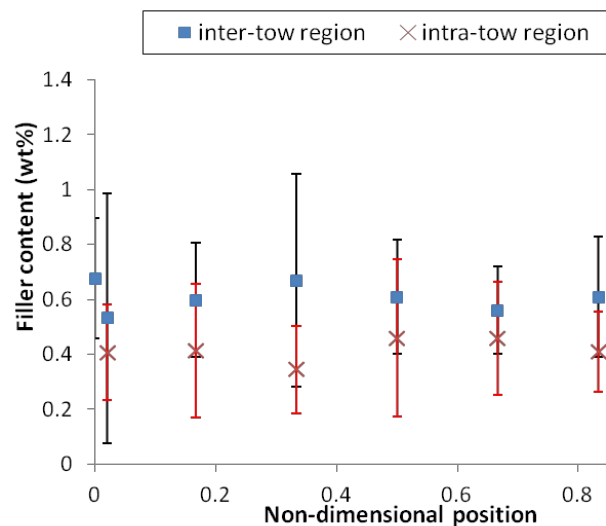


Figure 7. The concentrations of CNT-silver particles with initial concentration of 1wt%, fiber volume fraction of 0.3, injection pressure of 1 atm, dispersion process of 20 hours.

However, they were still lower than values in the inter-tow region slightly because some particles might be filtrated at the interface of fiber tow. Particle distribution in the inter-tow region had nearly the same values in the whole part.

Fig. 8 shows the results when fiber volume fraction was 50%. A lot of fiber tows in the mold compressed by each other, CNT-silver particles might have difficulty in penetrating into the tow. Nonetheless, higher concentrations than those in the case of 30% volume fraction were measured in the intra-tow region. It might be due to active filtration in narrow channels of that region.

4 Conclusions

Filtration phenomena occur when particle-suspended resin flows into fibrous media during the LCM process. To investigate the filtration aspects, a new method to measure the concentration of filler particles in a cured composite part was proposed. Quantitative elemental analyses using EPMA device enabled microscopic measurements of the concentrations both

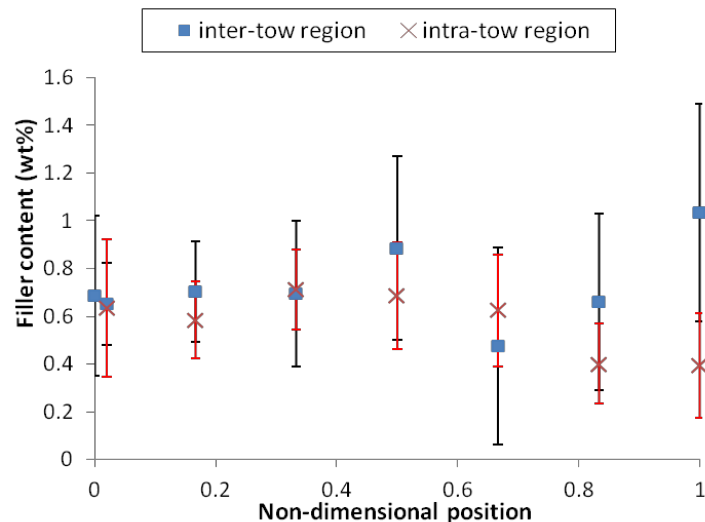


Figure 8. The concentrations of CNT-silver particles with initial concentration of 1wt%, fiber volume fraction of 0.5, injection pressure of 2 atm, dispersion process of 20 hours.

of nano-sized and micro-sized particles. Introduction of CNT-silver particles made it possible to measure the distribution of particles of high aspect ratios like CNTs. It has been hard to measure CNTs in the polymer matrix because polymer is mainly composed of carbon element. With the proposed method, the distributions of filler particles could be obtained in the inter-tow region and in the intra-tow region separately.

It was found that nano-sized TiO_2 particles could move freely in both regions, so they showed almost uniform distribution through the whole part. When the micro-sized TiO_2 particles were added, the concentration values in the intra-tow region varied according to the process conditions like particle size and initial concentration while those in inter-tow region were quite uniform. When the CNT-silver particles which have the high aspect ratio were used as fillers, they could not enter the intra-tow region easily compared to spherical particles so the concentrations in that region varied considerably according to the conditions such as dispersion process time and fiber volume fraction. Particles that did not enter the fiber tow increased concentrations in the inter-tow region along the direction of the resin flow in some cases.

It is expected that specific mechanisms and the effects of parameters of the manufacturing process on particle filtration can be investigated using the proposed measurement technique.

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