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In situ assessment of carbon nanotube flow and filtration monitoring through glass fabric using electrical resistance measurement

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ABSTRACT

Filtration of nanofillers into porous fabric media is still an issue during the preparation of advanced fiber-reinforced composites. The assessment of resin/multiwall carbon nanotube (MWCNT) flow, MWCNT filtration, and the cure monitoring of glass fiber/carbon nanotube-polyester composites by means of the measurement of the electrical resistance was introduced. The vacuum-assisted resin transfer molding technique was used. The electrical resistances measured over the span of a composite were qualitatively correlated with MWCNT flow and the degree of MWCNT filtration. It was found that while the complexity of the fabrics could likely introduce preferential deposition of MWCNTs, their filtration is mainly affected by their dispersion state in the resin suspension. Relationships among critical parameters such as the lengths and diameters of MWCNTs, the inter- and intra-tow dimensions of glass fabrics, the dispersion level of MWCNTs, and the viscosity of nanocomposite samples are discussed and correlated to the filtration, cure, and flow phenomena. We showed that our method can also serve as an early warning to obviate defects in the resulting composite.

1. Introduction

Glass fiber is one of the most attractive plastic reinforcement materials today, primarily because of its unrivalled performance-to-cost ratio. In order to take greater advantage of the cost-effectiveness of glass-fiber-reinforced plastics (GFRPs), many researchers [1,2] have tried to broaden the application fields of these composites by engineering conductive GFRPs with the aid of conductive nanomaterials, such as carbon nanotubes (CNTs), exfoliated graphite nanoplatelets (xGnPs) and graphene. This resulted in multiscale composites with improved mechanical, electrical, and thermal properties. As such, GFRP can be regarded as a multifunctional material which can be simultaneously used for structure electromagnetic interference shielding, self-sensing applications [3], etc. One of the most traditional manufacturing methods of these multiscale composites involves carbon nanomaterials (CNMs) first being "pre-dispersed" in the resin, and subsequently incorporated within the microscale fiber reinforcements for composite fabrication. In so doing, CNMs/resin nanocomposites are therefore distributed throughout the composite volume, filling up the porous glass fabric. The efficiency to transfer the properties of nanoreinforcements to a macroscale FRP relies on the ability to disperse and distribute them effectively in the host matrix, as well as to ensure a good distribution in the fabric [4–8]. Nanoreinforcements in their manufactured state tend to cluster together in any suspension due to the strong van der Waals forces. Shear mixing, such as three-roll milling, dissolver disk, planetary mixing, and ultrasonic processing, or a combination of these, have been used to disperse nanofillers in a polymer resin with varying degrees of success [9–12]. Ultrasonication often causes damage to nanofillers, resulting in the reduction of their aspect ratio and altering the final nanoreinforced polymer. Three-roll milling has recently provided good results for nanoreinforcement dispersion [13]. It exerts shear forces over the particles and avoids the presence of compression forces during the process. In this way, the agglomerated nanofillers can be separated without being damaged, provided that the processing parameters, such as gaps between rolls, roll speeds, and the number of passes, are optimized for each specific type of nanofiller.

The flow channels inside the fibrous media can be classified into two categories: inter-tow and intra-tow regions. The channel width of the inter-tow region may be up to several hundreds of microns, while that of the intra-tow region is several microns or nanometer-scale. When nanofiller agglomerates are larger than

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the gaps, fabrics tend to introduce a filtering effect, where nanofillers may block these porous gaps, leading to a very slow and even insufficient nanocomposite impregnation. This phenomenon is most prominent around the inlet, while the rest of the composite part tends to lack nanofillers even for well-dispersed resins or suspensions.

In general, filler size and fibrous pore size dictate the flow of a particle in a fibrous medium. As the resin is forced to flow through the porous medium, three cases can be experimentally observed; these are depicted in Fig. 1. If particles are very small compared with the pore size, the suspension flows through the medium easily, and, therefore, there is no or very little retention (Fig. 1 (a)). If the particle size is larger than a critical size that depends on the porous medium characteristics, the particles will accumulate on the medium and form a "cake," leading to a *cake filtration* [5] (Fig. 1(b)). If the suspension flows within the medium but the medium progressively captures the particles (retention), we will have a *deep bed filtration*. This occurs when some particle sizes, but not all, are greater than the pore size (Fig. 1(c)). In some cases, the amount of retained particles is such that the network is clogged-up. Retention is the case that is most likely to happen in industrial applications. Filler retention and filtration results in inhomogeneous filler content, leading to defective composite parts with non-uniform properties. In the most severe conditions, when the use of high-fiber content fabrics or high filler content is necessary, mold filling becomes difficult or hindered.

Recognizing the difficulty in experimentally evaluating the aforementioned filtration phenomenon, many filtration models [14–19] were developed to simulate and predict the particle flow behavior, but these models suffer from precision, and are often much too subjective. The few experimental works [5,20–22] available rely on tools such as visual flow front distance assessment or composite cross-section observations, which require that the composites be destroyed. To meet the demand for high-performance multiscale composites, it is important to develop a nondestructive experimental method for evaluating the impregnation state of a large-scale dimension composite, both on the surface and throughout its thickness simultaneously.

For CNTs in particular, it has been exceedingly difficult to observe filtration phenomena experimentally, because CNTs are made up of carbon atoms, which are the constituents of most polymer resins. Therefore, when CNTs are added as filler particles in the polymer matrix, elemental analysis cannot distinguish between the two components. Yum et al. [21] recently added silver to CNT, and used an electron probe microanalyzer. They successfully performed quantitative and qualitative analysis to assess particle distribution. Unfortunately, this is possible only for micro-medium composites, and again requires that the composite be shattered. Some researchers [5,20] have also investigated CNT filtration phenomena in fibrous media using SEM and TEM, but these methods only provide qualitative information, rather than evaluating the part as a whole.

In this work, we seek to introduce a novel approach for the process monitoring of glass fiber/multiwall carbon nanotube (MWCNT)-unsaturated polyester (UPE) composites using a percolated MWCNT conductive network. A systematic MWCNT dispersion route using a three-roll mill is followed. Parametric studies and their interaction, involving resin viscosity, MWCNT type, concentration, and degree of MWCNT dispersion, were investigated to discover which state minimizes MWCNT filtration. The filtration level was characterized *in situ* by monitoring the change in electrical resistance of the glass fibers during infusion. Concomitantly, flow and cure monitoring of the nanocomposite resins were also assessed *in situ*.

2. Materials and methods

2.1. Materials

Chemical vapor deposition-grown multi-walled carbon nanotubes (MWCNTs) were purchased from Hanwha Nanotech (Incheon, Korea). The supplier cited a purity of >95% (Fig. 2 (a) and (b)), a 5–10 nm inner diameter, a 60–100 nm outer diameter, and two different lengths: 100 μm (CM-100) and 250 μm (CM-250). Microstructural analyses performed on about 20 nanotubes confirmed the effective inner diameter is in the range of 5–10 nm. However, the outer diameter appeared to be thinner (10–50 nm), as shown by the high-resolution transmission electron microscopy (HR-TEM) and scanning electron microscope (SEM)

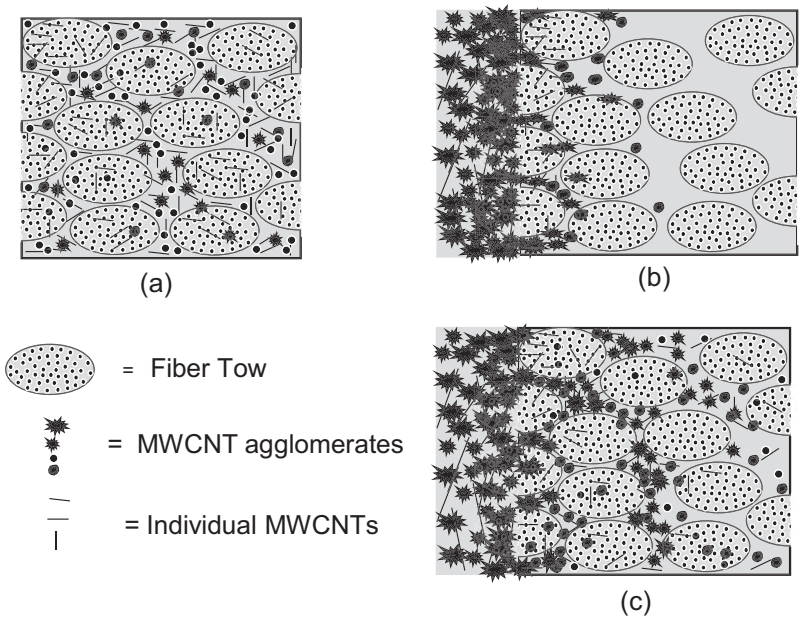

Fig. 1. Illustration of filtration cases: (a) particles are very small compared with the pore size, (b) particle size is larger than the pore size, and (c) intermediate case.