

DEVELOPMENT OF THE DISPLACED FOAM DISPERSION TECHNIQUE FOR THE MANUFACTURE OF MULTISCALE COMPOSITES

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1.0 Introduction

Over the past five decades, the utilization of advanced composites has shown increasing promise with their well documented advantages of high stiffness to weight ratios, corrosion resistance, and functional integration. As such, the market share of structural composites has continued to experience exponential growth. Traditional fiber reinforced composites (FRCs) have matured with respect to their material properties. For instance, their in-plane, fiber-dominant properties make them highly desirable compared to metals, but their through-thickness or z-axis properties are matrix-dominant and, thus, have limited their use. [1-2].

Researchers have worked on improving the through-thickness properties of composites by introducing nanomaterials to manufacture multiscale composites. This has also allowed for multifunctionality in composite structures.

2.0 Manufacture of Multiscale Composites

2.1 Current Processes

FRCs have found extensive use in aerospace, automotive, construction, recreational equipment and industrial sectors but their previously stated limitations have prohibited them from reaching their full potential [**Error! Reference source not found.**]. The incorporation of nanoparticles in polymers opens a new prototype where polymer matrices can be tailored to optimize specific properties, just as fiber orientation is used to optimize conventional advanced composites. For instance, nanoparticles such as carbon nanofibers (CNFs) and carbon nanotubes (CNTs) have been recognized as promising nanoconstituents in polymer nanocomposites (PNCs). This is because CNFs and CNTs possess excellent electrical,

thermal, and mechanical properties [**Error! Reference source not found.**].

Some of the more widely used methods for manufacturing conventional composite parts are wet lay-up, pultrusion, resin transfer molding (RTM), and vacuum assisted resin transfer molding (VaRTM). Others include autoclave processing, resin film infusion (RFI), prepreg method, filament winding, and fiber placement technology [5].

Multiscale composites, especially with the use of carbon nanotubes (CNTs), have yielded enhanced structural (through thickness) properties, and increased electrical and thermal conductivities. The manufacturing of such composite structures have however proved difficult or cumbersome, primarily because the introduction of CNTs increases the viscosity of the resins. The current processes through which CNTs are integrated are time consuming, can be hazardous, and often require a high technical knowledge/skill level, limiting the number of qualified handlers. This in turn can hinder and slow, productivity. Additionally, the processes may yield undesirable results; for example, voids weaken areas of the composite; filtration impedes the complete impregnation of CNTs within the desired part; and non-uniform dispersion gives way to a variation in the material properties over the area of the composite. This makes laminate manufacture through resin infusion, difficult with many researchers resorting to open mold techniques. Moreover, current techniques mostly result in the application of CNTs throughout the entire laminates, rather than in selected areas. Subsequently, one of the main barriers, to the widespread use of CNT applied composites, is an efficient mass-producible manufacturing process. In this paper the novel

Displaced Foam Dispersion (DFD) technique will address some of these issues.

2.1.1 Nanocomposites and Multiscale Composites

Researchers using CNFs and CNTs in the manufacture of polymer nanocomposites (PNCs) have reported mechanical, electrical, and thermal property enhancements which result from the synergy of the matrix and the nanoparticles [6]. Studies have shown that chemically modifying the surfaces of nanoparticles helps them disperse better in polymer matrices and results in improved physical properties [7]. Thus, enhancing the PNC matrix properties should lead to property enhancements in the FRC system and result in a composite with the potential to perform in a multifunctional capacity. Modifying the fiber reinforcement constituent within a FRC system by grafting [8] or electrophoretically depositing [9] nanoparticles onto the fiber can serve as another way to develop multifunctional composites. Thus, multi-scale fiber reinforced composites (M-FRCs) can be manufactured by either modifying the resin matrix or fiber reinforcement. Qiu et al. [9] studied CNT-Glass-epoxy multiscale composites, and reported a 27% increase in tensile modulus, and 16% increase in tensile strength, based on 1 wt% functionalized CNT inclusions. In studies that have modified the fiber reinforcement, researchers have also reported improved mechanical and thermomechanical properties [10]. Bekyarova et al. [4] studied the effect of electrophoretically dispersing (EPD) 0.25 wt% functionalized CNTs onto carbon fiber preforms followed by fabrication of M-FRCs using the VARTM process. They observed a 27% enhancement in interlaminar shear strength (ILSS). The mechanical property enhancements were attributed to the use of functionalized CNTs which enhanced their dispersion, and improved the CNT-polymer matrix interfacial bonding. In a study investigating the dimensional stability of epoxy/CNT/glass-fiber M-FRC, other researchers reported that their 1 wt% MFRC sample exhibited a 25% reduction in coefficient of thermal expansion (CTE) relative to their neat sample [4]. The CTE reduction was suggestive of well dispersed CNTs throughout the matrix of the M-FRC. In the same research they reported an 11°C reduction in the glass transition temperature (T_g) of their 1 wt% M-FRC

sample relative to the neat FRC sample [9]. The T_g reduction was suggestive that the cross link density decreases due to interference of the functional groups on the CNTs during curing. As a result, the presence of the functionalized CNTs disrupts the optimized epoxy resin-curing agent ratio in the curing reaction.

2.1.2 Problems Currently Existing in the Manufacture of Multi-Scale Composites

A major barrier to the widespread use of composites is the inability to efficiently mass produce them. The incorporation of carbon nanotubes which have been reported to improve the mechanical, thermal, and electrical properties of resin systems [1, 2], further complicates the problem. Two main issues need to be addressed to effectively improve the material properties of polymers when adding carbon nanotubes as filler constituents. These issues are the interfacial bonding, and the proper dispersion of the individual CNTs in the polymeric matrix. Investigations focusing on the interfacial bonding have been performed by Wagner and colleagues [8]. They performed pull-out tests of individual carbon nanotubes embedded in a polymer matrix to evaluate the interfacial shear strength of the nanotube polymer system. The interfacial adhesion to the polymer can be enhanced by chemical functionalization of the nanotube surface. Molecular dynamics simulations by Gates et al. [11] predicted an influence of chemical bonding between the nanotubes and the matrix on the interfacial adhesion.

The dispersion of the CNTs in the matrix system is imperative. Nano-scaled particles exhibit an enormous surface area being several orders of magnitude larger than the surface of conventional fillers. This surface area acts as interface for stress transfer, but is also responsible for the strong tendency of the CNTs to form agglomerates. An efficient exploitation of their properties in polymers is therefore related to their homogeneous dispersion in the matrix, a break-up of the agglomerates and a good wetting with the polymer.

The manufacturing of M-FRCs has also been difficult due to the rather significant increase in resin viscosity once CNTs have been added. This change in resin morphology impedes resin infusion through

fiber bundles. This has been reported by several workers including Fan et al. [12].

2.2 Displaced Foam Dispersion

The neoteric Displaced Foam Dispersion (DFD) technique utilizes CNTs or other nanomaterials encapsulated in foams to readily enable the manufacture of multiscale composites.

The DFD technique provides an efficient and robust method for integrating nanomaterials into multiscale composites in a simple, safe and controllable manner. It utilizes depleteable foam carrier systems to selectively place nanomaterials in advanced composite laminates.

In the DFD process, sheets of foam encapsulating the nanomaterials are placed between layers of reinforcing fabrics as show in Fig.1.

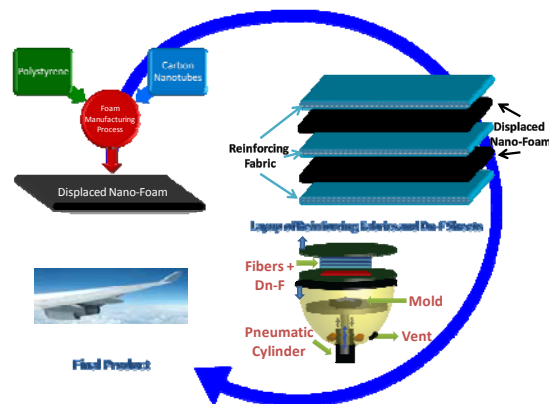


Fig. 1. Schematic of the DFD process.

As resin is infused, the foam carrier system is dissolved and becomes part of the resin system, leaving the nanomaterials where required by design. This may create the ability for direct manipulation of properties (mechanical, thermal, electrical) in selected areas. Fig. 2 is a schema depicting the utilization of the DFD process to manufacture a composite laminate with localized structural, electrical, and thermal properties.

The process described in this paper used CNTs as the nanomaterials which are dispersed in polystyrene (PS) to form nanocomposite films. The resulting CNT-PS films are foamed by a batch process. . Foaming is facilitated by the well dispersed CNTs in

the PS, which greatly enhances bubble nucleation. The foams are placed in predetermined areas between fiber preforms prior to resin infusion.

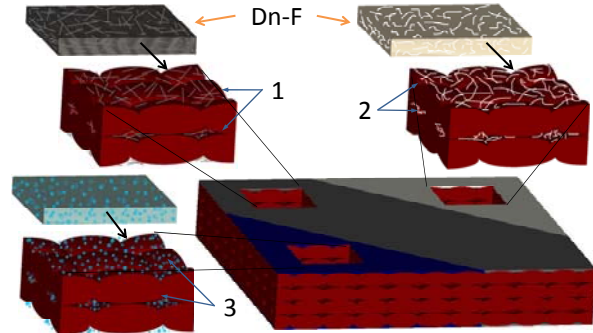


Fig. 2. Multiscale composite with localized (1) structural, (2) electrical, and (3) thermal properties.

Once resin is infused, the polystyrene foam is dissolved and becomes part of the resin matrix, leaving the CNTs in place. Tensile tests and microstructural evaluations were conducted to determine the extent of the viability of the technique.

3.0 Experimental

3.1 Methodology

The DFD process utilizes depleteable nano-enriched foams (Dn-Fs) to achieve nano particle integration and placement in multiscale composites. The Dn-Fs in the current work were made by expanding nanocomposite films made of well dispersed CNTs and polystyrene.

3.1.1 CNT- PS Films

Multi walled carbon nanotubes utilized in this work were from Nanocyl Inc. and CNano. As in a typical process, 50 mg nanotubes were mixed with 200 mL Dimethyleformamide (DMF) in a beaker. The beaker was placed in an ice bath to control the temperature, and the contents were sonicated to diperse the CNTs. A Misonix Sonicator 3000 was used with the processing time set at 8 hours with a 10 sec pulse and a 2 sec rest.

Separately, polystyrene pellets (5 g) were dissolved in 100 mL DMF. Moderate heat and magnetic stirring were used to facilitate the dissolution. The CNT-DMF suspension was then added to the PS-DMF solution and stirred for an additional 30

minutes. This was followed by further sonication for 30 minutes with a 10 sec pulse and a 2 sec rest.

Following sonication, the mixture was added drop-wise to 1500 ml DMF DI water mixture (volume ratio 1:5) under vigorous mixing using a homogenizer. The precipitates were collected by filtration and dried (Fig. 3).



Fig. 3. Filtration and drying cycle of the PS-CNT nanomaterial.

The dried PS-CNT material were pressed into thin films using two mirror finished plates (10×10cm) and a Wabash hot press. The press temperature was kept at approximately 220°C (428°F). After the T_g of polystyrene (95°C) was reached pressure was applied to the mold gradually increasing by 5psi every 5 minutes until 15psi was reached. The resulting PS-CNT thin films were allowed to cool under pressure, and then removed from mold.

3.1.2 Foaming Process

Pentane was used as the foaming agent. The PS-CNT thin films were submerged in pentane for 7 days (168 hours) to allow absorption of pentane into the nanocomposite. Subsequently the thin films were removed and foamed by placing them on a heating plate set at 95°C.. The foams were allowed to grow/bubble for approximately 5 minutes after which, the samples were allowed to set for 24-48

hours before handling and implicating into the DFD Laminates.

3.1.3 Manufacture of DFD Laminates

Multiscale laminates were manufactured using the vacuum infusion process. PS-CNT foam samples were cut to strips and between layers of glass fibers as seen in Fig. 4 (a). The assembly was placed between a vacuum bag, and evacuated. Resin (vinyl ester) was infused until reinforcing fabric was wetted out. Subsequently, the depletion of the PS-CNT Dn-F was initiated as seen in Fig. 4(b), leaving the encapsulated CNTs in place where desired.

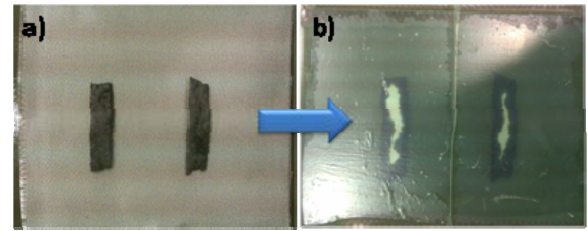


Fig. 4. a) CNT foam pieces: 1.0% MWNT acid treated (left) and 1.0% pristine MWNT (right) lie on single layer of glass fiber weave b) PS-CNT foam between two layers of glass fiber weave showing resin depletion of PS

3.2 Results

Tensile tests were conducted on the manufactured DFD laminates, and the results are given in Table 1.

Table 1: Comparison of the tensile properties of the DFD laminates

Sample	Stress (MPa)	Strain (%)	Modulus (GPa)
GFRC	169.15	4.31	39.28
M-GFRC	192.33	4.08	47.03

From Table 1, a 14% increase in tensile strength is seen with the DFD multiscale laminates when compared with the glass fiber reinforced composite (GFRC) laminates. A 20% increase in tensile modulus was also observed. Both are further illustrated in Fig. 5.

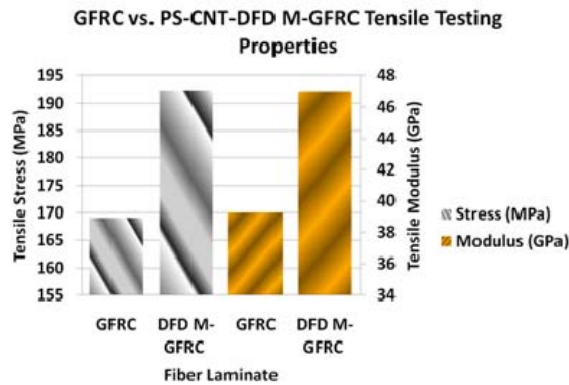


Fig. 5. Tensile properties of GFRC compared with DFD M-GFRC

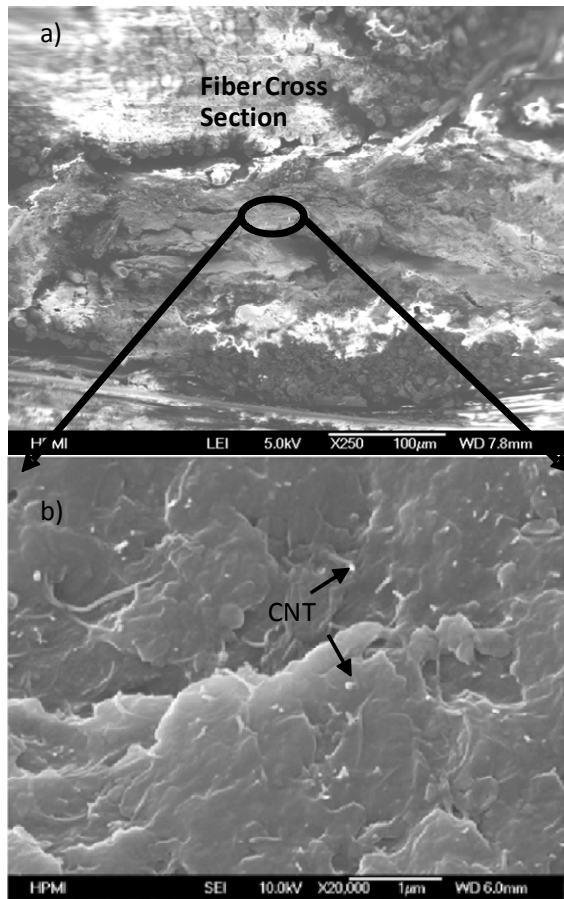


Fig.6. 1.0 wt.% MWCNT matrix dispersion utilizing DFD technique – a) x250 and b) x20,000

Fig. 6 shows a cross-section of a DFD laminate indicating good dispersion of CNTs in the area where the Dn-Fs were placed.

Complete removal of the PS foam is required for the DFD technique to be viable. Nonetheless, closer examination does indicate desired localized CNT placement after resin infusion, demonstrating the feasibility of the DFD technique.

4. Conclusion

This paper describes the development of the DFD technique, which utilizes a depleteable polystyrene foam encapsulation carrier system for CNT/nanomaterial placement. Several multiscale laminates were made demonstrating the feasibility of the technique. Tensile tests showed a 14% increase in tensile strength and a 20% increase in tensile modulus. Microstructural evaluations indicated the presence of dispersed CNTs only at the Dn-F placement locations, thus demonstrating the ability for selective placement of nanomaterials.

References

- [1] D. Askland, P. Phule. "The science and engineering of materials". 4th edition, Pacific Grove, CA: Brooks/Cole-Thompson Learning, 2003.
- [2] K. Chawla. "Composite materials science and engineering". 2nd edition, New York, NY: Springer Science and Business Media, Inc., 1998.
- [3] P. Mallick. "Fiber-Reinforced Composites Materials. Manufacturing and design". 2nd edition, Marcel Dekker, Inc.: New York, NY, 1993.
- [4] E. Bekyarova, E. Thostenson, A. Yu, H. Kim, J. Gao, J. Tang, et al. "Multiscale carbon nanotube-carbon fiber reinforcement for advanced epoxy composites". *Langmuir* Vol. 23, No. 7, pp 3970–3974, 2007.
- [5] S. K. Mazumder "Composites Manufacturing, Materials, Product and Process Engineering". CRC Taylor & Francis, 2002.
- [6] F. Hussain, D. Derrick, A. Haque and A. M. Shamsuzzoha "S2 Glass/Vinyl Ester Polymer Nanocomposites: Manufacturing, Structures, Thermal and Mechanical Properties". *Journal of Advanced Materials*, Vol. 37, No. 1, pp 16–27, 2005.

- [7] S. Banerjee, S. Wong “Synthesis and characterization of carbon nanotube-nanocrystal heterostructures”. *Nano Letters* Vol. 2, pp 195–200, 2002.
- [8] L. Vaisman, H. D. Wagner, G. Marom “The role of surfactants in dispersion of carbon nanotubes”. *Adv Colloid Interface Science*, No. 128–130, pp 37–46, 2006.
- [9] J. Qiu, C. Zhang, B. Wang, R. Liang “Carbon nanotube integrated multifunctional multiscale composites”. *Nanotechnology* Vol. 18, No. 27, pp275708, 2007.
- [10] F. H. Chowdhury, M. V. Hosur, S. Jeelani “Studies on the flexural and thermomechanical properties of woven carbon/nanoclay-epoxy laminates”. *Material Science Engineering A*, Vol. 421, No. 1-2, pp298–306, 2006
- [11] T. S. Gates, G. M. Odegard, S. J. V. Frankland, T. C. Clancy “Computational materials: Multi-scale modeling and simulation of nanostructured materials”. *Composites Science and Technology* Vol. 65, pp 2416–2434, 2005.
- [12] Z. Fan, K. Hsiao, S. G. Advani “Experimental investigation of dispersion during flow of multi-walled carbon nanotube/polymer suspension in fibrous porous media”. *Carbon*, Vol. 42, pp871–876, 2004.