AC 2007-2018: NANOENGINEERING OF STRUCTURAL MATERIALS

Ajit Kelkar, North Carolina A&T State University

Dr. Ajit D.Kelkar is a Director of Computational Science and Engineering and Professor of Mechanical Engineering at North Carolina A&T State University. He also serves as an Associate Director for the Center for Advanced Materials and Smart Structures. His research interests include manufacturing of composite materials, finite element modeling, fracture mechanics, high temperature materials, ceramics and composites. Specifically, his work has included the low cost manufacturing of composite materials, damage characterization of thin and thick composite laminates subjected to low velocity impact loadings, three dimensional finite element micro mechanics modeling of composites, modeling of textile composites, geometrically nonlinear plate and membrane problems, modeling of ceramic composites, fracture toughness studies of high strength materials, finite element modeling of offset car crash simulations. He is the member of several professional societies including ASME, AIAA, MRS, SAMPE and ASEE.

Ronnie Bolick, North Carolina A&T State University

Dr. Ronnie Bolick is Research Scientist in the Department of Mechanical Engineering at North Carolina A&T State University. His research areas have been in embedded fiber optic sensors, fatigue and durability studies for the automotive industry for replacement of mechanical fasteners, manufacturing of composite materials, high temperature materials, both ceramics and composites and low cost manufacturing process development for composite laminates. He has extensive experience in testing and data acquisition ranging from: low velocity impact studies, stress and strain measurement using laser displacement sensors, strain gauges and load cells, and component life/endurance limit prediction. He is a member of several professional societies including ASEE, ISA and SAE.

Ram Mohan, North Carolina A&T State University

Dr. Ram Mohan is Senior Research Scientist in the Center for Advanced Materials and Smart Structures. His research interests include process modeling of manufacturing of composite materials, finite element modeling, high performance coputing, molecular dynamic simulations. He is the member of several professional societies including SAMPE, ASME and ASEE.

Oladapo Akinyede, North Carolina A&T State University

© American Society for Engineering Education, 2007

NANOENGINEERING OF STRUCTURAL MATERIALS

Abstract

For the past five years, the research involving the fabrication and processing of reinforced polymer nanocomposites has grown exponentially. These new materials are helping in the discovery, development and incorporation of improved organic matrix nanocomposite materials with ease of manufacturing methodologies for several defense and industrial applications. These materials eventually will enable the U.S. to fully utilize nanocomposites in not only reinforcing applications but also in multifunctional applications where sensing and the unique optical, thermal, electrical and magnetic properties of nanoparticles can be combined with mechanical reinforcement to offer the greatest opportunities for significant advances in material design and function. With the loss of the conventional manufacturing jobs in the United States, it is extremely important to maintain our role in basic scientific and engineering research in the nanotechnology manufacturing area, which will help US to maintain its lead in the high tech materials area. Therefore it is important to introduce the basic fundamentals of nanoengineered materials to engineering students at undergraduate level. Presently we are introducing fabrication and processing aspects of the nanocomposites in several courses including Modern Engineering Materials, Introduction to Composite Materials and Engineering manufacturing. This paper will present different nanocomposite methodologies that can be introduced at an undergraduate curriculum without involvement of significant cost. The paper will address three different fabrication processes that has been developed and implemented. These three methods include (a) dispersing carbon nanotubes and or alumina particles using high energy mixing (using ultrasonication, high shear and pulverization), (b) electrospinning technique to manufacture and deposit nanofibers (c) X-Y Computer controlled spray technique to deposit single wall carbon nanotubes on the woven fabric. The fabricated nanocomposite materials are then tested by students in Strength of Materials Laboratory using conventional tensile testing machine. This paper demonstrates limitless bounds of nanomaterials, as well as would eventually help to modify and strengthen the existing engineering curriculums in materials, manufacturing, and mechanical and engineering technology.

Introduction

For the past five years, the research involving the fabrication and processing of reinforced polymer nanocomposites has grown exponentially. These new materials are helping in the discovery, development and incorporation of improved organic matrix nanocomposite materials with ease of manufacturing methodologies for defense and industrial applications. These materials eventually will enable the U.S. to fully utilize nanocomposites in not only reinforcing applications but also in multifunctional applications where sensing and the unique optical, thermal, electrical and magnetic properties of nanoparticles can be combined with mechanical reinforcement to offer the greatest opportunities for significant advances in material design and function[1]. With the loss of the conventional manufacturing jobs in the United States, it is extremely important to maintain our role in basic scientific and engineering research in the nanotechnology manufacturing area, which will help US to maintain its lead in the high tech materials area. Therefore it is important to introduce the basic fundamentals of nanoengineered materials to engineering students at undergraduate level. Presently we are introducing fabrication and processing aspects of the nanocomposites in several courses including Modern Engineering Materials, Introduction to Composite Materials and Engineering manufacturing.

This paper presents different nanocomposite methodologies that can be introduced at an undergraduate curriculum without involvement of significant cost. The paper will address three different fabrication processes that has been developed and implemented. These three methods include (a) dispersing alumina particles using high energy mixing (using ultrasonication, high shear and pulverization), (b) electrospinning technique to manufacture and deposit nanofibers (c) X-Y Computer controlled spray technique to deposit single wall carbon nanotubes on the woven fabric. This paper demonstrates limitless bounds of nanomaterials, as well as would eventually help to modify and strengthen the existing engineering curriculums in materials, manufacturing, and mechanical and engineering technology.

Nanocomposite Fabrication Methods

(a) Dispersion of nano alumina particles[2]:

Polymer composites have become an essential material and formidable choice for application and selection by designers in advanced structures for aerospace and marine applications, and the hybrid nanocomposite material systems further enhance the desirable properties along with the added benefits of the nano level material constituents. As such, effective processing techniques are required to integrate the nanomaterial particulates into the material systems at a larger component and structural level. Vacuum assisted resin transfer molding (VARTM) is a low cost manufacturing process regularly used for the processing of polymer composite laminate structures. The introduction of nano level material systems into the conventional processing methods for the manufacture of hybrid composite laminates with nanomaterial constituents can be achieved by the modification of a resin. In the development of the steps for the manufacturing process, we introduce sub-micron alumina particles into a traditional polymer composite material system to form a hybrid nanocomposite system. In particular, the focus is to employ conventional manufacturing processes to improve compatibility between polymeric matrix and the particulate reinforcements. Compatibilization is effected by the functionalization of alumina by the use of a silane coupling agent e.g. tris-2-methylethyl vinylsilane. Thus resin modification is carried out on using non-functionalized and functionalized alumina. In a hybrid polymer composite material configuration, two reinforcements are used, fiberglass fabric and nano-particle alumina, and they are sought to provide load bearing and load transfer function in the material system. Good load transfer mechanisms in polymeric composites are very important to reduce the interfacial stresses and reduce susceptibility of material system to failure modes such as an early matrix cracking and the interface debonding.

Material System

The fabrication process involved a three phase material system consisting of epoxy resin EPON 9504 cured with a proprietary polyamine EPIKURE 9554, a fabric reinforcement of S2 glass fiber composite and 110nm alumina particulate reinforcement (Generic name Alumina Dispal 23, manufactured by Sasol Inc.). Alumina was dispersed to form the hybrid nano composites prior to processing using resin modification. Prior to resin modification, functionalization of alumina is carried out to improve compatibility as discussed below.

Particulate Functionalization:

Alumina particles were functionalized with tris-2-methyoxyethoxy vinylsilane (T2MEVS). The procedure involves the dispersion of alumina in a polar solvent of water and methanol in equal proportions. Quantities of proportional alumina particles for the material design are then added to the polar solvent. Exfoliated dispersion is carried out by ultrasonic agitation using a 500W, 20 KHz sonicator with a tip size diameter of 13mm. The amplitude was set to 40% of maximum amplitude. Sonication procedure is carried out at a unit mass rate 2-3 min. / gm of alumina. Upon sonication and dissociation of nano-particle in organic solvent, proportional quantities of T2MEVS was then added to the solution and stirred. The mixture is further sonicated for about two minutes and stirred for simultaneous ultrasonic and mechanical mixing. The dispersed functionalized alumina is then ready for embedding in the resin.

Resin Modification:

Resin modification procedure is the exfoliated dispersion of non-functionalized or functionalized alumina in the resin system. This is a pre-processing procedure that is carried out before VARTM process for the fabrication of structural hybrid composite laminate. For the non-functionalized alumina, the procedure involves the ultrasonic agitation of composition(s) (%wt of resin weight) of alumina in EPON™ resin. A 500W sonicator with a 20Khz frequency is used to disperse alumina in the low viscosity resin. Sonication is carried out at 40% maximum amplitude with a unit mass rate of 3-5 mins. / gm of alumina. High amplitude and elongated sonication can cause localized elevation of temperature in resin. This rate is also higher than alumina dispersion in water and methanol mixture due to the higher viscosity of the resin system. It is also important to note that mechanical stirring is also carried out during sonication procedure to circulate the mixture and to avoid intercalated dispersion.

For functionalized alumina, the procedure involves a more elaborate dispersive scheme. Procedure for particulate functionalization discussed above is carried out. The solution is then heated at about 200^{o}F to remove water and methanol until 85-90% of moisture has been removed to prevent alumina caking. Due to the lower boiling point of methanol, most of the methanol gets evaporated during this procedure. The slurry is then mixed with the neat EPON™ resin and mechanically stirred. The resin is then ultrasonically agitated for exfoliated dispersion of the partially hydrated alumina particles. The dispersion is carried out at 40% maximum amplitude displacement and a unit mass rate of about 5-6 min/ gm of alumina. The partially hydrated and exfoliated EPON™ - alumina mixture is then placed in an oven at 200^{o}F for 8-10 hours until 95-99% of moisture is removed. The modified resin solution is then ready for VARTM process.

The hybrid nanocomposite material is then fabricated by impregnation of modified resin mixed with curing agent into a 4-ply fiber bed using the conventional single sided low cost Vacuum Assisted Resin Transfer Molding (VARTM) process[3].

(b) Electro-spinning

There are several things that can be learnt from the nature. For example take a case of spider web. The thread of the web is so strong that it can withstand weight of the entire spider. The electro-spinning process imitates a spider spinning its web. This process is multi-disciplinary and allows students to refresh their education from preliminary college courses in chemistry, electronics, computer programming and mechanical engineering.

The first step in the process utilizes chemistry. The students are refreshed on chemicals handling risks and their safety precautions. The students then combine chemicals to form a binder. The binder is combined with silica dioxide. One drop per second is titrated into the silica dioxide mixture which is being continuously stirred. This mixture is stirred for 24 hours. The solution is then reduced in volume until approximately two-thirds of the original mixture remains and is termed as sol-gel. Students are also trained to measure the viscosity. The viscosity of the original mixture is approximately 40 centi-poise. After reduction, the viscosity is approximately 500 centi-poise. The solution is then poured into a syringe and a tube is attached to the blunt needle of the syringe. Another needle tip is placed on the end of the tubing.

In step two, the syringe is placed into a syringe pump. An alligator clip from the positive voltage of a high voltage power supply is attached to the needle tip. The negative or ground of the power is attached to a plate that fabric is clamped on. Figure 1 illustrates an XYZ table, the electrified needle tip and the S2 fiberglass fabric on the mounting plate. Equipment such as the High Voltage power supply, the syringe pump which is programmable and is used to disperse the sol gel solution is computer controlled. The syringe pump software controls delivery of the sol gel at a rate of milliliters per second. The high voltage power supply controls the current and voltage depositing the solution, and the rate at which the XYZ table moves is also controlled via computer. The mounting plate with fiberglass fabric first moves in the X direction. At the end of the fabric the X controller stops and the Y axis controller moves the plate downward. The X axis controller then moves the plate to the opposite end of the plate. This process continues until the entire fabric is covered. The Z axis moves the plate toward or away from the needle tip. This distance determines the size of the spray pattern on the fabric. All of the equipment is enclosed in a temperature and humidity chamber that is also monitored.

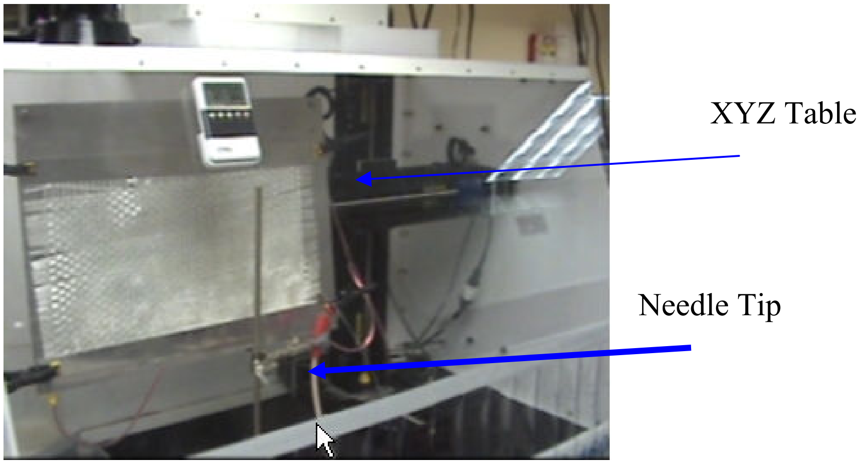

Figure 1. Electro-spinning Setup.

The actual electro-spinning of fibers starts in the following manner. The X controller begins moving the plate in the X direction and the syringe pump begins dispensing sol gel through the syringe into the tube to the electrified needle on the end of the tube. When the sol gel solution leaves the needle, the potential voltage deposits the solution onto the grounded fabric. As the electric potential moves around and over the fabric, the sol-gel is electro-spun onto the fabric. Figure 2 illustrates the voltage jumping to ground potential that completes the circuit. The entire panel is moved in the X and Y directions until the entire panel is covered with electro-spun fibers.

Another step in the training of students is the use of optical micro-scopes. After processing the entire panel, they remove the panel and view the electro-spun fibers under the microscope. Figure 3 illustrates a micrograph of the electro-spun fibers of approximately 105 microns. Using the low cost VARTM procedure[3], these electrospun laminates are infused with the resin to form the composite laminate.

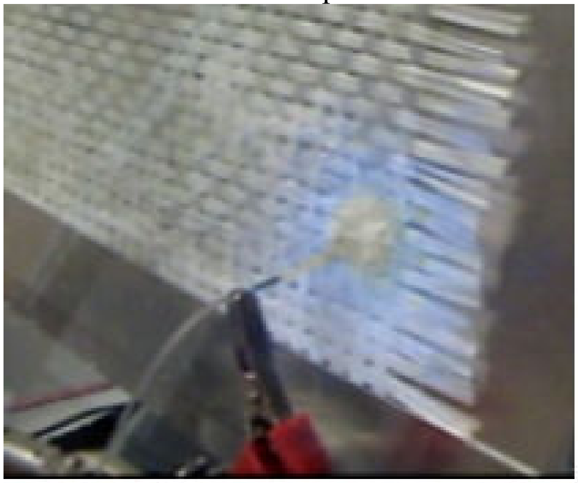

Figure 2. Voltage jumping to ground.

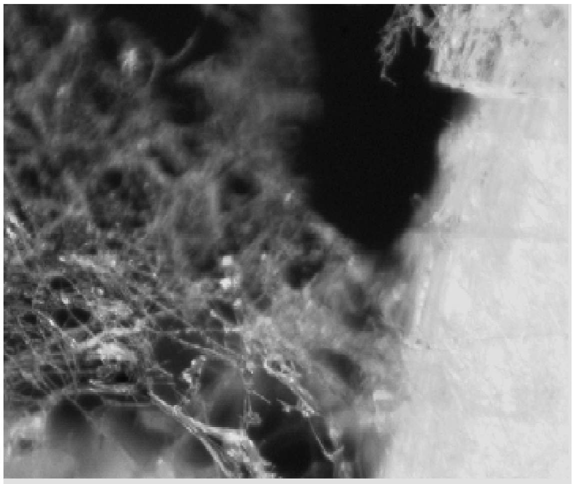

Figure 3. Electro-spun fibers.

(c) <u>Carbon Nanotubes Deposition</u>

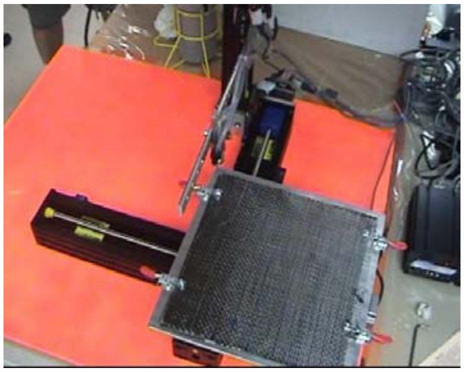

Figure 4. XY Spray Table.

In this process a fabric material is mounted on the XY table, see Figure 4. The sprayer is aligned over the edge of the fabric at one corner. The nano-particles are mixed with a solvent which acts as a carrier. The solvent allows the nano-particles to be dispersed. The sprayer is computer controlled to spray a predetermined volume at a certain rate per second. The combination of the XY table movement and the spaying of the nano-particles, disperse nano-particles in a uniform pattern onto the material below. Illustrations of three resin test specimens of different concentrations of carbon nanotubes: top-highest concentration, middle-medium concentration and bottom just neat resin are shown in Figure 5.

Figure 5. Test specimens with various concentrations of carbon nano tubes.

Students are trained in quality control, computer programming and combining of machinery, computer software, chemistry and design of experiment in this course. Once the fabrics have been correctly covered with carbon nano-particles, the panels are then manufactured using low cost VARTM method [3] and fabricated panels are cut into tensile coupons to obtain the fundamental mechanical properties.

Performance Evaluation [4]

Static tensile tests are employed to understand the behavior of the hybrid composite panels and the particulate non-fiber composite panels that were manufactured as discussed in the previous sections. Coupons were prepared from the laminates to ASTM standard 3039 for the hybrid composite and ASTM 6038 for the particulate composite. Mechanical evaluation consists of a tensile test for the determination of the material strength, modulus and elongation.

Concluding Remarks

Several undergraduate students were trained in the area of nano engineering of structural materials. These undergraduate students were trained in three different areas: (a) nanoparticle dispersion methodology (b) electrospinning and (c) carbon nanotubes deposition. Using these three methods, students were trained to manufacture stronger composites using conventional low cost VARTM method in conjunction with the modified resin/fabric. When these techniques were taught to undergraduate students, there were numerous challenges. Most of the students were not familiar with the nanotechnology. Furthermore most of them had any experience with handling carbon nanotubes or alumina particles. Safety issues were of prime importance, in particular when carbon nanotubes are used in manufacturing. Since the proposed activities involve many areas, it was difficult to introduce these experiments into mechanical undergraduate curriculum. We have decided to implement the proposed activity into three different laboratories, first material science, second strength of materials and third manufacturing processes. Once these experiments are introduced, we plan to collect student feed back and modify the experiments accordingly. The simplicity of the processing methodology presents an easy avenue for the introduction into the undergraduate curriculum without any significant additional cost. The variation in the properties that is influenced by the processing methodologies presents an excellent opportunity to educate the students on the process-property interactions and cross-dependencies in the material science and composite material systems.

Bibliography

1. Mark J Schulz, Ajit D Kelkar and Mannur J Sundaresan, “Nanoengineering of Structural, Functional and Smart Materials”, Cat. #: 1653, ISBN: 0849316537, 2005, CRC Press
2. R. Mohan, O. Akinyede, Ajit D. Kelkar and J. Sankar, “Processing and Evaluation of Hybrid Composite Laminates with Nanomaterial Functionalized Fiber and Resin Systems”, SAMPE Proceedings 2006, Long Beach, May 2006.
3. Ajit D. Kelkar, Jitendra S. Tate and Ron Bolick; “Introduction to Low Cost Manufacturing of Composite Laminates”, ASEE 2003 Annual Conference & Exposition, Nashville, TN, USA, June 22- 25, 2003, Session 2003 – 2526
4. R. Mohan, O. Akinyede, and Ajit D. Kelkar, “Processing and Evaluation of Hybrid Composite Laminates with Nanoparticle Functiaonlaized Fiber and Resin Systems,” SAMPE Proceedings 2006, May 2006.