Fabrication and Evaluation on Nano-Phased Unidirectional Carbon Fiber Reinforced Epoxy

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Abstract

In the present investigation, we have developed a novel manufacturing technique to fabricate unidirectional nanophased carbon prepregs using solution impregnation and filament winding methods. Siliconcarbide nanoparticles (β-SiC) were first infused in a high-temperature epoxy through a high-frequency ultrasonic cavitation technique. The loading of nanoparticles was 1.5% by weight of the resin. After infusion, nanophased resin was used to impregnate a continuous strand of dry carbon fiber tows in a filament winding set up. As the process continued, excess resin was squeezed out and the prepregs were run through a heater to partially cure the resin and evaporate out the solvent used for dissolving the resin. In the next step prepregs were wound onto spools. The same filament winder was then used to wrap the nanophased prepregs over a cylindrical mandrel of Marcore foam especially built for this purpose. Once the desired thickness was achieved, the prepregs on the cylinder was longitudinally cut, opened into a rectangular flat sheet and cured in a compression molding machine. Test coupons were then prepared from these rectangular panels. In parallel, control panels were also fabricated in identical manner from the neat resin without any particle infusion. Extensive thermal and mechanical characterizations were performed to evaluate the performances of the neat and nanophased systems. Thermo-gravimetric analysis (TGA) results indicated that by incorporating nanoparticles, the thermal decomposition temperature increased by about by about 7-8^{0}C due to enhancement in the cross-linking of the polymer. This enhancement in cross-linking was also substantiated by the differential scanning calorimetry (DSC) tests. Significant improvement in flexural properties of nanophased laminates was also observed when compared to the neat system. Improvement in strength and stiffness was observed to be around 32% and 20%, respectively over the neat system. Failure mechanisms, fiber orientations and dispersion of nanoparticles in the nanophased system were studied by Scanning electron microscopy (SEM). These results indicate that the carbon filaments and SiC nanoparticles are distributed uniformly without agglomeration over the entire volume of the resin, and there are no distinct differences in the failure processes of the two systems.

Introduction

The incorporation of inorganic particulate fillers has proven to be an effective way of improving the mechanical properties, such as modulus and strength, of resin. However, the typical filler content needed for significant enhancement of these properties can be as high as 10-20% by volume. At such high particle volume fractions, the processing of the material often becomes difficult. Since the inorganic filler has a higher density than the resin, the density of the filled resin is also increased. Nanoparticle filled resins are attracting considerable attention since they can produce

property enhancement that are sometimes even higher than that of conventional filled polymers at volume fractions in the range of 1 to 5%. It has been established that with the addition of small amounts of nanoparticles (<5 wt.%) to a matrix system can increase thermal and mechanical properties without compromising the weight or processability of the composite [1-5].

Unidirectional carbon prepreg tapes/tows have long been the reinforcement of choice for the manufacturer of components requiring the highest performance. Carbon prepreg laminates and filament wound structures are used for a diverse set of applications. These include commercial aircraft structures for Boeing and Airbus as well as many products in the recreational, automotive and industrial markets. Freeway column wrapping, bridges and oil field equipment are beginning to make more use of carbon fiber composites for added strength and stiffness. The principal reason for these increasing applications is due to the fact that carbon prepreg provides a balance of high strength, high modulus and high chemical resistance at relatively low density.

Largely driven by these applications, extensive studies have been made in recent years to improve mechanical properties and processability of carbon prepreg. For example, in a study of Sherman *et al*. [6], monolithic thin alumina plates have been used to modify unidirectional carbon/epoxy prepreg. Barton *et al.* [7] has prepared carbon fiber pre-impregnated tapes from a range of prepolymers comprising blends of propenyl-functionalized cyanate ester oligomers with commercial bis-maleimide monomers using dip-winding technique. Ide *et al.* [8] prepared prepreg containing unidirectional carbon fibers, co-directional stranded steel filaments and a matrix resin. Wang W. X. *et al*. [9] used spray method to distribute SiC whiskers along the interface of composite laminates during the lay-up process. All above modifications of unidirectional carbon/epoxy prepregs are about filling conventional fillers into the matrix. In the year of 2000, Hayes *et al.* [10] incorporated alumina particles (5 μm and 0.05 μm) and nano fibers into a model epoxy resin and impregnated those into unidirectional carbon fibers. Prepregs were also developed where the alumina materials were dispersed throughout the matrix as well as placed only on the prepreg surface by using double pass impregnation. They observed an increase in interlaminar shear strength. Up to now, nanophased carbon prepregs were not well studied and the manufacturing techniques for the processing of nanophased fiber reinforced composites were not well known.

In this paper, a novel manufacturing technique was developed to fabricate unidirectional, nanophased carbon prepregs using solution impregnation and filament winding methods. β-phase silicon carbide nanoparticles with a loading of 1.5% by weight of the resin were incorporated in a high temperature epoxy-resin system and impregnated into a continuous strand of carbon fiber reinforcing tows. TGA, DSC and flexural tests were performed to evaluate the performances of the neat and nanophased carbon-epoxy laminates systems. After the flexural test, failure mechanisms, fiber orientations, and dispersion of nanoparticles in the nanophased system were studied by SEM.

Fabrication Procedure for the Nano-Phased Composite

Online solution impregnation and filament winding were used as the method of manufacturing nanophased unidirectional laminates. The method involved five principle steps: (1) uniform dispersion of nano particles in the resin system; (2) application of resin reaction mixture onto the reinforcing tows; (3) removal of excess

resin and solvent from the prepreg; (4) filament winding; and (5) consolidation of prepregs into laminates.

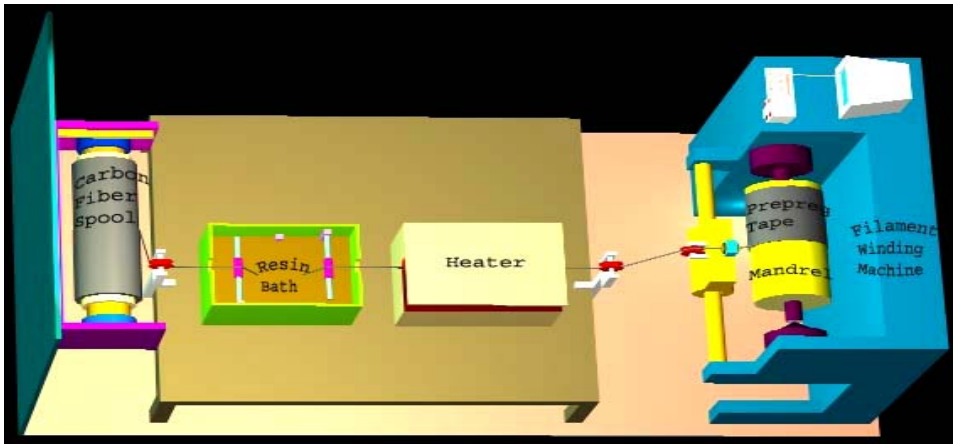

Figure 1. Schematic of solution impregnation and filament winding

Commercially available high temperature prepreg resin CH46T (Applied Poleramic, Inc., USA, stored as solid under sub-zero temperatures) was first dissolved in acetone (dimethyl ketone, class 1B, Fisher Scientific Co. LLC, USA), at a ratio of 65:35 by mechanical stirring at 1500 RPM for about 4 hours. Spherical shaped silicon carbide nanoparticles (β-SiC, MER Corporation, USA, ~ 30 nm diameter) were carefully measured to have a 1.5% loading by weight of the resin and mechanically mixed with the liquid resin. The mixture was then irradiated with high intensity *Sonic Vibra Cell* ultrasonic liquid processor (Ti-horn, 20 kHz, 100 W/cm^2) at 50% of the amplitude for about 30 minutes. This ensured uniform mixing of nano particles over the entire volume of the resin. To avoid temperature rise during sonication, cooling was employed by submerging the mixing beaker in a water bath maintained at 10^{0}C. The nanophased resin reaction mixture was then transferred into a heating bath maintained at a constant temperature of 40^{0}C throughout the fabrication. A continuous strand of carbon fiber (T700SC, Toray Carbon Fibers America, Inc., USA, filaments 12000) from a spool attached in the spindle bracket assembly was allowed to pass through the resin bath at a rate of about 1 meter per minute. In this case, the resin reaction mixture individually wet each filament within the fiber tow. Once the fiber was coated with nanophased resin the excess solvent was removed from the prepreg by passing the wet strand through a high temperature heater maintained at 70^{0}C. The nanophased prepreg tow was then routed and fed through a fiber delivery system and was precisely hoop-wound on a rotating foam mandrel attached to the filament winding machine as shown in Figure 1. During the fiber placement, the winding angle was kept at 89.875^0 to avoid excessive gaps or overlaps between adjacent courses. Eight layers of tows were successively laid down without allowing the previous layer to dry. When the desired thickness was achieved, the prepregs on the cylinder were longitudinally cut open into a rectangular sheet as shown in Figure 2. These rectangular sheets were then placed in a compression molding setup by putting symmetric layers of plastic film, bleeder cloth, and teflon on the top and bottom. The whole setup was then placed in compression molding machine, as shown in Figure 3. Mold temperature was set at 177^{0}C and mold pressure was kept as 276 KPa for about 4 hours to obtain a 2 mm thick SiC nanophased

unidirectional laminate (as shown in Figure 5). A typical consolidation cycle is shown in Figure 4.

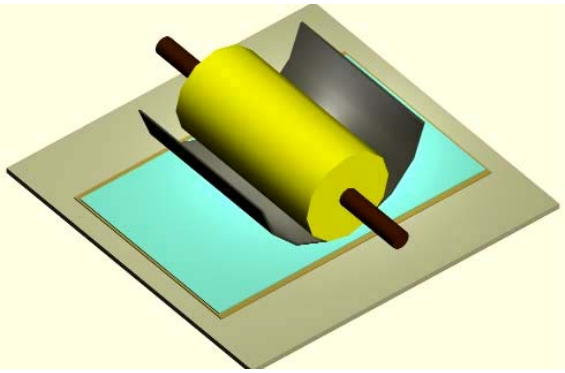

Figure 2. Schematic of unidirectional laminate preparation

Figure 3. Compression Molding

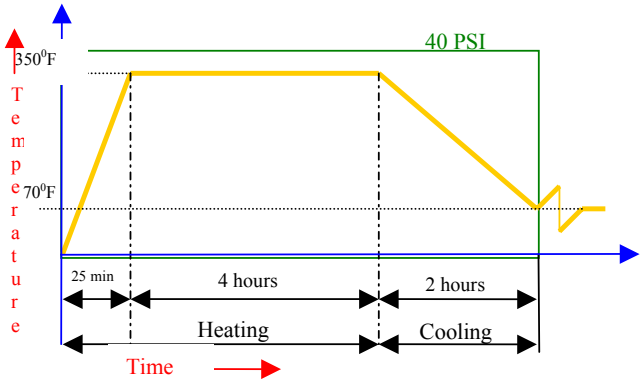

Figure 4. Consolidation cycle

Figure 5. Unidirectional Panel

Experimental

Flexure tests were performed on an MTS servohydraulic test machine equipped with a 100 KN load cell. Test coupons were prepared according to ASTM D790. Five specimens with span-to-depth ratio of 16 to 1 were cut from both neat and nanophased laminate along the fiber direction. Typical specimen dimensions were 56 mm in length, 25 mm in width and 2 mm in thickness. Span length was kept at 32.2 mm. Displacement controlled three-point bending tests were carried out at a crosshead speed of 0.9 mm/min until specimen failed. Tensile test were performed at the same machine, strain rate is 0.00 1/s. *TestWare-SX* PC installed software on the machine was used to control the movements and record loads and corresponding displacements. Two parameters were evaluated from stress-strain curves: modulus (E) and failure strength (σ_b).

Results and discussion

Typical flexural and tensile stress strain plots of neat and nanophased lanimates are shown in Figures 6 a and b. The curves show considerable non-linear deformation after 0.6% strain and the irregularities in the curves were attributed to

random filament breakage during loading. The specimens failed rapidly after reaching the maximum stress and pinging noise were also observed while individual filament broke or inter layer delaminated. Stress strain curves shown in Figure 6 also revealed that by infusing 1.5% by weight SiC nanoparticles, strength and modulus were significantly improved. Nanophased system showed about 32% increase in flexural strength and 20% in flexure modulus with respect to the neat ones. Five specimens were tested in each case, and average mechanical properties of neat and nanophased laminates are shown in Table I and II.

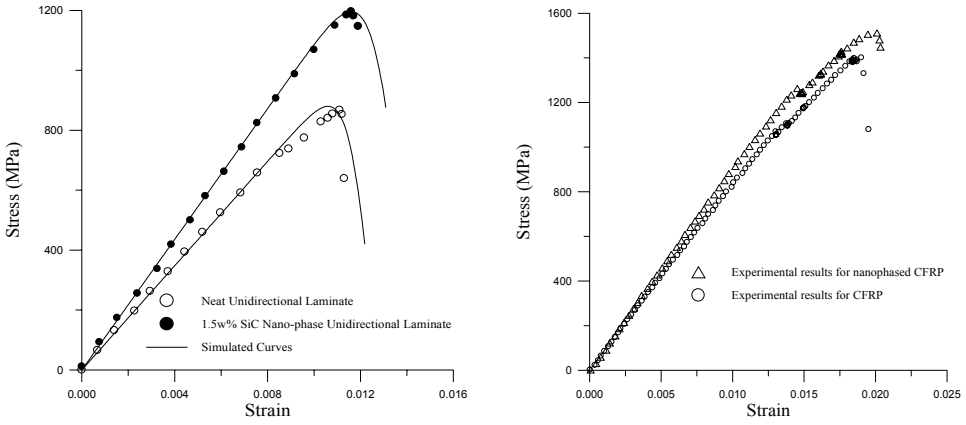

Figure 6. Stress-strain of neat and nanophased laminates (A: flexure; B: tensile)

Table I. Flexure test data for carbon prepreg laminates

Material	Flexural Strength (MPa)	Average Flexural Strength (MPa)	Gain/Loss Strength in (%)	Flexural Modulus (GPa)	Average Flexural Modulus (GPa)	Gain/Loss Modulus in (%)
Neat	841.01 886.22 867.45 860.02 871.92	865.32	--	94.74 92.77 94.64 92.61 88.71	92.69	--
+1.5% SiC	1146.54 1093.71 1112.74 1196.61 1177.53	1145.43	+32.37	109.36 113.17 114.39 105.54 115.68	111.63	+20.43

Table II. Tensile test data for carbon prepreg laminates

Material	Tensile Strength (GPa)	Average Strength (GPa)	Gain/Loss Strength in (%)	Tensile Modulus (GPa)	Average Modulus (GPa)	Gain/Loss Modulus in (%)
Neat	1.32 1.41 1.39 1.42 1.34	1.38	--	79.75 77.82 78.45 81.72 79.91	79.53	--
+1.5% SiC	1.48 1.39 1.51 1.49 1.55	1.48	+7.25	87.59 82.40 84.62 88.96 85.75	85.86	+7.96

Figures 7 are the SEM micrographs of the failed specimen in flexure test. They also show interfiber micro-cracks and delamination cracks. These micrographs also reveal that the carbon fibers are highly oriented with uniform resin distribution. Figure 7(b) shows the surface of a filament on which SiC nanoparticles are distributed uniformly without agglomeration. Filament diameter was found to be 8-10 microns and SiC nanoparticle to be of about 30-40 nm.

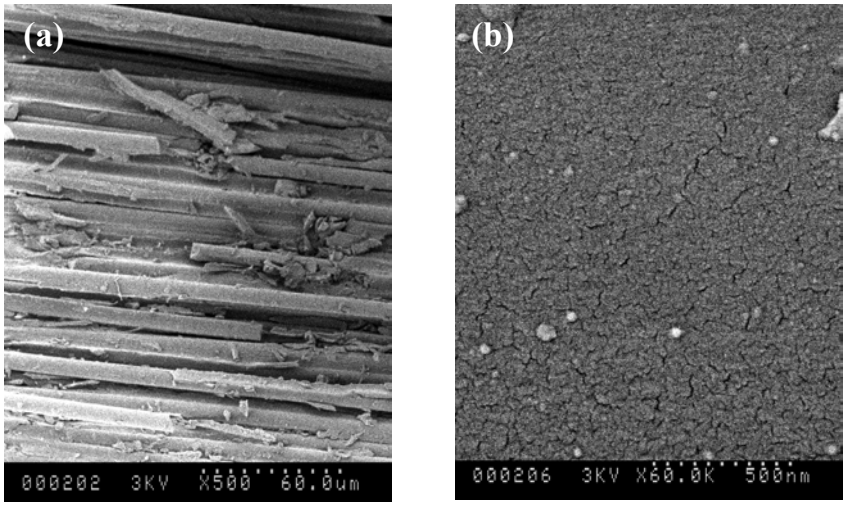

Figure 7. SEM micrographs

Summary

- An innovative technique was established to fabricate carbon fiber prepregs from a nanoparticle infused matrix.

- The nanophased prepregs have been utilized in a filament winding process to manufacture unidirectional layered composites.
- These composites were consolidated in a regular hot press.
- Thermal studies on the consolidated samples have indicated that there is enhanced cross-linking and an increase in the degradation temperature (about 7^0C) of the nanophased composite.
- Mechanical tests also indicated improvement in the nanophased composite properties. Nanophased system showed approximately 32% increase in flexural strength and 20% in modulus with respect to the neat ones. Nanophased system also exhibit 7.25% improvement in tensile strength and 7.96% improvement in tensile modulus

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