Synthesis of a CNT Nano-Coating on Carbon Fibers: It's Role on Strength, Toughness and Damage Tolerance of Polymer Matrix Composites

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ABSTRACT

Carbon fibers are used as reinforcement in high performance composites. Nanotubes of carbon (CNTs) are another form of carbon with outstanding mechanical, electrical and thermal properties and therefore can be used along with carbon fibers to produce carbon fiber reinforced nanotube dispersed composites with relatively superior performance. One of the limitations in achieving the full benefits from the use of carbon nanotubes as reinforcement is the problem of dispersing the nanotubes uniformly in a matrix. In the present work a novel method of incorporating CNTs in a polymer matrix has been developed. This consists of in-situ synthesis of a nanocoating of carbon nanotubes on the surface of carbon fibers to be used as reinforcement and available in the form of tows or woven fabrics. The CNTs remain anchored to the surface of the carbon fibers and thus get dispersed in the matrix along with the fibers.

Composite samples in the form of laminates have been prepared and tested for mechanical properties and for response to low energy impact loading. The measurement of mechanical properties showed a significant increase in tensile strength, toughness and shear modulus when CNTs were introduced in the matrix along with carbon fibers. Presence of carbon nanotubes on the surface of carbon fibers also showed improved damage tolerance and altered damage distribution in the samples during ultrasonic C-scan observations.

Keywords: Nano-composites, CNT nano-coating, damage tolerance, Ultrasonic C-scan, C-fiber composite

1 INTRODUCTION

Carbon in its form as nanotubes has outstanding mechanical, electrical and thermal properties [1-4]. This has made carbon nanotubes (CNTs) an excellent candidate material for applications as reinforcement in advanced high performance composites. It has been shown that the properties of these nano constituents can be transferred to macro-level behavior of materials such as polymers, metals and ceramics [5] by incorporating the nanotubes as reinforcement in their composites. The properties of the products, however, are largely influenced by the quality of CNTs, the choice of the matrix material and the nature and properties of the CNT/matrix interface [6]. Limitations in achieving the optimal benefits from the incorporation of CNTs in composites also arise due to the difficulties in dispersing the individual nanotubes uniformly in the matrix, controlling their orientation and their tendency to form clusters. Proper dispersion and alignment of CNTs along a preferred orientation will help in achieving superior properties in the direction of orientation of the tubes [7]. Considerable research and development efforts have focused on each of these problems and innovative solutions have been proposed [8]. A novel method of incorporating MWCNTs into a composite matrix has been developed by our group. This consists of in-situ synthesis of CNTs directly on the surface of a functional substrate such as carbon fibers to be used as reinforcement. The CNTs remain anchored to the substrate during subsequent processing and thus get incorporated in the composite matrix. The presence of CNTs on the fiber surface is found to give significant improvements in properties of composites in relation to those of plain carbon fiber reinforced composites [9, 10]. The procedure used for the in-situ synthesis of CNTs on carbon fibers, preparation of polymer matrix laminate samples and observations on the role of CNT incorporation on mechanical properties and damage tolerance during low energy impact tests is presented in this paper.

2 EXPERIMENTAL PROCEDURE

2.1 Synthesis of CNTs

The synthesis of CNTs has been carried out using CVD process with nickel nanoparticles as catalyst and acetylene as a carbon precursor. Sizing on the fibers was removed before processing for nanotube synthesis by immersing the tows and mats in concentrated nitric acid for an hour followed by washing overnight with running water. The fibers were then dried in an oven at 80 ^{o}C. Optimum yield and good quality MWCNT deposit with good fiber surface coverage was obtained for synthesis temperature of 750 ^{o}C and deposition time of one hour (figure 1). Removal of the sizing gave better yield. Examination of CNTs on scanning and transmission electron microscopes (JSM-840A JEOL scanning SEM and CM-200 TEM) showed that the tip

growth mechanism was operating; catalyst nanoparticles located at the tips of the MWCNTs were observed and the tubes remained anchored to the surface of substrate (figure 2). CNT growth was perpendicular to the fiber surface initially but as growth continued a network of CNTs developed enveloping individual fibers in the form of a sheath [Fig.3]. XRD pattern taken on the processed carbon fibers confirmed the presence of the CNTs (figure 4)

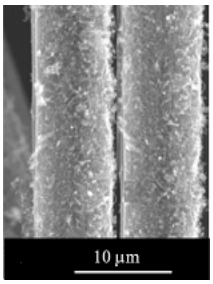

Figure 1

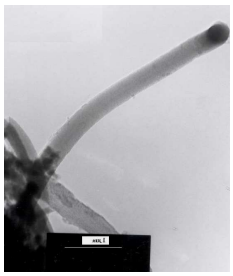

Figure 2

Figure 1. MWCNT deposit on carbon fiber surface.
Figure 2. Nickel nanoparticle at the tip of a MWCNT.

Figure 3

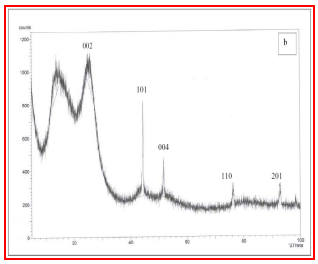

Figure 4

Figure 3. Network of CNT in the form of a mesh.
Figure 4. XRD pattern of c fibers coated with CNTs

2.2 Specimen Preparation

T-300, 6k Carbon Fibers and LY-556 Epoxy along with HY 951hardener were used to prepare samples for mechanical testing. Tensile, compression, flexture, shear and hardness tests were carried out on specimens of appropriate dimensions (figure 5) .For low energy impact tests 2-D laminates of 200 x 200 x 6 mms were prepared using 0-90 lay up of carbon fiber mats.

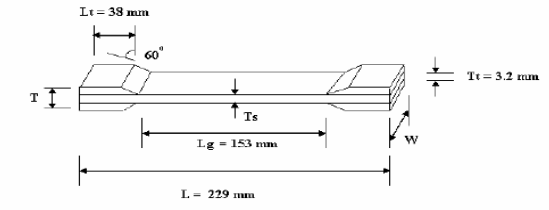

Figure 5. Specimen geometry of tensile test specimen

3 RESULTS AND OBSERVATIONS

3.1 Synthesis of CNTs

Examination of CNT nano-coating on scanning and high resolution transmission microscope showed multiwall nanotubes (MWCNT); the length of nanotubes was of the order of a few microns and these appeared to form quasi continuous envelop of a mesh around individual fibers. Bundles of nanotubes also appeared as individual filaments at lower magnifications. The diameter of multiwall nanotubes was of the order of 30 to 70 nanometers (figure 6). Cleaning with hydrogen peroxide for over 24 hours was found effective in obtaining a fairly clean network of MWCNTs (figure 7)

Figure 6

Figure 7

Figure 6: TEM image of a MWCNT
Figure 7.TEM picture of CNTs after cleaning with H_2O_2

3.2 Mechanical Properties

Mechanical property measurements showed a relative increase in values of all properties in the presence of CNT surface nanocoating on fibers. Flexural strength and modulus showed an increase of around 25% and 100% respectively. Tensile strength showed an increase of 65% and shear strength showed an increase of around 20%. Fractographic observations on tensile test specimens showed relatively low fiber pullout on the fracture surface indicating that the presence of CNTS on the surface of the carbon fiber possibly helped in improved anchoring of the fibers in the matrix and more effective load transfer. (Figure 8)

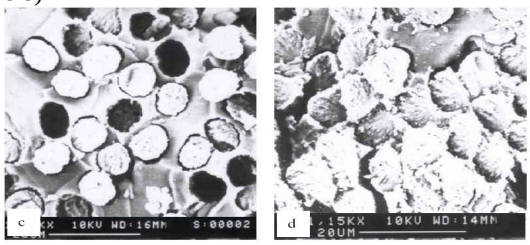

Figure 8. Fractographs showing relative absence of pullout in the right side image for CNT coated C-fiber specimen

3.3 Low Energy Impact Test and Ultrasonic C-Scan Examination

Low energy impact tests showed superior performance of composite samples with CNT coated carbon fiber reinforcement. Ultrasonic C-Scan observations were carried out on all test specimens using automated portable ultrasonic C-scan imaging facility. The C-scans show (figure 9) that damage distribution in the volume of the samples changes significantly in the presence of CNTs. In case of CNT coated carbon fiber composites damage indications were found to be more localized whereas in the absence of CNTs the damage was found to be more or less distributed over the entire volume of the samples tested. The relative energy levels for minimum observable damage were also found to be higher in case. This is attributed mainly to superior fiber-matrix interface performance in the presence of CNTs and more effective dissipation of impact strain energy in the volume of the specimens in the presence of CNTs.

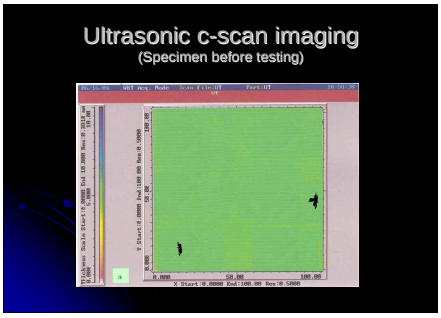

Figure 9. Ultrasonic C-scan image of a specimen before testing

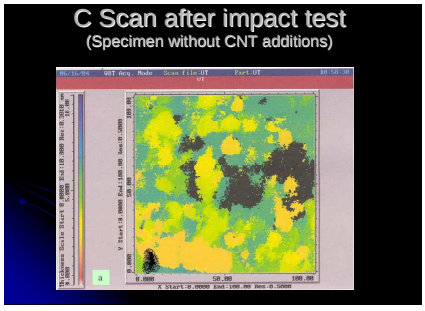

Figure 10.Ultrasonic C-scan image of a specimen without CNT impregnation showing random damage distribution after low energy impact testing

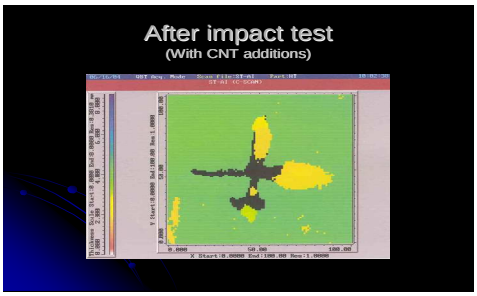

Figure 11.Ultrasonic C-scan image of a composite laminate after low energy impact test showing relatively localized damage

4 DISCUSSIONS AND CONCLUSIONS

In-situ synthesis of carbon naotubes on carbon fibers has been effectively developed and used to disperse MWCNTs in polymer matrix. The process can be adapted to other reinforcements on which CNTs can be grown and other matrix materials such metals and ceramics. Incorporation of CNTs has shown significant increase in mechanical properties and in damage tolerance of composite samples in the presence of CNT nano-coating on carbon fiber surface. This is attributed to improved fiber-matrix interface behavior.

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