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Enhanced crack detection sensitivity of carbon fiber composites by carbon nanotubes directly grown on carbon fibers

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ABSTRACT

The ability of highly conductive hybrid carbon–fiber/carbon nanotube loaded epoxy composites to sense matrix cracking damage *in situ* is demonstrated. Multi-walled carbon-nanotubes (MWCNTs) are grown perpendicular to and on the surface of a woven carbon–fiber fabric using a chemical vapor deposition process. An increase in sensitivity of resistance change under interlaminar fracture is shown through a series of double cantilever beam (DCB) tests on samples prepared with MWCNTs grown on both sides of carbon–fiber fabric lamina placed at the top and bottom surfaces of an 8-layer test panel whereas samples with MWCNTs inside the samples did not show much increase in sensitivity of resistance change compared with the baseline samples without MWCNTs. The results suggest that the addition of surface positioned hierarchical carbon-nanotube lamina on composite structures has the potential for autonomic sensing of internal matrix damage.

1. Introduction

The last several decades have seen continual research, development and improvement in the properties of fiber-reinforced polymer composites. The improvement in the mechanical properties, durability and reliability of composite materials and systems has allowed them to be applied to widening applications in every aspect of society, not only aerospace, but automotive, sporting goods and construction. Currently, major structural components in commercial and military aviation as well as space systems use large scale composite parts. For example, Boeing's new 787 commercial airliner uses more than 50% composite material, a 50 times increase over its usage in the 747 [1]. This expanding use of composite materials raises the important need for accurate methods to detect damage in structures that may arise from numerous sources such as fatigue from cyclic loading, impact damage or degradation due to environmental conditions. Often this damage is not readily visible and expensive or time-consuming techniques such as ultrasound or X-ray scanning must be employed [2]. Such inspections must often be conducted with the structure taken out of service and further, these tests are done on a periodic basis with no accommodation for what damage might occur or propagate between inspections.

The development of electrical internal sensors for damage detection in composite systems has focused on using either naturally conducting reinforcing materials, such as carbon fiber, or the addition of conducting fibers or particles in the insulating matrix [3–5]. Numerous studies have been conducted to improve the electrical conducting properties of various matrix materials by adding conducting fillers [6]. Typically the electrical conductivity is related to the volume fraction of filler in the material and reaches a conducting level at the percolation threshold which allows electrons to pass along a network of conducting particles within the composite. Reaching the percolation threshold volume fraction of filler often corresponds to a dramatic increase and then leveling off of conductivity in bulk filler-matrix composites. Many studies are available that discuss the effect of filler concentration on conductivity and they show the same trend of a sharp increase in conductivity at a certain filler percentage which is attributed to reaching the percolation threshold [7,8]. One problem with the filler approach is the associated degradation of other material properties with increasing filler percentage. The advantage to using nanoparticle fillers is that they allow for a significant reduction of the volume percentage required to reach the percolation threshold due to the high aspect ratios that increase the formation of conducting pathways among the particles in otherwise insulating polymers [9]. In a broad study of carbon nanotubes (CNTs) and epoxy composite properties, Gojny et al. found that multi-walled carbon nanotubes (MWCNTs) formed conducting networks at concentrations as low as 0.1 wt.% [10]. Agglomeration, which effectively reduces surface area by creating large-scale particulates, is a consistent challenge in the production of nanocomposites, hindering the realization of improvements in both mechanical and electrical properties [11]. As an alternative to direct mixing of

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nanoparticles and matrix materials, the process of direct application of nanoparticles onto the reinforcing fibers has been developed. One such method uses chemical vapor deposition (CVD) processing to grow CNTs from the fiber surfaces. Veedu et al. used a CVD process to grow MWCNTs on SiC woven fabric with the intent of both improving mechanical and electrical properties, reporting an improvement in through-thickness electrical conductivity from 0.075×10^{-6} S/cm in the base composite to 0.408 S/cm in the nanocomposite [12]. In a similar study, Garcia et al. fabricated laminate panels using alumina fiber woven fabric with CVD grown CNTs on the surface. They reported through thickness resistivity decreasing from $\sim 10^6\,\Omega$ mm in a baseline sample to $\sim 10^2\,\Omega$ mm in the nanocomposite [13].

A commonly used technique for testing the fracture toughness of the interlaminar matrix material in carbon fiber reinforced plastics applications is the double cantilever beam (DCB) test. In the Mode I fracture toughness test, a specimen with a pre-crack is pulled apart and the load and crack propagation are measured to quantify fracture behavior [14]. An early study by Fischer et al. showed that there is a close correlation between the change in resistance through the thickness of the sample and crack length during the test [15]. This result indicated that it is possible to detect internal damage and crack propagation using resistance change methods and many subsequent studies have borne this out. Zhang et al. studied the use of MWCNTs in epoxy for use in detecting fatigue damage and crack growth by tracking volume resistance changes using $R = \frac{\rho l}{A}$ for volume resistivity and $dR/R = d\rho/\rho + dl/l - dA/A$, where R is resistance, ρ is resistivity, l is the conduction path length and A is the cross-section area. In a Mode I DCB test on 8-layer woven graphite fiber and MWCNT-epoxy composite samples, they found a high sensitivity of through-thickness resistance to the length and growth rate of delamination [16]. Many additional studies have shown the effectiveness of adding carbon nanotube fillers to normally nonconductive epoxy matrix composites for sensing damage in both carbon and glass fiber composites. Bogër et al. introduced conducting carbon black and CNTs as fillers in glass fiber and epoxy composites at 0.3 wt.%. Through a combination of ILSS and both static and dynamic tensile loading tests the authors showed a minimum 10% increase in resistance change values versus loading when compared to unmodified samples. In the cyclic loading case, they reported a rising and irreversible increase in resistance corresponding to building residual strain in the nanocomposites that further promoted the suitability of the technique for damage detection [17]. In a work reported by Park et al. single carbon fibers were immersed in epoxy polymers containing dispersions of CNTs, carbon nanofibers (CNF) and carbon black (CB) varying in volume percentage from 0.5% up to 50% in order to compare stress/strain sensing abilities. They first found that the CNT loaded composites had lower volume resistivity, $\sim 1 \times 10^2\,\Omega$ cm, compared to $\sim 4 \times 10^2\,\Omega$ cm for CNF for the same concentration of 2 vol%, whereas the carbon black samples did not show any conductivity below 7 vol%. Cyclic tensile loading combined with resistance change measurements taken from points on the embedded carbon fiber and around the perimeter of the carbon nanoparticle/epoxy matrix showed a high degree of correlation with increasing damage with even the lowest volume percentage (0.5%) of CNT/epoxy detecting resistance changes. Further results from pullout testing showed that the CNT/epoxy had the highest sensitivity to stress and strain when compared to the same concentrations of CNF or CB, indicating that inherent damage sensing ability [18]. A study by Thostenson on glass fiber/epoxy composites filled with a conducting carbon nanotube demonstrated the ability of the CNTs to form a sensing network for damage under several modes of failure and is the method is applicable to normally non-conducting composite systems. It was shown first that as little as 0.1 vol% of MWCNT in the composite resulted in a dramatic drop in resistivity corresponding to the formation of a percolation network of CNTs. The results showed that the sensing network could be used for accurately monitoring the onset and accumulation of microcracks. Notably, on successive loading of an already damaged specimen the resistance change curve increased significantly in slope, indicating that the sensing network may also be applied to testing the efficacy of self-healing methods, if the resistance curve moves back toward the undamaged reference after healing [19]. In a theoretical study of CNT filled composites Li et al. developed a resistor network finite element model to predict damage detection behavior. Their work suggests several modes of resistance increasing with matrix cracking depending on whether the crack is small enough to still allow electron tunneling, a reduction in tunneling or if the percolating network, and thus conducting path, is actually broken [20]. Some correlation to this result is reported in more recent work by Thostenson et al. on cyclic loading of CNT-Epon 862 epoxy and glass–fiber composites. Aside from detecting damage with resistance change, their SEM analysis showed the loading and eventual pull out of individual CNTs from the matrix and demonstrated that microstructural crack initiation and propagation can be sensed *in situ* [21].

Glass fiber composites were investigated in most of the above studies. CNT's capability of crack detection can be manifested in glass fiber composites whose electrical conductivity is very low. However, the out-of-plane electrical conductivity of carbon fiber composites with reasonable fiber volume fractions (>50%) could be higher than 10^{-1} S/m [22,23] and the crack propagation can be detected by measurement of the electrical resistance change even without incorporation of conducting nanoparticles such as CNTs as shown in Fischer et al.'s study [15]. In this study, hierarchical composites (hybrid of carbon fibers and CNTs grown on carbon fibers) concept was investigated to show increase in crack detection sensitivity of carbon fiber composites and advantages of this concept for real life applications.

2. Experimental setup

2.1. Sample fabrication

For this study the base materials are a plain weave carbon fiber fabric consisting of AS4 fibers provided by Hexcel Corp. and an epoxy resin matrix. The thickness of a single ply of fiber fabric is approximately 0.25 mm. Samples of the carbon–fiber fabric of approximately 25 mm × 100 mm were sent to the Frontier Energy and Electronic Materials Laboratory at Pohang University of Science and Technology (POSTECH) in Korea for chemical vapor deposition of multiwalled carbon nanotubes (MWCNTs) on the surface. The chemical vapor deposition process starts with the application by e-beam evaporation of a 1 nm Fe catalyst layer. Then, in an argon gas environment, the substrate is heated to either 993 K or 1023 K. For thirty minutes, hydrogen process gas and carbon-containing acetylene gas are bled into the reaction area so that carbon nanotube growth is initiated at the Fe sites. Acetylene is broken down at the surface of the Fe catalyst and carbon moves to the outside to start the formation of tubes. Lengths of the grown tubes were approximately 14 μm. A representative SEM image for each length of CNTs grown is shown in Fig. 1. These images show that dense 'forests' of aligned MWCNTs are created on the surface of the AS4 fabric. These 'forests' were grown either on a single side of the fabric or on both sides.

The epoxy resin is a two part system consisting of Epon 862 epoxy and EpiKure W curing agent (Miller-Stephenson Chemical Company, Inc.) in a 100/26.5 weight ratio of epoxy to curing agent. Epon 862 is a low viscosity epoxy resin made from epichlorohydrin