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NEW INSIGHTS INTO CONTROLLING SUB-MICRON FAILURE MECHANISMS IN COMPOSITES USING DISCRETE FUNCTIONALIZED MULTIWALL CARBON NANOTUBES

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ABSTRACT

New technology has been developed that enables multiwall carbon nanotubes to be discrete, high aspect ratio and well bonded to the composite matrix of choice. Several composite types are examined using tubes of diameter about 12 nm and length about 700nm. Fully discrete, well-bonded tubes are shown to significantly enhance the matrix resistance to fracture and can be placed between fiber plies of composites. The challenges of maintaining the exfoliated state of discrete multiwall carbon nanotubes during composite part assembly from the liquid prepolymer to the cured part are discussed.

INTRODUCTION

For enhanced durability and reliability in advanced matrix-fiber composites, the structure of composites from scales at the molecular level to the engineered part are important to select and control to maximize their resistance to failure initiation and crack growth [1-3]. In advanced aircraft composites, for example, the network structure of the crosslinked epoxy is managed with chemistry at the angstrom scale, and possibly with toughening agents such as block polymers at the nanoscale. The next level of structure is at the many micrometer scale with the fibers, and so on. Fracture initiation in these types of epoxy fiber matt composites under load often occurs at the sub-micron scale between fibers due to inter-laminar forces [4]. These sub-micron cracks then coalesce with time under load, leading to their catastrophic failure.

Carbon nanotubes with their individual tube properties of high tensile modulus (~800 GPa), and tensile strength (~100 GPa) are well-recognized to potentially improve both the impact as well the fatigue durability of epoxy composites. There are comprehensive reviews of the challenges of dispersing carbon nanotubes in epoxies and the subsequent mechanical properties [5,6]. In early work described by Sandler et al., multiwall carbon nanotubes, MWNT, from Hyperion were dispersed in a bisphenol A epoxy up to 0.15% wt. Although addition of the MWNT showed some mechanical performance improvement, the tubes were seen to be agglomerated [7]. Agglomerations generally act as structural defects. In attempts to transfuse fiber mat reinforced composites with MWNT-modified epoxy, the MWNT agglomerations are filtered by the fiber mat.

Studies by Gojny et al. [8] illustrated that oxidizing the surfaces of MWNT can improve their dispersion and bonding in epoxy, but they still obtained agglomerates. Surfactant modified MWNTs as well as extensive mixing methods using sonication and high rate shear were also studied [6]. Zang et al. have shown the toughness of cycloaliphatic epoxy resin (ERL-4221) was improved by using a

combination of hydroxyl group functionalized MWNT's, high shear rate mixing and sonication [9]. A significant increase in the tensile strength of the composite from 32 to 60 MPa was obtained by adding less than 0.5% wt. of functionalized MWNTs. Scanning electron microscopy demonstrated the nanofiber-crack bridging mechanisms of toughening. However, at 1% wt. functionalized MWNT and above a significant reduction in strength was seen due to agglomerations of the tubes. Thus, the challenge still remains to maximize the performance gains theoretically possible with MWNT addition to epoxy composites. Success will entail obtaining effective dispersion of MWNT at higher concentrations, selecting MWNT aspect ratio for the balance of resin viscosity for composite manufacturing and mechanical performance, and bonding of the discrete MWNT to the matrix during epoxy curing.

Multiwall carbon nanotubes are commonly made from catalytic chemical vapor deposition techniques. They usually consist of macro-clusters of entangled tubes ranging in diameter from 10-500 μm. Individual MWNT lengths are in excess of 4-10 μm. Molecular Rebar Design LLC has developed a commercial process to produce functionalized MWNT, Molecular Rebar™, MR, that have an average diameter around 12 nm with an aspect ratio around 60 which allows for an excellent balance of resin viscosity and mechanical performance at a given loading [10]. As the surface area of the discrete carbon nanotubes is about 200 m^2/gram, small changes in the thermodynamic interaction of the tube surface and the matrix can result in re-agglomeration after initial dispersion of the tubes, for example during curing due to chemical and thermal variations. Consequently, to maintain both their discrete nature and to be well-bonded to the matrix requires the MWNT functionalization to be carefully tailored, dependent on the epoxy resin type and hardener, composite assembly and curing conditions of time and temperature.

MATERIALS AND TESTING

Several epoxy systems with tailored functionalized MR have been evaluated, including cycloaliphatic epoxy with methyltetrahydrophthalic anhydride hardener, bisphenol F and bisphenol A epoxies with diethylenetetramine and tetra-ethylenetetramine (TETA) hardeners, and tetra-functional epoxy Araldite MY 721 with 3,3'-diamino-diphenylsulfone hardener. Investigations have included, prior to mixing and curing, putting MR into the epoxy and the hardener components, either singly or in both. Before curing, the mixtures were degassed at 50°C and partial vacuum for an hour. Each epoxy resin type requires its own curing profile which was obtained from the resin supplier. Control plaques with no MR were made following the same procedure.

Mechanical properties were determined with a MTS Instron 3367. Samples were tested in tensile mode at 0.83mm/s at 25°C. Single edged notched specimen (3 to 4 mm in thickness, 12.5 mm width) of razor notch 1mm depth were tested in tension at a rate of 0.25 mm/s at 25°C. No pre-crack was introduced using fatigue loading. Fatigue testing was performed on the same notched specimen depth with conditions $\sigma_{min}/\sigma_{max}$ 0.1, σ_{max} in the range 16-23 MPa, frequency 1Hz, 25°C. The curing characteristics and glass transitions were determined using a TA DMA Q800 with a heating rate of 5°C/min from 50 to 350°C at a strain of 0.03% and at 1Hz.

RESULTS AND DISCUSSION

On addition of 0.5% wt. MR in bisphenol F epoxy cured using TETA, the tensile modulus increased by 30% and the tensile strength by about 25% (68 MPa for the neat cured resin and 86 MPa for the composite) with retention of strain to break versus the control (about 0.1). Kq values obtained from single edged notched tensile specimen with 0.5% wt. MR also showed much improvement, 1.05 $MPa.m^{0.5}$ versus the control at 0.72 $MPa.m^{0.5}$. Optical micrographs of the specimen fracture surfaces of the control bisphenol F epoxy and with 0.5% wt. MR are shown in Figure 1. The razor notch is seen on the left of the figure. Observed is the characteristic pop-in representing the fracture initiation site, a region of slow crack growth seen by a rough surface texture, followed by the rapid crack growth region seen as a smooth surface. Of note, the MR significantly reduced the size of the pop-in region even though the stress at failure is higher. The extended region of slow crack growth across the specimen width for the samples with MR is consistent with the higher Kq values.

For a bisphenol F epoxy containing 1% wt. MR closer examinations of the gold-sputtered fracture surface in the slow crack growth region, close to the pop-in region, are shown in Figures 2a&b at 10,000x and 124,000x magnification, respectively. First, in Figure 2a the MR is seen to be discrete and

uniformly dispersed. The fracture surface is characteristic of coalescence of multiple small planar cracks of size about 0.1-0.2 um, that coalesce further to domains of about 1-2 μm. Seen in Figure 2b, the tubes have good bonding to the epoxy matrix. Some lengths of tubes are observed as would be expected from a crack bridging mechanism; however, holes in the surface that would be characteristic of some fiber pull-out were not observed, although they may have been covered by the gold sputtering. Another thought is that tubes with length in the plane of the crack growth have debonded. Many tubes have observed to have been snapped close to the fracture surface. The fast fracture region of the same specimen is shown in Figure 3. The surface is smooth and carbon nanotubes have been snapped very close to, or at the crack surface. Of note, no carbon nanotubes were observed lying on the surface.

Fatigue testing of the notched specimen highlighted the increased fracture initiation and growth resistance on addition of MR to bisphenol F epoxy. Below K_{max} 0.35 MPa.m$^{0.5}$ the unmodified bisphenol F epoxy failed within 1000-3000 cycles, whereas with 0.5% MR addition the samples lasted over 17,000 cycles.

Studies are in progress with higher Tg (200°C) epoxy Araldite MY 721 of the type currently being used in composites with carbon fibers for aircraft. These epoxies are generally brittle and very difficult to toughen. As stated earlier a key goal is to place the MR between fibers to increase the interlaminar crack resistance. A simple experiment was conducted to see if the carbon fiber matt would allow the MR to pass through without filtering. An aluminum plate was laid flat in the oven at 120^{0}C and a spatula of resin mix with MR was placed on the plate. A piece of both Twill Weave and Plain Weave 3k 5.7oz AS4 Aerospace Grade carbon fiber fabric was used to cover the two puddles of resin and a tongue depressor used to press the fabric into the resin mix. Black resin immediately was visible covering the top of the fabric indicating the MR was not filtered out. A top plate was clamped to cover the resin mixture and the sample cured. The cured composite was microtomed to slices of about 60 μm thickness and Figure 4 shows a typical STEM micrograph of the composite at 50,000x. Individual tubes of MR are seen in the resin phase with no aggregates found. Mechanical property evaluations are in progress.

CONCLUSIONS

Functionalized carbon nanotubes have been made that provide significant improvements in the durability of epoxies. The surfaces of the tubes must be specifically tailored to maintain discrete tubes within the resin after curing with the hardener. Furthermore, the tubes must also have a measure of bonding to the network after curing. Once the carbon nanotubes are discrete they can pass through and distribute within the spaces of the glass or carbon fiber mats of the composites where, after curing, they are expected to provide enhanced interlaminar crack initiation and growth resistance.

ACKNOWLEDGEMENTS

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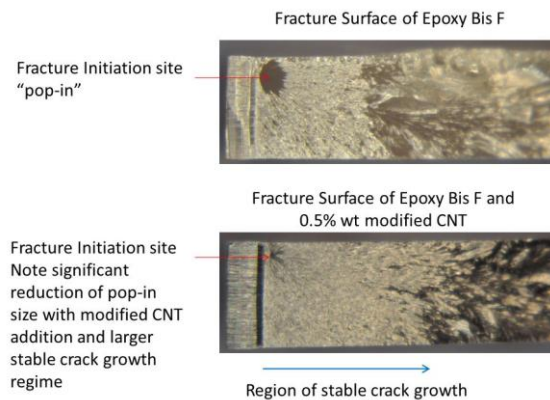
Figure 1. Optical micrographs of the fractured edge-notched specimen of bisphenol F epoxy, above unmodified epoxy, below with 0.5% wt. MR
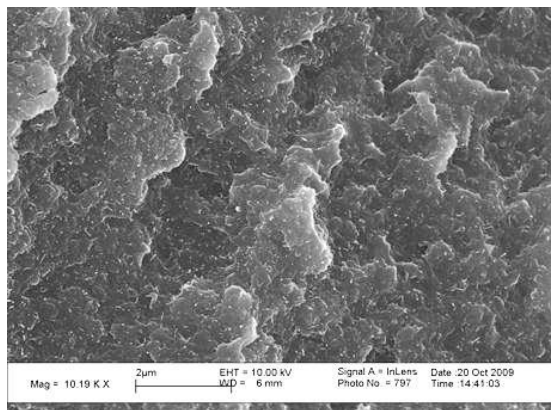

Figure 2a. SEM micrographs of the fractured edge-notched specimen of bisphenol F epoxy modified by 1.0 % wt. MR close to the pop-in site of fracture initiation at magnification 10 Kx.
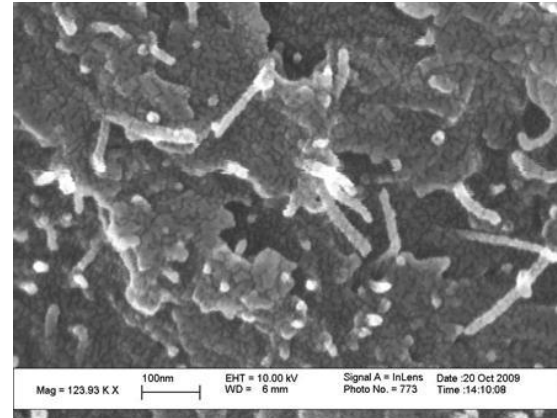

Figure 2b. SEM micrographs of the fractured edge-notched specimen of bisphenol F epoxy modified by 1.0% wt. MR close to the pop-in site of fracture initiation at magnification 124 Kx.
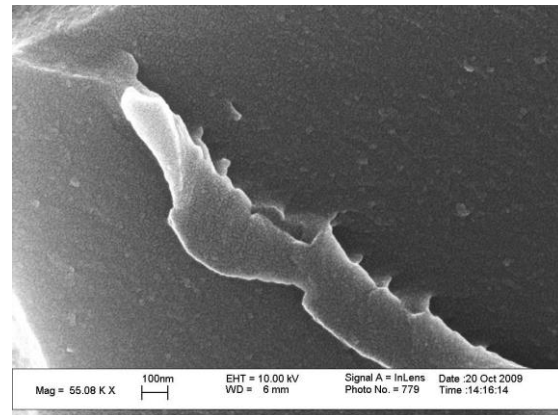

Figure 3. SEM micrographs of the fractured edge-notched specimen of bisphenol F epoxy modified by 1.0% wt. MR in the unstable fracture region at magnification 55 Kx.
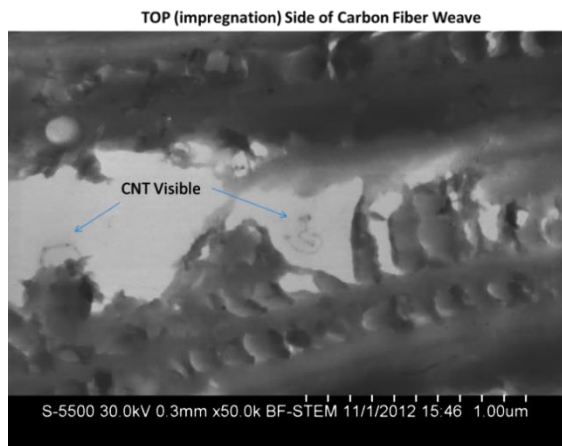
Figure 4. STEM micrographs of microtomed Araldite MY 721 epoxy with 0.3% wt. MR and carbon fiber matt at magnification 50 Kx.