

Mechanical Characterization of Nanofiber-Reinforced Composite Adhesives

L. Roy Xu^{1,*}, Lang Li², Charles M. Lukehart², and Huacheng Kuai¹

¹Department of Civil and Environmental Engineering and ²Department of Chemistry, Vanderbilt Institute of Nanoscale Science and Engineering, Vanderbilt University, Nashville, TN 37235, USA

Tensile and shear strength tests of metal/metal and polymer/polymer joints featuring a new functionalized nanofiber/epoxy composite adhesive were conducted. Strength increase is not as high as we expected (only up to 30%) although we used GCNF-ODA reactive linkers to improve the interface. The moderate strength increase is due to high interfacial stress developed in nanocomposites because of the high stiffness property mismatch, and inefficient interfacial shear stress transfer through shear-lag mechanism. In order to design strong nanocomposite materials, continuous or at least aligned nanofibers/nanotubes should be employed.

Keywords: Adhesive Joints, Nanocomposite Materials, Graphite Nanofibers, Mechanical Property.

Since carbon nanotubes have extraordinary mechanical properties, they tend to be used as reinforcements in polymers and other matrices to form so-called “nanocomposite materials.”^{1–9} Nanocomposites are a novel class of composite materials where one of the constituents has dimensions in the range of 1–100 nm. Alternative reinforcement materials for nanocomposites include nanofibers, nanoplatelets, nanoclays, etc. In order to develop nanocomposite materials with excellent mechanical properties, strong chemical bonding between the reinforcement and the matrix is a necessary, but not sufficient condition. Zhong et al.⁶ employed Graphitic Carbon Nano-Fibers (GCNFs) as reinforcements in polymeric matrix nanocomposites. Strong and stiff GCNFs (Young’s modulus $E > 600$ GPa) have average diameters as small as 25 nm and demonstrate atomic structures such that edge carbon atom surface sites are present along the entire length of the carbon nanofiber. Chemical modification of these surface carbon sites and subsequent reaction with bifunctional linker molecules provides surface-derivatized GCNFs that can covalently bind to polymer resin molecules. This nanofiber/polymer covalent binding is expected to delay interfacial debonding. So far, it has been difficult to quantify the improved interfacial bonding between the matrix and the nanofibers accurately (i.e., by direct measurement at the nano-scale). However, mechanical properties of the final macro-scale nanocomposite materials can be easily measured using various kinds of standard

tests for engineering materials. Our macro-scale mechanical property characterizations including bending, tensile, and fracture properties (the minimum specimen dimension is 5 mm) showed that there was only very little increase in mechanical properties of nanocomposites, although we used reactive linkers to improve the fiber/matrix interface as reported by Xu et al.⁹ Therefore, we decide to reinforce adhesive layers using nanofibers because the thickness of an adhesive layer is usually several microns, which is close to the length of a nanofiber. Also, several micro-cracks will occur inside the adhesive layer if the adhesive joint is subjected to shear load,¹⁰ so nanofibers may provide resistance to suppress these micro-shear cracks and improve shear strengths. As shown in Figure 1, this type of new adhesive is expected to apply to metal/composite joints.

GCNFs having a herringbone atomic structure were prepared and surface derivatized by covalently attaching 3,4'-oxydianiline (ODA) linker molecules to surface carbon sites at a number density of ca. 1 ODA group/300 total bulk C atoms. These GCNF-ODA nanofibers contain a pendant primary amino functional group. Reaction of these derivatized nanofibers with butyl glycidyl ether (an epoxy resin monomer) under ultra-sonication gives reactive carbon nanofibers (r-GCNF-ODA) of small average length in which the surface linker molecules have been chemically terminated with epoxy resin-like functional groups. Herringbone-type carbon nanofibers were grown by the interaction of a carbon source gas with mixed-metal powder growth catalyst. Detailed procedures on synthesis of herringbone GCNFs and GCNF-ODA are described in

*Author to whom correspondence should be addressed.

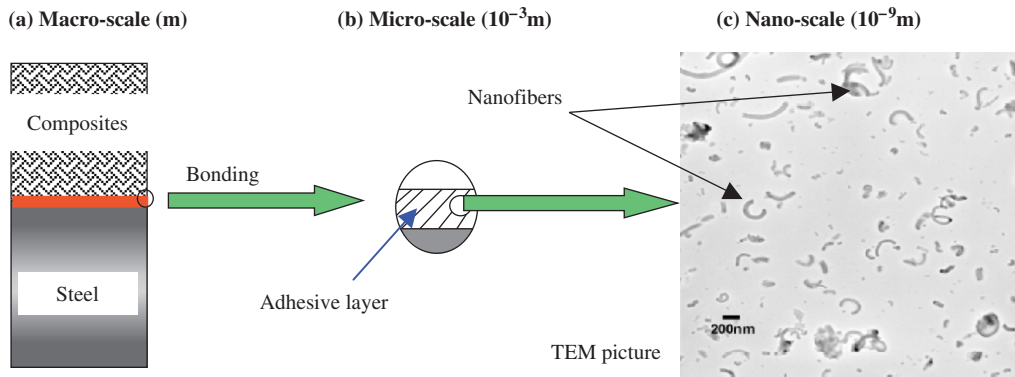


Fig. 1. A multi-length-scale illustration of nanocomposite bonding.

Zhong et al.⁶ As-prepared herringbone GCNF and surface-derivatized GCNF-ODA nanofibers have dimensions of 50 to 200 nm in diameter and 5 to 10 microns in length.

The derivatized GCNF-ODA nanofibers were used as reinforcement additives to form nanocomposite materials. Commercial bisphenol A type epoxy resins such as Epon[®] 826 and Epon[®] 828 from Miller-Stephenson Chemical Company Inc., were used as matrix materials (100 parts in weight), and borontrifluoride-monoethylamine (BF₃-MEA) (Aldrich Chemical Company) was used as the curing agent (2.75 parts in weight). Blends of epoxy, curing agent and nanofibers were mixed at a temperature of 90 °C, sonicated at controlled power levels and duration, filtered to remove any residual large agglomerated particles, and cast into a standard mold. Air bubbles were eliminated by placing the composite samples in a vacuum oven and then cured at 120 °C for one hour and then 170 °C for two hours, followed by cooling at the natural cooling rate of the oven. In Figure 1, for a sonicated nanocomposite sample, uniform dispersion of nanofibers inside the epoxy resin was observed in a transmission electronic microscopy (TEM) micrograph. Two types of adhesive joints were employed to test nanofiber-reinforced adhesives: aluminum to aluminum and PMMA to PMMA (Plexiglas). These bonding surfaces are sand-blasted before the adhesive is applied to these bonding areas.

The nanofiber composites in this investigation contain randomly distributed nanofibers so their macro-scale mechanical properties are effectively isotropic. Also, since the nanofiber dimension and volume are quite small, the nanocomposites can be approximated as homogenous materials. Hence, we mainly use test standards for polymeric materials to evaluate the mechanical properties of nanocomposite materials. Butt-joint tensile tests and Iosipescu shear tests were conducted to characterize mechanical properties of the nanocomposite bonding. All tests were conducted on an MTS 810 testing machine and the loading rate was 1.0 mm/min. About 4–6 specimens in each group and several different groups with different processing conditions and fiber contents were tested.

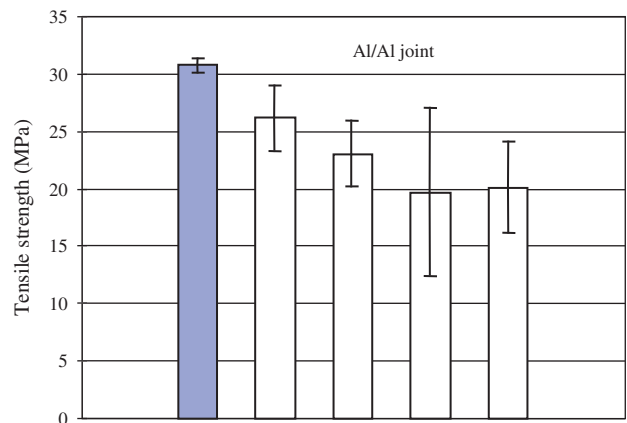


Fig. 2. Tensile strength comparisons of various Al/Al bonds featuring nanofiber-reinforced composites with different fiber weight percents and processing conditions (left bar—pure epoxy bonding).

Figure 2 shows tensile strength comparisons of various aluminum-to-aluminum bonds featuring nanofiber-reinforced adhesives with different fiber weight percents and processing conditions (left bar—pure epoxy bonding). All the tensile strengths with nanofiber-reinforced adhesives are below the tensile strength featuring pure epoxy.

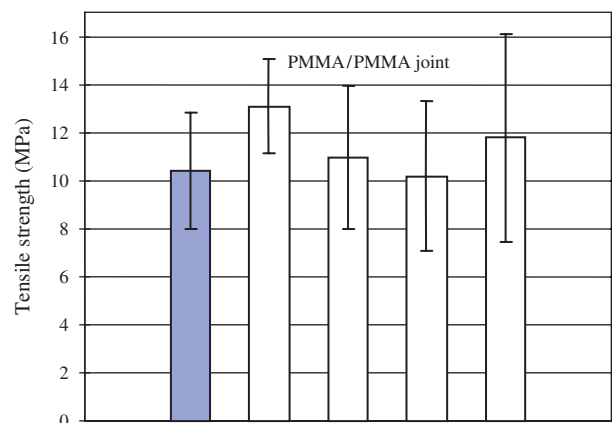


Fig. 3. Tensile strength comparisons of various PMMA/PMMA bonds featuring nanofiber-reinforced composites with different fiber weight percents and processing conditions (left bar—pure epoxy bonding).

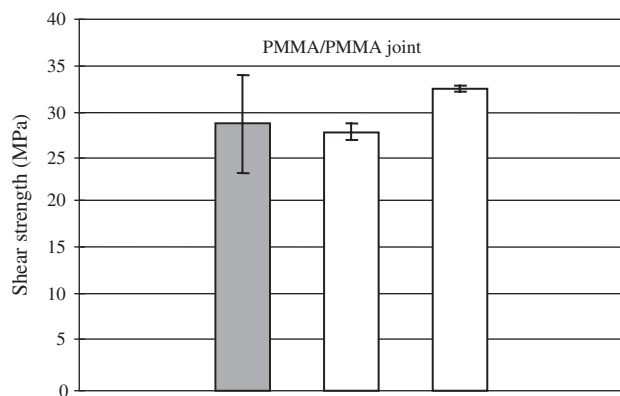


Fig. 4. Shear strength comparisons of various PMMA/PMMA bonds featuring nanofiber-reinforced composites with different fiber weight percents and processing conditions (left bar—pure epoxy bonding).

Very small initial debonding areas were found after we examined the failed bonding surface. These debonding which are induced in processing lead to strength reduction in nanofiber-reinforced adhesives. Figure 3 shows tensile strength comparisons of various PMMA/PMMA bonds featuring nanofiber-reinforced adhesives with different fiber weight percents (from 0.3–0.8 weight percent) and processing conditions (from low to high level sonication). We find that almost all the tensile strengths of nanofiber adhesives exceed the tensile strength of pure epoxy bonding (increase up to 30%). However, the shear strengths of the nanofiber adhesives are almost same as the pure epoxy as seen in Figure 4. Therefore, our conclusion is that very limited strength increase is achieved for nanofiber-reinforced adhesives.

The limited strength increase in our previous large specimens (in terms of mm) to current nanofiber-reinforced adhesives (in terms of micron) is due to the same mechanics factor. Although discontinuous nanotubes/nanofibers with high strength and stiffness, when added as reinforcement to matrices, are undermined by the high stress singularity at the fiber–matrix interface,¹¹ and also by inefficient

interfacial shear stress transfer through shear-lag mechanism. Thus the strong nanofiber or nanotubes cannot carry high load. However, continuous forms of nanofibers or nanotubes without finite ends, on the other hand, preclude the presence of extra matrix material at the ends of fibers and hence eliminate stress concentration/shear-lag stress transferring. For future nanocomposite material design with an objective of strength or fracture toughness increase, nanofibers or nanotubes should be very long or at least aligned although it is new challenging from the material development and processing viewpoint.

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