Nanocomposite Adhesive Bonding Using Graphite Nanofibers

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Summary

Graphitic carbon nanofibers were used to reinforce epoxy resin to form nanocomposite adhesive bonding. Good dispersion and polymer wetting of the GCNF component is evident on the nanoscale. Tensile and shear joint strength measurements were conducted for metal-metal and polymer-polymer joints using pure epoxy and nanocomposite bonding. Very little bonding strength increase, or some bonding strength decrease, was measured.

Introduction

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 [1-3]. Nanocomposites are a novel class of composite materials where one of the constituents has dimensions in the range between 1 and 100 nm [4]. Wagner [5] reported that load transfer through a shear stress mechanism was seen at the molecular level. It has been reported that nanotubes increased the composite strength by as much as 25% [6]. However, multi wall nanotubes (MWNTs) are limited in their applications because of weak inter-shell interactions [7]. Single wall nanotubes (SWNTs) on the other hand are quite expensive and difficult to manufacture. Alternative reinforcement materials for nanocomposites include graphitic carbon nano-fibers (GCNFs) and graphite nanoplatelets etc [8]. GCNFs also have excellent properties and can be used as reinforcements in various kinds of matrices. They offer chemically facile sites that can be functionalized with additives thereby resulting in a strong interfacial bond with the matrix. Generally, the three main mechanisms of interfacial load transfer are micromechanical interlocking, chemical bonding and the weak van der Waals force between the matrix and the reinforcements [9]. In order to form a nanocomposite material with excellent mechanical properties, strong chemical bonding between the reinforcement and the matrix is a necessary condition, but might not be a sufficient condition. From the length-scale argument it is known that the effective toughening may not be energetically favorable at the nano length-scale [10]. This generally necessitates a filler size greater than 100 nm [11]. However, there might be significant difference in mechanical behaviors between a continuous fiber reinforced composite and a nanofiber reinforced composite, even if both have very strong interfacial bonding. It has been proved that a continuous fiber reinforced composite can effectively

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arrest the propagation of a major crack, while the short nanofiber/nanotubes might not have this kind of effect [12]. Here the length of nanofibers/nanotubes plays an important role in the toughening mechanism of nanocomposites as reported in some recent investigations [13-15].



Figure 1: (a) Nano-fiber reinforced adhesive bonding applied to a hybrid metalpolymer joint (b) Transmission Electron Microscope (TEM) image of nanofibers as uniformly dispersed in epoxy matrix

Graphitic carbon nanofibers (GCNFs) are attractive additives for fabricating carbon fiber/polymer composite materials of enhanced strength and electrical conductivity due to their unusual atomic structure. Greatly enhanced performance of nanocomposite materials reinforced with nanotube or nanofiber additives has not been fully achieved because of difficulties in achieving efficient dispersion and wetting of the nanoscale component within the matrix material, even when using surface-functionalized additives. We now report the fabrication of GCNF/epoxy nanocomposites using CGNFs to reinforce an epoxy resin. As illustrated in Fig.1 (a), nanofiber-reinforced adhesives will be used to bond hybrid joints of metals and polymers. Processing conditions have been optimized to give a hybrid material containing derivatized carbon nanofibers highly dispersed within a thermoset matrix. In the present study, ultrasonic methods, including low-power sonication using an ultrasonic cleaner and high-power sonication using a commercial sonifier, are investigated as a means to disperse nanofibers in epoxy resin and to initiate nanofiber/epoxy resin covalent binding. The dispersion quality of the resulting hybrid nanocomposite is clearly seen in a TEM picture as seen in Fig. 1(b).

Experimental Procedures

Herringbone-type carbon nanofibers were grown by the interaction of a carbon source gas with mixed-metal powder growth catalyst. Iron-copper powder with

atomic ratio of 7:3 was prepared by the co-precipitation of the respective metal nitrate solutions with ammonium bicarbonate. The precipitate was dried in an oven at 110 °C and ground into fine powder. This powder was put into a quartz boat in a horizontal tubular furnace and was converted into metal-oxides mixture by calcining in air at 400 °C for 4 h. The growth of carbon nanofibers was completed at 600°C after 90 min. The product was cooled to room temperature under helium. The collected oxidized GCNFs were washed with deionized water until the filtrate reached a pH value of about 7 and then were dried in vacuum at room temperature. The drv oxidized GCNFs were activated by reaction with thionyl chloride at 70 °C for 24 h with a small amount of dimethylformamide (DMF). The reaction mixture was cooled and then filtered. The collected fibers were washed with tetrahydrofuran (THF) under nitrogen until the supernatant was clear. The as-prepared GCNFs were used as reinforcement to nanocomposite bonding. A commercial epoxy resin, DER 736, was used as the epoxy matrix material. Blends of epoxy, curing agent and nanofibers were mixed at room temperature, sonicated at controlled power levels and duration, filtered to remove any residual large agglomerated particles. After vacuum degassing for one hour at 40°C, the nanofiber-reinforced adhesive was applied onto the bonding surfaces of the joint specimens. Then, the fixture was put into an oven and the specimens were cured at 60°C overnight.

Due to their simplicity, the Iosipescu shear and butt-joint tension tests were conducted for the characterization of shear and tensile bonding strengths. An MTS 810 testing machine was used and the loading rate was 1 mm/min. In order to understand the possible stress field change between a standard Iosipescu shear specimen (one material) and a bonded Iosipescu shear specimen (dissimilar materials), finite element analysis has been conducted for accurate shear strength measurements.

Results and Discussion

Fig. 2 shows tensile strength comparison of two joints using nanocomposite bonding. It is not surprising to see a decrease in strength of aluminum/aluminum joints since initial defects were easily introduced in the processing of nanocomposite materials. However, some joint strength increase was achieved in PMMA/PMMA joints. Shear strength tests also revealed a similar trend. More bonding strength measurements will be conducted for further investigation. The low strength increase of nanofiber composites is due to interfacial stress transfer and interfacial failure, which is caused by a severe property mismatch between nanofibers and matrices.

It is generally true that the stiffness of nanocomposites could be improved although the waviness and agglomeration of nanotubes/nanofibers will significantly affect the stiffness properties. The strengths or fracture toughness values of nanocom-



Figure 2: Tensile strength comparison of Aluminum/Aluminum and PMMA/PMMA bonds featuring nanofiber reinforced composites with different fiber weight percents and processing conditions (left bar-pure epoxy bonding)

posite materials could be slightly lower than that of pure matrices [15]. Hence, we should pay great attention to the presence of stress singularity at the ends of nanofibers/nanotubes inside a matrix. It is well known that a high stress singular-

ity/concentration occurs at the locations where discontinuity either in material or geometry exists [16]. It was found that interfacial shear stress concentration is quite high when the moduli ratio of the fiber and the matrix E_f/E_m is high [17]. These results based on previous traditional composites are still applicable to nanocomposite materials although the Young's moduli of nanofibers or nanotubes are much higher than the Young's moduli of any other traditional reinforcements. Therefore, the interfacial shear stress singularity/concentration of the nanocomposite should be much severe than that of traditional composites. In order to characterize the stress singularity/concentration at the interface between the matrix and reinforcements, we mainly use two Dundurs' parameters (α and β) to characterize the Young's modulus and bulk modulus for nanotubes or nanofibers so far, we only employ one Dundurs' parameter to analyze nonocomposites:

$$a = \frac{E_f - E_m}{E_f + E_m} \tag{1}$$

We compare two composite systems with the same epoxy matrix (Young's modulus E=2.6 GPa [18]) reinforced by E-glass fibers (E =72 GPa) and nanofibers (E=600 GPa). Obviously, $\alpha_{nanofiber/epoxy}=0.99 > \alpha_{glass/epoxy}=0.93$ and β , which can be calculated if we know the bulk modulus or Poisson's ratio of nanofiber/nanotubes, should be quite large too for nanofiber/nanotubes composites. Since these two material constants are related to property mismatch and interfacial stress, we can conclude that the interfacial stress level is quite high in nanocomposite materials. Higher interfacial stress will be directly related to the final failure strain of nanocomposites so it is probably the major reason contributing to the low failure strains in nanocomposites over their matrices. Although the composite stiffness can be increased by some degree, the final strength of the composites is determined by the failure strain of the nanocomposites. Therefore, it is not surprising that the nanocomposite strength is even less that that of the pure matrix if the failure strain is determined by interfacial failure between the matrix and the nanoscale reinforcement.

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