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Dynamic fracture of carbon nanotube/epoxy composites under high strain-rate loading

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ABSTRACT

We investigate dynamic fracture of three types of multiwalled carbon nanotube (MWCNT)/epoxy composites and neat epoxy under high strain-rate loading (10^5–10^6 s^{-1}). The composites include randomly dispersed, 1 wt%, functionalized and pristine CNT/epoxy composites, as well as laminated, ~50 wt% CNT buckypaper/epoxy composites. The pristine and functionalized CNT composites demonstrate spall strength and fracture toughness slightly higher and lower than that of neat epoxy, respectively, and the spall strength of laminated CNT buckypaper/epoxy composites is considerably lower; both types of CNTs reduce the extent of damage. Pullout, sliding and immediate fracture modes are observed; the fracture mechanisms depend on the CNT–epoxy interface strength and fiber strength, and other microstructures such as the interface between CNT laminates. Compared to the functionalized CNT composites, weaker CNT–epoxy interface strength and higher fiber strength lead to a higher probability of sliding fracture and higher tensile strength in the pristine CNT composites at high strain rates. On the contrary, sliding fracture is more pronounced in the functionalized CNT composites under quasistatic loading, a manifestation of a loading-rate effect on fracture modes. Despite their helpful sliding fracture mode and large CNT content, the weak laminate–laminate interfaces play a detrimental role in fracture of the laminated CNT buckypaper/epoxy composites. Regardless of materials, increasing strain rates leads to pronounced rise in tensile strength and fracture toughness.

1. Introduction

Dynamic response of polymers and their composites is of broad interest for many engineering applications as well as fundamental understanding of structure–loading–property relations under elevated stresses and strain rates as in shock wave loading. Previous studies investigated shock response of the elastomer polychloroprene [1], compression and release behaviors, and dynamic shear strengths of glass fiber-reinforced polymer composites [2,3], shock equation of state of carbon-fiber epoxy composite [4], the effect of orientation on the shock response of a carbon fiber-epoxy composite [5], dynamic tensile strengths of a glass fiber reinforced epoxy composite [6] and of organic fiber-reinforced epoxy microcomposites [7], and punch damage of a woven carbon fiber reinforced-epoxy composite with carbon nanotube additions [8]. Mechanical properties of composites depend on such factors as composition, spatial distribution and geometry of fillers, and manufacture processes, giving rise to complexities in describing and predicting their performances under different loading conditions. For instance, fracture of glass- and organic-fiber (10 μm in diameter) reinforced epoxy composites is investigated with plate impact experiments, and it is found that introducing fibers into the matrix may have positive or negative effects on the mechanical properties such as dynamic tensile or spall strength, σ_{sp} [6–8]. At smaller fiber sizes (10 nm scale), nanomaterials offer opportunities for developing novel nanocomposites [9–12], and characterizing mechanical properties of such materials under dynamic loading and revealing underlying mechanisms are of immediate necessity.

Owing to their remarkable mechanical, electronic and thermal properties [13–15], it is of great interest to use carbon nanotubes (CNTs) to reinforce polymers, including the epoxy resin which is one of the most important thermosetting polymers [9–12]. However, a technical issue is how to disperse CNTs homogeneously in a polymer, since CNTs tend to become highly entangled due to

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their huge aspect ratios, and this agglomeration is detrimental to the mechanical properties of the resultant composites. The fiber–matrix interface strength ($\sigma_{f\text{-}m}$), and the tensile strength or fiber strength (σ_f) of CNTs, are also contributing factors. Higher $\sigma_{f\text{-}m}$ indicates improved compatibility of two phases of composites and facilitated stress transfer from the matrix to CNTs, but excessive $\sigma_{f\text{-}m}$ can be counterproductive since it may reduce the probability of frictional sliding to accommodate deformation for energy dissipation [7,16,17]. Higher fiber strength is always beneficial. In quasi-static or *low strain-rate* loading, three fracture modes were identified in MWCNT/epoxy composites [16,18]: pullout, sliding fracture and immediate fracture; apparent tensile strength and fracture toughness of the composites are improved for functionalized CNTs because of the elevated $\sigma_{f\text{-}m}$ and sliding fracture mode, despite a decrease in the CNT tensile strength.

Despite the potential applications of CNT/epoxy composites to dynamic extremes, high strain-rate loading experiments on such materials are essentially nonexistent. Characterizing their properties under high strain rates and revealing underlying mechanisms are important to materials design for high strain-rate loading. Since fiber sliding and fracture are strain-rate dependent [6,7,15,19–22], we investigate in this work damage of nanocomposites under high strain-rate planar impact loading (strain rate $\dot{\varepsilon} \sim 10^5$—$10^6$ s^{-1}). We explore low CNT-content, functionalized and pristine, MWCNT/epoxy composites to examine the effects of $\sigma_{f\text{-}m}, \sigma_f$ and $\dot{\varepsilon}$. In order to significantly increase the CNT content, we fabricate laminated, MWCNT buckypaper/epoxy composites. High CNT content can not be achieved simply via random mixing of CNTs with epoxy, because CNTs agglomerate and become highly entangled in epoxy. To circumvent this issue, buckypaper layers [23–26] are stacked to form a bulk, high effective CNT-content, CNT/epoxy composites. We perform gas gun impact loading with *in situ* velocimetry on these three types of CNT composites as well as neat epoxy for comparison, and the shock-recovered samples are examined with scanning electron microscope (SEM). Our results suggest that fracture mode and tensile strength are loading rate- and microstructure-dependent. In particular, higher $\sigma_{f\text{-}m}$ does not necessarily lead to better performances under high strain-rate loading of nano/microfiber-epoxy composites.

2. Materials and methods

We use bisphenol-A epoxy with an epoxy equivalent weight of 185 g/eq to synthesize the neat epoxy resin. The curing agent, Albidur HE600, is 4-methylhexahy-drophtahlic anhydride accelerated with a trace amount of tertiary amine. The MWCNTs (Baytubes C 150P, from Bayer Material Science AG) are synthesized in a high-yield catalytic process via chemical vapor deposition, and the C content is more than 95 wt%. The length of multiwalled CNTs ranges from 1 μm to 10 μm, and their outer and inner diameters are about 15 nm and 4 nm, respectively. To improve the CNT–epoxy interfacial bonding, some MWCNTs are treated with ozone for 4 h at ambient temperature [27].

To prepare CNT/epoxy composites with randomly mixed CNTs, we disperse pristine (unfunctionalized) or ozone-treated (functionalized) multiwalled CNTs within the neat epoxy resin in a high-speed dissolver, and a master batch containing 2 wt% CNTs is prepared. The master batch is further processed using a three-roll mill; the mill is composed of three adjacent cylindrical rolls which turn at different angular velocities. The first and third rolls rotate in the same direction while the center roll rotates in the opposite direction. We optimize the gap and nip force between rolls to achieve high shearing stresses in order to break up the nanotube agglomerates and generate highly dispersed nanotube/epoxy dispersion. The master batch is then diluted in an appropriate amount of neat epoxy resin and mechanically mixed with anhydride curing agent at 60 °C. The suspension is de-gassed, poured into preheated steel molds, and cured in an oven. We use a four-step curing procedure: 30 min at 90 °C, 60 min at 120 °C, 30 min at 140 °C, and finally 120 min at 160 °C. After curing, the samples are cooled down slowly to room temperature in the oven. The composites prepared with pristine and functionalized CNTs are referred to P-CNT and F-CNT composites, respectively, and the CNT content is about 1 wt%. More details can be found in Refs. [16–18,28,29]. Previous studies show that F-CNTs improve the CNT–epoxy interfacial strength $\sigma_{f\text{-}m}$ [9,16,18,29], but the tensile strength σ_f of F-CNTs is reduced relative to P-CNTs [17].

In addition, we synthesize ~50 wt% laminated MWCNT buckypaper/epoxy composites (L-CNT). The buckypaper/epoxy laminates, with 52.8 wt% buckypaper and 47.2 wt% epoxy, are prepared through a prepreg molding process. Buckypaper is fabricated by vacuum filtration method. The MWCNTs (6–8 nm in diameter, up to 50 μm in length, and purity > 93%; FloTubeTM 7000, CNano Technology Ltd., Beijing, China) are ultrasonically dispersed in deionized water with the aid of the surfactant (Triton X-100); the dispersion is centrifuged at 4000 rpm for 30 min to eliminate the catalyst and aggregations. Thereafter, the supernatant is filtrated through a polyvinylidene fluoride microporous filter membrane under vacuum. After filtration, the buckypaper is thoroughly washed with plenty of deionized water to remove the adsorbed surfactant, dried in air, and peeled off from the filter membrane carefully. More details of buckypaper fabrication were presented elsewhere [23–26]. The same epoxy system is used to infiltrate the buckypaper. The epoxy is mechanically mixed with the cure agent at a stoichiometric ratio at 60 °C for 30 min. The mixture is degassed to remove the air bubbles in a vacuum oven and afterwards diluted by acetone to adjust the viscosity. The buckypaper is then soaked in the epoxy solution at 40°C to be fully infiltrated by the resin with the aid of vacuum. After the acetone is completely volatilized, the buckypaper is retrieved from the resin (referred to as prepreg). The prepregs are stacked into the mould layer by layer, vacuumed and compressed in a press at 0.1 MPa to eliminate the bubbles and redundant resin between the layers. The sample is cured in an oven under some weights (the effective pressure is approximately 0.1 MPa), following the same curing procedure as the randomly mixed system. Finally, the cured sample is cooled slowly to room temperature in the oven and machined to the desired dimensions.

The initial densities (ρ_0) of epoxy, F-CNT, P-CNT and L-CNT as measured with the Archimedes' method are 1.18–1.24 g cm^{-3}. Their longitudinal sound velocities (C_L) determined from ultrasonic measurements also vary in a narrow range of 2320–2400 m s^{-1}. The Poisson's ratio $\nu \sim 0.38$ [6,30,31], and the bulk sound speed C_0 can then be obtained.

The flyer-plate planar impact experiments are a standard, well established, high strain-rate loading method. The working principles of dynamic loading, measurement and data interpretation, and representative examples can be found in Refs. [1–8,22,32]. Flyer plate impact experiments are conducted with a 10-mm bore, single-stage, tabletop gas gun to investigate dynamic compression and tension responses of the CNT/epoxy composites. The schematic setup of the impact experiments is shown in Fig. 1. A flyer plate (3) is attached to polycarbonate sabot (1), with a recess (2) immediately behind it. When a solenoid valve is fired, compressed N_2 or He is released from a high-pressure gas reservoir into the gun barrel (9), accelerating the sabot and flyer plate assembly. Upon exiting the muzzle, the flyer plate impacts the target or sample under consideration (4). The flyer plate velocity is measured with an optical beam block system (OBB, 8), and the free surface velocity of the target, with a dual-laser Doppler pin (DPS) system (7). DPS is essentially a displacement interferometer similar to photon Doppler velocimeter. The muzzle, target and diagnostics are located in a