INTERFACE FRACTURE ENERGIES OF INDIVIDUAL CARBON NANOFIBERS

Ioannis Chasiotis[*a)], Tanil Ozkan[*]
[*]*Department of Aerospace Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801,U.S.A.*

Summary Single nanofiber pull-out experiments were carried out to quantify the role of surface roughness and functionalization on the interfacial fracture energy of carbon nanofibers with 250 nm diameter embedded in a polymer epoxy. A novel MEMS-based method was developed for controlled nanofiber loading and geometry, while an elasticity model was employed to compute the interfacial fracture energy. Carbon nanofibers with 5-30 nm peak-to-valley surface roughness resulted in interfacial fracture energy of 1.9±0.9 J/m^2. Reduction of the peak-to-valley surface roughness to 1-2 nm and a decrease in surface defects drastically reduced the interfacial fracture energy, and its scatter, to 0.65±0.14 J/m^2. Finally, oxidative surface functionalization of nanofibers with smooth surface resulted in much higher interfacial fracture energy of 3.3±1.0 J/m^2. The results, which were independent of nanofiber length and diameter for all three types on nanofibers, pointed out to the critical role of surface roughness and covalent bonding in interfacial adhesion of nanoscale fibers.

INTRODUCTION

Carbon nanofibers and nanotubes, have received major attention as composite fillers due to their immense specific surface area and high tensile strength. The latter supports polymer matrix strengthening assuming that very good interfacial adhesion and nanofiber alignment can be achieved. In this regard, the nanofiber surface morphology and functionalization are critical in improving interfacial adhesion and load transfer. Unfortunately, such quantitative data at the individual nanofiber level are lacking today with only few pioneering experimental efforts reported in literature [1-5]. Major difficulties in the aforementioned works arise from the imprecise definition of the embedded carbon nanofiber/nanotube segment, the lack of knowledge of the precise nanofiber orientation, and an uncontrolled amount of polymer matrix surrounding a nanofiber or nanotube. This paper presents a new method for pull-out experiments with single nanofibers, as well as results for different nanofiber surface conditions. Three different types of nanofibers were employed to examine the effects of surface defect density and roughness, and surface functionalization. An experimental method that benefits from the precision of MEMS-based microtools for nanoscale metrology, following on methods developed before by this group [6,7] supported the objectives of the present study, including the capability to study the interface between a carbon nanofiber and a thermosetting polymer epoxy.

METHODS, RESULTS AND DISCUSSION

Three grades of commercial Pyrograf®-III carbon nanofibers with 250 nm average diameter and hollow core, and Epon 828 based epoxy polymer were employed in this study. The first nanofiber type had 5-30 nm peak-to-valley surface roughness, the second nanofiber type had peak-to-valley surface roughness of 1-2 nm, and the third nanofiber type was produced from the second type with subsequent oxidative surface functionalization to increase covalent bonding. All nanofibers were individually embedded in surface micromachined channels for epoxy matrix, with embedded lengths in the range of 250 - 2,000 nm. The pull-out force was determined by an on-chip Microelectromechanical System (MEMS) force sensor and the use of a robust method for nanometer scale resolution measurements using optics and MEMS [6-9] as shown in Fig. 1. The approach in reference [10] was adopted in the formulation of the energy balance, and the tensile and shear stress components of the total strain energy were derived by modifying the relations in reference [11] according to the specific geometry of the present experiments. Details of the calculations are provided in [12]. The resulting expression provides an upper bound for the interfacial fracture energy, $G_{c,max}$, of the single carbon nanofiber-epoxy matrix system by relating the critical load for interfacial crack initiation to the nanofiber geometry and the elastic constants of the materials involved. No frictional dissipation terms were included in this calculation because the pull-out process with fully cured epoxy matrix proceeded instantaneously.

The analytical model for $G_{c,max}$ was strictly elastic. The pull-out force vs. nanofiber cross-head displacement curve was straight during the entire experiment supporting the validity of the elastic interfacial model for $G_{c,max}$. The value of the latter quantity was quite independent of the nanofiber diameter and embedded length for all three types of nanofibers, as shown in Fig. 2. The interfacial fracture energy of the rough carbon nanofibers, was 1.94±0.9 J/m^2 ranging between 0.87 - 3.78 J/m^2. The very large standard deviation, corresponding to 45% of the mean value, originated in the variability in surface defect density (the particular nanofibers were not heat-treated) and the surface roughness that locally varied as much as 5-30 nm. On the other hand, the interfacial fracture energy for the smooth nanofibers, which were high temperature heat-treated but not surface functionalized, was 0.65±0.14 J/m^2 varying in the narrow range of 0.44-0.86 J/m^2. The smaller standard deviation (22% of the mean) compared to the first class of rougher carbon nanofibers is evidence for the effect of the reduction of surface roughness on the uniformity of the work of fracture. Finally, the interfacial fracture energy of functionalized nanofibers with smooth surfaces (which were previously high temperature heat-treated) was 3.3±0.1 J/m^2 with a range of values between 2.71 J/m^2 and 5.70 J/m^2.

[a)] Corresponding author. Email: chasioti@illinois.edu

This increased $G_{c,max}$ value underscores the important role of bonded interactions with the epoxy matrix. Furthermore, despite the fairly large standard deviation of ~30% of the average $G_{c,max}$, the lower bound of the interfacial fracture energy for the oxidatively treated nanofibers was always higher than the interfacial fracture energy for rough nanofibers, indicating that the effects of chemical surface functionalization are much more decisive than topographical factors, such as large nanoscale surface roughness and defect density. Hydrogen and covalent bonding of the epoxy and amine groups with the functional groups (-COOH, -OH) introduced to the surface of the carbon nanofibers during wet chemical treatment ensured the high interfacial strength.

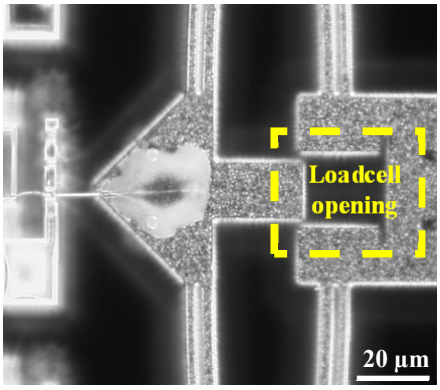

Fig. 1. Optical image of a carbon nanofiber pulled-out of a microfabricated channel. The loadcell opening provides the applied force.

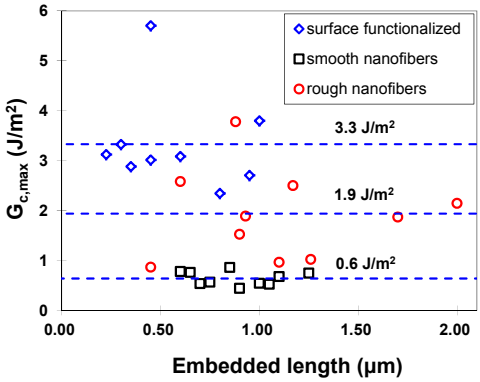

Fig. 2. Elastic interfacial fracture energy vs. nanofiber embedded length for carbon nanofibers with three surface conditions embedded a thermosetting polymer.

CONCLUSIONS

The interfacial fracture energy of individual carbon nanofibers embedded in a polymer epoxy was determined using a new MEMS-based method for nanoscale pull-out experiments. Smooth nanofiber surfaces resulted in dramatic reduction (50%) of the interfacial fracture energy and interfacial shear strength pointing out to the fact that surface asperities and defects increase the van der Waals interactions with the polymer matrix. Oxidative surface functionalization of smooth nanofibers resulted in high interfacial fracture energy values emphasizing the catalytic role of covalent bonding. In all cases, only adhesive interfacial failure was observed (as viewed in high resolution SEM images) indicating that the shear strength of the matrix within the load transfer region surrounding the nanofiber could reach quite higher values than the bulk polymer, potentially due to the presence of the carbon nanofiber that alters the local cross-link and molecular structure of the polymer. The debond strength and interfacial fracture energy were independent of length and diameter for all three categories of nanofibers. Compared to pull-out experiments with individual carbon nanotubes and nanofibers reported in literature, the debond strengths measured in this study were characterized by much smaller data scatter, not exceeding ~27% of the average values.

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