Measurement of carbon nanotube–polymer interfacial strength

Asa H. Barber Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

Sidney R. Cohen Chemical Research Support, Weizmann Institute of Science, Rehovot 76100, Israel

H. Daniel Wagner^{a)} Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

(Received 23 October 2002; accepted 1 April 2003)

The force required to separate a carbon nanotube from a solid polymer matrix has been measured by performing reproducible nanopullout experiments using atomic force microscopy. The separation stress is found to be remarkably high, indicating that carbon nanotubes are effective at reinforcing a polymer. These results imply that the polymer matrix in close vicinity of the carbon nanotube is able to withstand stresses that would otherwise cause considerable yield in a bulk polymer specimen. © 2003 American Institute of Physics. [DOI: 10.1063/1.1579568]

Since the discovery¹ of carbon microtubules in 1991, carbon nanotubes (CNTs) have been considered to be the "ultimate" fiber due to exceptionally high strength, stiffness, and compressive behavior.²⁻⁶ It is because of their outstanding mechanical properties that carbon nanotubes show promise as fiber reinforcements in strong, lightweight polymer composite materials. As the mechanical properties of composites depend directly upon the embedded fiber mechanical behavior, replacing conventional microsized fibers with CNTs can cause composite properties, such as tensile strength and elastic modulus, to be potentially improved. In fact, several experimental and theoretical works hint at the existence of strong adhesion at the nanotube-polymer interface, which would lead to effective stress transfer.⁷⁻⁹ This adhesion will be a strong function of physical and chemical influences, such as the polymer properties in the vicinity of the fiber and covalent bonding between the polymer and defect sites on the nanotube.

Until now, all experimental measurements of the nanotube-polymer interaction have been indirect. Polymer wetting of nanotubes has been observed¹⁰ in nanocomposite samples using transmission electron microscopy but this does not give any quantitative or accurate information as to the magnitude of the interfacial adhesion. Other methods have been attempted to evaluate interfacial quality, including using Raman spectroscopy to monitor the deformation of nanotubes in a polymer,¹¹ examination of individual nanotube fragmentation under composite loading,¹² and mechanical characterization of bulk nanotube-polymer composite systems.^{13–15} While these methods have been used to give nanotube stress sensors¹⁶ and information on nanotube failure mechanisms, the assessment of the interfacial strength has been unresolved. Experimental measurements of the interfacial strength are severely hindered by the scales involved when using nanotubes, and have led to some comsimulation work of the nanotube-polymer puter interface.^{17,18} In recent preliminary experiments, we have shown that an individual CNT can be detached from a polymer matrix.¹⁹ This work hinted at the possibility of a highstrength nanotube–polymer interface. In the present letter, we measure the adhesive interactions between a single CNT and polymer matrix using a nanopullout technique. This method for pulling out a single CNT embedded within a polymer matrix is analogous to the microfiber pullout²⁰ test, widely used in composite testing, which is effective in measuring the adhesion between reinforcements and polymers.

Atomic force microscopy (AFM) has been shown to be a powerful tool for examining the mechanical properties of nanotube materials. Bending and buckling,² frictional properties,²¹ and tensile strength tests⁵ of CNTs have all been measured using AFM. To carry out a nanopullout experiment, we use AFM to manipulate the CNT in relation to the polymer. A single multiwalled CNT (MWCNT, Nanolabs, Massachusetts) was attached to an AFM tip (MikroMasch, Estonia), with spring constant of around 1 Nm⁻¹ (Fig. 1) using an established technique.²² Several such tips were employed, each calibrated by measuring the sensor response on a hard surface, and using scanning electron microscopy (SEM)-determined dimensions to calculate the spring constant. Thin films (~300 nm) of polyethylene-butene,²³ an



FIG. 1. A single MWCNT-AFM tip (nanotube diameter \sim 80 nm) before pullout and after pullout (left inset, scaled to 40%). Note the clean tube both before and after the pullout process. MWCNT diameters for all the pullout experiments varied between 32 and 136 nm.

4140

Downloaded 03 Jun 2003 to 132.77.4.43. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

^{a)}Electronic mail: daniel.wagner@weizmann.ac.il

^{© 2003} American Institute of Physics



FIG. 2. Typical plot of pullout force (taken from the AFM cantilever deflection) against pullout time. At (a), the nanotube is embedded in the polymer. As the nanotube is pulled away from the polymer, the cantilever bends away (b) until the maximum force, corresponding to the maximum cantilever bending deflection, is achieved (c). Pullout then occurs (d), resulting in the eventual complete separation of the nanotube from the polymer (e).

amorphous thermoplastic polymer, were spin-coated onto a sapphire plate. The surface of the polymer film was imaged in semi-contact mode using the nanotube tip with AFM (NT-MDT Solver P47, Zelenograd). The polymer film was heated in situ under AFM with the nanotube tip in feedback, or in close proximity over the polymer. Once within the softening/ melt range of the polymer (47-52 °C), AFM was used to push the nanotube tip into the polymer. We observed a "jump-in" of the nanotube tip into the polymer at the initial contact point. This was due to the polymer showing a limited degree of wetting of the nanotube, and resulted in the tube being pulled into the polymer by about 10 nm, as measured from the cantilever deflection during this process. To increase the embedded length of nanotube within the polymer, we increased the set-point force on the nanotube. For smalldiameter MWCNTs, there is a tendency for the nanotube to bend rather than continue within the polymer at the highest forces applied (vide infra). Immediately upon reaching the desired embedded length, the polymer was rapidly cooled. The nanotube was pulled out of the matrix just above room temperature (about 30 °C) by retraction of the z-piezo while recording the AFM cantilever deflection during the pullout process (Fig. 2). Initially, the cantilever bends away from the polymer surface until a peak force, or maximum bending of the cantilever, is reached. This critical force causes failure at the interface, resulting in the nanotube being pulled out of the polymer. Eventually, a large drop in the force is observed, corresponding to the nanotube fully separating from the polymer.

AFM imaging of the polymer surface after the nanopullout experiment is shown in Fig. 3. The surface shows a clear exit hole corresponding to the removal of the nanotube. Undesired bending of the nanotube during the push-in process can cause distortion of the pullout hole from a circular shape, which was used to evaluate whether the nanotube push-in was normal to the polymer surface or not. If the push-in was not normal to the polymer surface, the measurement was discarded. The embedded length was measured from the lowest position in the exit hole using the AFM height image data. As a double check, the *z*-piezo and cantilever deflections were used to estimate the total movement of the nano-



FIG. 3. AFM height imaging of the pullout area reveals an exit hole (a) in the polymer surface, the depth of which can be taken (b) and used to calculate the embedded length. The geometry of the pullout area, clearly showing the hole previously containing the nanotube, is displayed from the AFM height data (c).

tube into the polymer during the jump-in and push-in processes. A good correlation was found between this total jump-in/push-in distance and the embedded length measured from AFM height image data. At small embedded lengths (L_{emb}) , the maximum fiber-polymer adhesion force (F_{max}) in a fiber pullout test is a linear function²⁴ of the embedded length: $F_{\text{max}} \sim L_{\text{emb}}$. In principle, this dependence is valid here as well since very small embedded lengths (average of 40 nm, not exceeding 70 nm) were used in our experiments. These embedded lengths are admittedly small, and therefore we cannot neglect the possibility of influence of an end effect, which is difficult to estimate in view of the lack of knowledge of the end geometry, structure, and nature of bonding. In Fig. 4, we have plotted F_{max} against the total embedded area A_{emb} of nanotube in the matrix, instead of the embedded length (because our experiments were performed with a variety of tube diameters), where A_{emb} $=2\pi r_{\rm NT}L_{\rm emb}$, and $r_{\rm NT}$ is the outer radius of the nanotube AFM tip. L_{emb} was measured from the AFM topography images. The average nanotube-polymer interfacial strength τ was then estimated from the slope of the linear fit in Fig. 4 through $F_{\text{max}} = \tau A_{\text{emb}}$. Neglecting any end effect, this fit gives a value of 47 MPa for the average interfacial stress required to remove a single MWCNT from the polyethylenebutene matrix.

a. As a double check, the *z*-piezo and cantilever deflecns were used to estimate the total movement of the nano-Downloaded 03 Jun 2003 to 132.77.4.43. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp



FIG. 4. Plot of pullout force, taken from the AFM force curves, against pullout area for the pullout of MWCNTs from polyethylene-butene. The gradient from the linear fit to the data (R^2 =0.89) can be used to calculate the interfacial separation stress of 47 MPa. There is large data scatter at low embedded areas/lengths, which results from the uncertainty in accurately measuring embedded area on a nonatomically smooth polymer surface. Error bars were calculated according to the uncertainty in measuring the spring constant of the cantilever.

polyethylene system was predicted, using van der Waals interactions, to be 2 MPa.¹⁸ When strong bonding, that is, covalent bonding, occurs between the reinforcement and polymer matrix, the computer simulated interfacial strength can be as high as 100 MPa for a polyethylene–CNT interface and higher for a polystyrene–nanotube system.¹⁷ While each polymer system is unique, these computer simulation predictions, together with our experimental data, are evidence for a relatively strong interface between MWCNTs and polyethylene-butene. We can therefore infer that covalent bonding exists between the polymer matrix and CNT, probably through defects in the outer shell of the nanotube itself.

The present experiments reveal that the polymer matrix around the nanotube is able to withstand high levels of stress that would otherwise see a similar bulk polymer sample fail. The typical tensile strength of the copolymer used here is about ten times lower than the average separation stress required to pull the nanotube away from the polymer. It would be expected that during pullout, the stresses around the nanotube would cause the polymer to yield and fail before the interface. Thus, the pulled-out nanotube would be surrounded by polymer that had yielded during the pullout process. Neither the exit hole nor the pulled-out nanotube in Figs. 1 and 3 show any evidence of this, leading us to believe that the properties of the polymer immediately surrounding the nanotube are different from those of the bulk, with the tensile strength in that area being an order of magnitude greater than the bulk tensile strength.

In conclusion, we have performed nanopullout experiments to measure the separation strength between a single MWCNT and a polymer matrix. The nanotube was embedded within the polymer and pulled out using AFM, with the stress required to separate the nanotube measured during the pullout. We find that the separation stress is relatively high, indicating that the bonding model should consider chemical, as well as physical, interactions. Further, the polymer mechanical properties in the vicinity of the nanotube appear to show differences when compared to those of the bulk polymer behavior. These results highlight the benefits of reinforcing a polymer with a carbon nanotube, and also show that the polymer matrix is surprisingly resilient during the pullout procedure. We are currently extending such measurements to higher embedded lengths.

This project was supported by the (CNT) Thematic European network on "Carbon Nanotubes for Future Industrial Composites" (EU), the G. M. J. Schmidt Minerva Center of Supramolecular Architectures, and by the Israeli Academy of Science. One of the authors (H.D.W.) is the recipient of the Livio Norzi Professorial Chair. The authors are very grateful to Dr. A. Lustiger at ExxonMobil for useful discussion and for providing the polyethylene-butene, and K. Gartsman at the Weizmann Electron Microscopy Unit for his assistance with the ESEM.

- ²M. R. Falvo, G. J. Clary, R. M. Taylor, V. Chi, F. P. Brooks, S. Washburn, and R. Superfine, Nature (London) **389**, 582 (1997).
- ³M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, Nature (London) **381**, 678 (1996).
- ⁴B. I. Yakobson, C. J. Brabec, and J. Bernholc, Phys. Rev. Lett. **76**, 2511 (1996).
- ⁵Y. Min-Feng, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, and R. S. Ruoff, Science (Washington, DC, U.S.) 287, 637 (2000).
- ⁶O. Lourie, D. M. Cox, and H. D. Wagner, Phys. Rev. Lett. **81**, 1638 (1998).
- ⁷E. T. Thostenson, R. Zhifeng, and T.-W. Chou, Compos. Sci. Technol. 61, 1899 (2001).
- ⁸D. Hull, An Introduction to Composite Materials, 2nd ed. (Cambridge University Press, Cambridge, 1996).
- ⁹ F. Li, H. M. Cheng, S. Bai, G. Su, and M. S. Dresselhaus, Appl. Phys. Lett. **77**, 3161 (2000).
- ¹⁰O. Lourie and H. D. Wagner, Appl. Phys. Lett. 73, 3527 (1998).
- ¹¹O. Lourie, H. D. Wagner, Y. Zhang, and S. Iijima, Adv. Mater. (Weinheim, Ger.) **11**, 931 (1999).
- ¹² H. D. Wagner, O. Lourie, Y. Feldman, and R. Tenne, Appl. Phys. Lett. **72**, 188 (1998).
- ¹³D. Qian, E. C. Dickey, R. Andrews, and T. Rantell, Appl. Phys. Lett. 76, 2868 (2000).
- ¹⁴P. M. Ajayan, L. S. Schadler, C. Giannaris, and A. Rubio, Adv. Mater. (Weinheim, Ger.) **12**, 750 (2000).
- ¹⁵L. S. Schadler, S. C. Giannaris, and P. M. Ajayan, Appl. Phys. Lett. 73, 3842 (1998).
- ¹⁶Q. Zhao, J. R. Wood, and H. D. Wagner, Appl. Phys. Lett. 78, 1748 (2001).
- ¹⁷K. Liao and S. Li, Appl. Phys. Lett. **79**, 4225 (2001).
- ¹⁸S. J. V. Frankland, A. Caglar, D. W. Brenner, and M. Griebel, J. Phys. Chem. B **106**, 3046 (2002).
- ¹⁹C. A. Cooper, S. R. Cohen, A. H. Barber, and H. D. Wagner, Appl. Phys. Lett. 81, 3873 (2002).
- ²⁰P. S. Chua and M. R. Piggott, Compos. Sci. Technol. 22, 33 (1985).
- ²¹ M. R. Falvo, R. M. Taylor II, A. Helser, V. Chi, F. P. Brooks Jr., S. Washburn, and R. Superfine, Nature (London) **397**, 236 (1999).
- ²² H. Nishijima, S. Kamo, S. Akita, Y. Nakayamaa, K. I. Hohmura, S. H. Yoshimura, and K. Takeyasu, Appl. Phys. Lett. **74**, 4061 (1999).
- ²³ The polyethylene-butene (trade name: Exact 4023, Exxon-Mobil, NJ) was used as received. Typical polymer properties can be found at: http:// www.exxonmobil.com/chemical/customer/products/families/exact/ grade_slate/pdf/americas/exact4023.pdf
- ²⁴ See Eq. (44) in K. R. Jiang and L. S. Penn, Compos. Sci. Technol. 45, 89 (1992).
- ²⁵ There are many examples of weak interface composite systems in the literature, a good case being a glass-fiber-polypropylene composite, see E. Mader, K. Jacobasch, K. Grundke, and T. Gietzelt, Composites, Part A 27, 907 (1996).

Downloaded 03 Jun 2003 to 132.77.4.43. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

¹S. Iijima, Nature (London) **354**, 56 (1991); carbon-based nanotubes were independently discovered several years earlier by Nesterenko *et al.* Their work remains largely unknown to the scientific community. [A. M. Nesterenko, N. F. Kolesnik, Y. S. Akhmatov, V. I. Sukhomlin, and O. V. Prilutski, Metals , 3 (1982); UDK 869.173.23; *News of the Academy of Science*, USSR, pp. 12–16].