3-6-2009

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Mark C. Strus
Birck Nanotechnology Center and School of Mechanical Engineering

Camilo I. Cano
School of Chemical Engineering, Purdue University

R. Byron Pipes
School of Chemical Engineering, School of Aeronautics and Astronautics, School of Materials Engineering, Purdue University

Cattien V. Nguyen
ELORET Corp, NASA Ames Research Center, Moffett Field, California, USA

Arvind Raman
Birck Nanotechnology Center and School of Mechanical Engineering, Purdue University, raman@purdue.edu

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Strus, Mark C.; Cano, Camilo I.; Pipes, R. Byron; Nguyen, Cattien V.; and Raman, Arvind, "Interfacial energy between carbon nanotubes and polymers measured from nanoscale peel tests in the atomic force microscope" (2009). Birck and NCN Publications. Paper 448.
http://docs.lib.purdue.edu/nanopub/448

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Interfacial energy between carbon nanotubes and polymers measured from nanoscale peel tests in the atomic force microscope

Mark C. Strus a, Camilo I. Cano b, R. Byron Pipes b,c,d, Cattien V. Nguyen e, Arvind Raman a,*

a Birck Nanotechnology Center and School of Mechanical Engineering, Purdue University, West Lafayette, Indiana, USA
b School of Chemical Engineering, Purdue University, West Lafayette, Indiana, USA
c School of Aeronautics and Astronautics, Purdue University, West Lafayette, Indiana, USA
d School of Materials Engineering, Purdue University, West Lafayette, Indiana, USA
e ELORET Corp, NASA Ames Research Center, Moffett Field, California, USA

ARTICLE INFO

Article history:
Received 20 December 2008
Received in revised form 17 February 2009
Accepted 19 February 2009
Available online 6 March 2009

Keywords:
A. Nanoscale peeling
B. Carbon nanotubes
C. Polymer nanocomposites
D. Interfacial fracture energy
E. Atomic force microscope
F. Surface energy

ABSTRACT

The future development of polymer composite materials with nanotubes or nanoscale fibers requires the ability to understand and improve the interfacial bonding at the nanotube–polymer matrix interface. In recent work [Strus MC, Zalamea L, Raman A, Pipes RB, Nguyen CV, Stach EA. Peeling force spectroscopy: exposing the adhesive nanomechanics of one-dimensional nanostructures. Nano Lett 2008;8(2):544–50], it has been shown that a new mode in the Atomic Force Microscope (AFM), peeling force spectroscopy, can be used to understand the adhesive mechanics of carbon nanotubes peeled from a surface. In the present work, we demonstrate how AFM peeling force spectroscopy can be used to distinguish between elastic and interfacial components during a nanoscale peel test, thus enabling the direct measurement of interfacial energy between an individual nanotube or nanofiber and a given material surface. The proposed method provides a convenient experimental framework to quickly screen different combinations of polymers and functionalized nanotubes for optimal interfacial strength.

1. Introduction

Carbon nanotubes (CNTs) are gaining significant interest as nanoreinforcements for strong, durable, lightweight polymer composite materials due to their unusually high tensile and compressive modulus [2,3]. When properly dispersed in a polymer matrix material, CNTs could allow for improvement in fracture toughness and fatigue properties since the CNT size is on the same order as defects in the material [4]. Many researchers have shown that the addition of a small volume fraction of CNTs to various polymers can improve the bulk modulus of the composite materials such as epoxy [5], polyimide [6], polyethylene [7], methyl-ethyl ethacrylate [8], or polyvinyl alcohol [9]. Additionally, the large electrical and thermal conductivities of carbon nanotubes have lead to the creation of unique nanocomposites that can quickly dissipate electrostatic charges [10] or withstand high temperatures with minimal mechanical degradation [11]. Since the first reported work on CNT–reinforced polymer nanocomposites materials [12], they have found widespread application in automotive, aerospace, defense, sporting goods, infrastructure, and medical sectors [13–15].

However, the advancement of CNT nanocomposites has been hindered, among other things, by the lack of understanding of the interfacial bonding between CNTs and the surrounding matrix [16]. Better interfacial strength, especially shear strength, is important to improve the nanocomposites bulk properties [17]. However, to date, only a few techniques [18–20] are able to directly measure the interfacial fracture energy between an individual CNT/nanofiber and surrounding matrix despite recent calls for individual fragment, pulling, and peeling experiments between polymers and CNTs/nanofibers [4].

In this work, we show how the recently developed peeling force spectroscopy using an atomic force microscope (AFM) [1] is capable of quantitatively comparing the interfacial fracture energy between multi-walled carbon nanotubes and different polymer materials. Through a continuum-based model of carbon nanotubes on graphite, we demonstrate how the interfacial and flexural energies acquired during peeling of a nanotube off a surface can be decoupled to find both the interfacial fracture energy (mode I fracture) between the nanotube and surface, as well as the flexural rigidity of the nanotube from a single force–distance curve in the AFM. We reveal experimental multi-walled CNT peeling results carried out with an AFM on substrates of graphite, epoxy, and polyimide. Based on hundreds of peeling experiments, we directly compare the interfacial energies between the CNTs and the different substrates representing typical polymer matrix materials for nanocomposites. The results show that peeling force spectroscopy is a promising tool that could be extended to compare, for example, the effects that specific matrix polymerization or nanotube/nanofiber functionalization [21] has on interfacial energy and load transfer in nanoreinforced nanocomposites.
2. Theoretical basis of proposed method

We begin with a theoretical model of a CNT being peeled from a flat surface with specific interaction forces. In carbon nanotube nanocomposites, three types of CNT–polymer matrix interaction forces are relevant: micro-mechanical interlocking [16], chemical bonding [22], and van der Waals interaction forces. We study CNT peeling that takes into account the van der Waals interaction forces based on the universal graphitic potential [23]. However, the model can be extended to include chemical bonding which becomes important for functionalized CNTs [21] or mechanical interlocking [24]. The developed computational model, described in detail in Strus et al. [1] and Zalamea [25] is used here to demonstrate how different regions of peeling force–displacement measurements can be used to decouple and quantify both the interfacial energy and the flexural stiffness of the CNT.

2.1. Nanotube configurations during peeling: point- and line-contact

In the formulation, the CNT is modeled as a large deformation, continuum inextensible elastica [26] that interacts with a graphite surface via van der Waals interaction forces [23]. The resulting non-linear boundary value problem is solved numerically to find the peeling forces applied to the fixed end of the nanotube as a function of the crack opening or peeling point displacement between the CNT and substrate (see Fig. 1a for a 1.5 µm multi-walled CNT with inner and outer diameters of 10 nm and 41 nm). As described in [1] and verified elsewhere [27], multiple solutions with differing forces and extensible elastica deformed shapes can exist for certain peeling point displacements (see Fig. 1a at peeling point displacement of 200 nm). However, in a typical peeling experiment the peeling probe will either approach or retract from the surface, thus allowing access only to some of the solution branches, as indicated by the dashed red (approach) and solid blue (retraction) arrowed lines in Fig. 1a. In both approach and retraction of the CNT, the peeling force may suddenly drop or jump as the CNT switches from one equilibrium solution branch to another. Generally, the peeling force jumps, which are observed experimentally, indicate a sudden change in the deformed shape of the CNT.

In general, there are three forms of CNT deformed shapes during a peeling event. When a CNT is in a s-shape configuration [28], it forms a line-contact with the underlying surface as shown in Fig. 1 and thus interfacial adhesion is greatest during this stage of peeling. In the arc-shape configuration [28], the CNT forms only a point-contact and thus interfacial adhesion is small. Because the external applied force acts through a known distance, the area under the force–displacement curve indicates the amount of work done during line-contact peeling.

1 For interpretation of color in Fig. 1, the reader is referred to the web version of this article.
point-contact peeling, assuming small CNT–substrate friction [29] and negligible substrate deformation [30], the work of the applied peeling force either creates new nanotube and substrate surfaces (interfacial energy) or deforms the nanotube (flexural energy).

With the computational model, the instantaneous interfacial energy can be calculated as a function of the peeling point displacement as shown in Fig. 1b simply by integrating the CNT–substrate interaction forces per unit length along the length of the CNT such that

\[
\text{Interfacial Energy} = \frac{E I}{L} \int_{0}^{L} f(z(s)) \sin \theta(s) ds
\]

where \(E\) is the CNT flexural elastic modulus, \(I\) is its area moment of inertia, \(L\) is the CNT length, \(Z\) is the CNT straightness. The interfacial and flexural energies have been shown as a function of peeling point displacement in Fig. 1 for a 1.5 \(\mu\)m CNT peeled from a graphite surface. The portions of the energies corresponding to the line- and point-contact peeling events in Fig. 1a have been labeled accordingly. Recall that the total work of peeling is simply the sum of the change in interfacial energy plus the change in flexural energy.

2.2. Predicting interfacial energy from line-contact peeling

By understanding the interfacial and flexural energy contributions in the line-contact and point-contact configurations of the CNT, it becomes possible to extract the interfacial and flexural energies separately. When the CNT is peeled from the substrate in its line-contact configuration, Fig. 1b and c shows most of the work of peeling changes the interfacial energy in the system, while just a small amount goes into changing the flexural energy in the CNT. Therefore, the area under the line-contact portion of a peeling experiment can be used to approximate the change in interfacial energy.

During point-contact CNT peeling, the change in interfacial energy is negligible (see Fig. 1b), indicating that nearly all of the work done by the external peeling force is transferred into flexural deformations of the CNT. Thus, the slope of the arc-shape peeling force–displacement provides a good estimate of the CNT bending compliance, \(c = L^2/3EI\). For the relatively stiff multi-walled CNT in Fig. 1, the peeling force–displacement slope in the line-contact peeling regime underpredicts the actual CNT flexural compliance by 10%. For less stiff single-walled CNTs, this flexural compliance approximation method becomes error prone.

The method to estimate interfacial energy change from the total work done during line-contact peeling is valid only for nanotubes or nanofibers with certain aspect ratios. Fig. 2 shows the ratio of the change in interfacial energy to the total work of peeling during line-contact peeling for various hollow single-walled CNTs and solid carbon fibers with different aspect ratios. When this ratio is near 100% it means that the work of peeling (area under the curve in the line-contact regime) can predict the interfacial energy between the CNT and the surface. This result will be the basis for the following experiments which quantitatively compare interfacial energies for different CNT–polymer substrate interactions.

3. Peeling experiments

3.1. Experimental setup

Dozens of multi-walled CNTs were attached to tipless microcantilevers from MikroMash™ and K-Tek Nanotechnology LLC™ as shown in Fig. 3, using a technique developed by Stevens et al. [31]. The attachment procedure is also described in our recent work [1]. Briefly, multi-walled CNTs, initially grown via chemical vapor deposition on a thin Pt/In wire, were properly aligned in a dark-field microscope and would naturally stick to the 10 nm thick nickel-coated tipless microcantilevers due to van der Waals forces. A voltage bias was applied to the microcantilever causing localized Joule heating at the point of highest resistance, the CNT–microcantilever interface, thus welding the CNT in place. In general, this CNT–microcantilever weld was strong enough to hold up for thousands of peeling experiments and the CNT would usually sever before the weld gave out.

Peel tests were carried out with an Agilent 5500™ AFM system in a dry nitrogen chamber with near 0% relative humidity. The bending stiffness of tipless AFM microcantilevers were experimentally calibrated between 2 and 20 N/m using the method of Sader and Chon [32]. All of the experimental results presented here were completed with the two CNTs shown in Fig. 3 with an initial deviation from straightness <1% [33], although the observed phenomena were also repeatable with CNTs with larger deviation from straightness.

Besides highly order pyrolytic graphite, two polymeric substrates, polyimide (LaRC-1A) and epoxy adhesive (Cycom 7714A) were obtained from Sigma–Aldrich™, while 4,4’-oxydiphthalic dianhydride (ODPA) and 3,4’-oxydianiline (ODA) were purchased from Chriskiev Company Inc.™. The LaRC-1A precursor solution was prepared at room temperature by dissolving equimolar amounts of ODPA and ODA in NMP.
(15% of solids by weight) in a round bottom flask equipped with a nitrogen blanket and mechanical stirring. This reaction was carried out for 24 h. All reagents were used as received. The polyimide substrate was obtained by spin coating a solution of the corresponding poly (amic acid) precursor solution (LaRC-1A) onto polished metal disks and letting it dry at 120 °C under vacuum for 48 h to reduce the NMP content as much as possible (some NMP will inevitably remain hydrogen bonded to the amic acid groups). After this drying step, the samples were put in a nitrogen-purged convection oven and the temperature was raised at a rate of 5 °C/min up to 300 °C and kept there for 2 h to guarantee full imide conversion. The slow heating rate was chosen to minimize void formation in the films during the imidization. Epoxy samples were prepared from B-staged resin dissolved in NMP then spin-coated on polished metal disks and left to dry at 120 °C for 48 h under nitrogen atmosphere. At the end of the drying stage, the films were completely cured and did not require any additional thermal treatment. A 5 × 5 μm² area of each sample was imaged with a conventional AFM probe to evaluate waviness and roughness. As shown in Fig. 4, both the graphite and polymer samples show negligible waviness while their line scans show height variations ±5 Å over 5 μm, well within the expected surface roughness of the multi-walled CNTs.

3.2. Peeling on graphite, epoxy, and polyimide substrates

Fig. 4 shows a typical static AFM peeling experiment, where CNT peeling forces are recorded as a function of peeling point displacement with probe A on graphite, epoxy, and polyimide substrates. From prior work [1], it is possible to separate the cantilever snap-in and pull-off (cantilever adhesion to substrate) from the CNT peeling (CNT adhesion to substrate) by noting the force hysteresis at the closest approach distance is the cantilever adhesion. Once the cantilever pulls off from the substrate the remaining force jumps correspond in sequence to (a) the transition from line to point-contact, (b) jumps between multiple point-contact states due to CNT imperfections and, (c) a final jump from point-contact to freestanding state. From Fig. 4 it is clear that the peeling signatures using probe A (Fig. 3a) on graphite, epoxy, and polyimide substrates show qualitatively similar force jumps indicating a passage through the same sequence of CNT configurations. Quantitatively, there are important differences. Because the aspect ratios of the multi-walled CNTs used here are greater than 50, the theory developed earlier in this paper can be easily applied to these data. Accordingly, the interfacial energy between the multi-walled CNT and the substrate can be calculated from the shaded solid green² region under the line-contact regime as indicated in Fig. 4. As shown in Fig. 4b, some curve extrapolations are needed to identify and measure the correct area in the line-contact regime. Similarly, the slope of the force–distance curve in the point-contact regime provides a measure of the flexural compliance of the multi-walled CNT.

CNT peeling experiments showed good repeatability under the same operating conditions. In Fig. 5a, the interfacial energies of the multi-walled CNT of peeling probe A are plotted, based on experiments performed with the same probe at five different locations on each of the three substrates a total of 25 times per location. The data were processed according to Fig. 4 to obtain the area under the line-contact part of the curve, in order to estimate the interfacial energy in each peel test. As expected, measurements at the several locations on the same substrate show a small distribution in interfacial energies, while measurements on the various substrates are clearly separated because their interfacial energies are quite different. Therefore, the mean values of interfacial energies measured on each substrate can be used to quantitatively compare interfacial energies, so that CNT–epoxy is estimated to have an interfacial energy 1.5 times larger than CNT–graphite and 2.7 times larger that CNT–polyimide.

Fig. 5b shows a set of experiments completed with probe B where 20 peel tests were performed at 16 separate locations on both graphite and epoxy. The larger number of sample locations and fewer tests per location highlights the larger distribution of data particularly on epoxy. In this case, the mean epoxy/graphite interfacial energy ratio is 3.8, slightly larger than was...
found with probe A. Although all experiments were carried out in a dry-nitrogen, adsorbed molecules or impurities such as amorphous carbon may contribute to the difference in interfacial energy ratios.

The proposed theory also suggests a recipe for measuring the flexural compliance of the nanotube from the point-contact regime of the experimental peeling force curve. In the Fig. 4, before the CNT transitions from point-contact to freestanding, the linear slope of each of the point-contact peeling curves can be used to estimate the CNT flexural compliance. Using this method, the CNT flexural compliance on graphite, epoxy, and polyimide is estimated to be 23.3 m/N, 21.7 m/N, and 19.2 m/N, respectively. These estimated compliances are similar on the three different substrates because only changes in flexural energy are expected during point-contact peeling. A similar theoretical compliance (22.6 m/N) could be achieved with $d_0 = 55$ nm, $d_1 = 10$ nm, $L = 2.2$ µm, and $E = 350$ GPa, all reasonable parameters for CVD-grown multi-walled CNTs.

These results clearly demonstrate how peeling force spectroscopy using an AFM can be used to measure the total interfacial energy during peeling (mode I fracture), and that the method clearly identifies the different interfacial energies between a given
nanotube and different polymer surfaces. Nonetheless, there are some important issues to keep in mind during such experiments:

- Interfacial energy ratios between substrates tested with the same probe on different days may vary because of substrate tilt relative to the CNT. Only mode I fracture/peeling (normal) is sensed by the microcantilever, but the CNT may also experience peeling in either mode II (friction-dominated) or mode III (lateral) type of crack opening, where sample tilt will play a significant role.

- Although the line-contact (immediately after cantilever pull-off) and point-contact (before return to freestanding) are readily recognized, additional force jumps are often observed (see Fig. 4a). These force jumps may either be additional line-contact peeling events, if the CNT was not initially well-adhered along its length, or point-contact events where the CNT tip geometry allows for sudden pivoting and/or slipping. Another possibility is the existence of a weak point in the CNT due to a defect, which leads to a sudden change in the overall bending stiffness of the CNT as it undergoes point-contact peeling.

Despite these challenges, these experiments have shown the clear measurement of CNT–epoxy and CNT–graphite interfacial energies with different probes and multiple trials demonstrating the robustness of the method.

4. Extracting interfacial fracture energy from peeling force spectroscopy

Although peeling force spectroscopy is very useful for readily comparing interfacial energies between nanotubes/nanofibers with different functionalizations and various polymers, the current experimental setup and accompanying model cannot provide interfacial energy per unit area, or interfacial fracture energy, for mode I fracture because the contact area of the CNT with the polymer substrate is unknown during s-shape peeling. Assuming full-length stiction of the CNT in Fig. 5a, one can obtain upper limit estimates of CNT–substrate interfacial energies per unit length on the three surfaces tested: 0.6 pJ/m for polyimide, 1.1 pJ/m for graphite, and 1.7 pJ/m for epoxy.

Though polyimide and epoxy are known to have similar free surface energies [34], the difference in their CNT–substrate interfacial energies may be due to local surface deformations during peeling, especially for epoxy, which generally has a lower bulk modulus [35,36]. In other words, if the measured interfacial energies were divided by a well-defined contact area, it is possible the CNT–substrate interfacial energy per unit area would be similar for these two polymers. Therefore, the reported interfacial measurements may depend both on the substrate’s surface and mechanical properties. Such is the case of graphite, which will deform little due to its large bulk modulus, but which shows a larger interfacial energy than polyimide because it has a much larger free surface energy [37]. Future improvements to AFM peel tests would benefit from inclusion of true contact length and area, perhaps by recent techniques where peeling experiments have been observed in a scanning electron microscope [38].

5. Conclusions

In this work, we have demonstrated the possibility of using nanoscale peeling with the AFM to quantitatively measure the interfacial bonding between nanotube–matrix interfaces in order to promote the development of stronger, tougher, and more robust nanocomposite materials. From an extension of previous work [1], we have shown that CNT peeling involves sudden transitions between different mechanical configurations or regimes (line-contact, point-contact and free standing). However, a key contribution was to identify that the force curves in different peeling regimes can be used to separate and quantify the interfacial energy and the flexural compliance of the CNT during the peeling process.

Using the proposed method, we have demonstrated through a series of peeling experiments, that CNTs have higher interfacial energies with epoxy than graphite, while CNTs and polyimides have the lowest interfacial energy of the three. This result clearly demonstrates the potential of the nanoscale peel test as a method of screening one-dimensional nanoreinforcement–matrix interfacial energies.

Before full acceptance as a screening tool, AFM peeling force spectroscopy requires improvements such as the elimination of sample tilt error, estimation of line-contact CNT adhesion contact area, the added ability to test nanotubes/nanofibers with large deviations from straightness and significant defects, and a better understanding of how mechanical properties measured at the polymer surface differ from those in the bulk configuration [39] where nanotube/nanofiber-reinforcements are typically added. Despite these shortcomings and in light of the few and often cumbersome alternatives [19,40], we have shown that the AFM peeling force spectroscopy method already offers the experimental ability to sensitively and quantitatively compare interfacial characteristics with minimal preparation, and will become a useful method for characterizing novel CNT/nanofiber functionalizations and
future polymerization techniques as the next generation of nano-
composites is developed.

Acknowledgement

This work was funded, in part, by the National Science Founda-
tion through the Grant CMMI-0826356 “Cyber enabled predictive
models for polymer nanocomposites: multi-resolution simulations
and experiments,” and the Bilisland Dissertation Fellowship from
the Purdue University graduate school. C.V.N is employed by ELO-
RET Corporation at NASA Ames Research Center, and his work is
supported by a subcontract from University Affiliated Research
Center (UARC) operated by the University of California Santa Cruz
at NASA Ames.

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