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Philip A. Yuya
University of Nebraska - Lincoln

Yongkui Wen
University of Nebraska - Lincoln

Joseph A. Turner
University of Nebraska - Lincoln, jaturner@unl.edu

Yuris A. Dzenis
University of Nebraska - Lincoln, ydzenis@unl.edu

Zheng Li
Peking University, Beijing 100871, China

Determination of Young's modulus of individual electrospun nanofibers by microcantilever vibration method

Philip A. Yuya, Yongkui Wen, Joseph A. Turner,[a] and Yuris A. Dzenis
Department of Engineering Mechanics, W317.4 Nebraska Hall, Lincoln, Nebraska 68588-0526

Zheng Li
Department of Mechanics and Engineering Science, Peking University, Beijing 100871, China

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The authors report a technique for measuring Young's modulus of a single electrospun nanofiber using the vibrations of two microcantilevers coupled with the nanofiber. The modulus is calculated from the resonant frequency shift resulting from the nanofiber. Polyacrylonitrile nanofibers (200 nm diameter) were collected during electrospinning and wrapped on two similar microcantilevers causing a shift in first resonance from 10.0 to 19.4 kHz. Finite element analysis was used to analyze the frequency shift using images from a scanning electron microscope giving a modulus of the as-spun polyacrylonitrile nanofiber of 26.8 GPa. © *2007 American Institute of Physics*.
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Continuous nanofibers manufactured by spinning fiber-forming solutions in high electric fields represent a class of nanomaterials with critical advantages for applications.[1] Their dual nanomacroscopic nature allows one to combine their potentially unique nanoscale-related properties with ease of processing characteristic of macroscopic materials. Continuous polymer, carbon, and ceramic nanofibers are being currently developed for applications in various areas of nanotechnology.[1–3] Many of these applications require reliable information on nanofiber mechanical properties. An ultrasmall nanofiber diameter precludes the use of conventional fiber testing techniques. For example, only larger fibers with diameters approaching 1 μm can be tested using modified tensile fiber testing methods.[4–6] Recently, atomic force microscopy (AFM)-based techniques similar to the ones used for characterization of carbon nanotubes and inorganic nanowires[7–10] have been applied to measure the elastic response of electrospun nanofibers.[11–14] The techniques requiring fixed nanofiber attachment (gluing) to a cantilever tip[14] were laborious and could be applied only to larger nanofibers. Bending of nanofibers suspended over pores[13] or shorter[11] or longer trenches[12] required easier specimen preparation and could generally be used on smaller nanofibers. However, scanning required to find a suitable nanofiber and its center-span point rendered these methods less suitable for high-throughput testing.

Vibrations excited by thermal or electrical loads were used to measure elastic properties of carbon nanotubes.[15–18] One end of carbon nanotubes was embedded into rigid substrate and vibrational amplitudes were evaluated *in situ* using transmission electron microscopy. Elastic properties of nanotubes were then derived from the measured resonant frequencies. Vibrational analysis can theoretically lead to fast and robust evaluation of stiffness of electrospun nanofibers.

In this letter, a microcantilever-based, vibrational method for determining Young's modulus of a single electrospun nanofiber is described. The nanofiber collected directly during electrospinning is attached to two AFM microcantilevers. An atomic force microscope is then used to determine the resonant frequencies of a microcantilever-nanofiber system from which Young's modulus of the nanofiber is obtained. Since the vibration amplitudes are kept sufficiently small, the vibrations of the system do not cause the nanofiber to slack. Therefore the nanofiber is modeled as a spring under tension with "spring constant" k. The technique is demonstrated on an example of electrospun polyacrylonitrile (PAN) nanofiber.

The theory for this technique is based on conventional beam dynamics for which an analytical relation between the fiber stiffness and the resonant frequencies is obtained for specific geometries.[19,20] A schematic of two similar prismatic beams, cantilevered at one end and coupled with a nanofiber of stiffness k at the other end is shown in Fig. 1. The boundary value problem for this system has governing equations given by

$$EIq_i''''(x,t) + \rho\ddot{q}_i(x,t) = 0 \quad (i = 1,2), \tag{1}$$

where $q(x,t)$ is the cantilever dynamic deflection, EI is the flexural rigidity of the beam of length L, ρ is the mass density per unit cross-sectional area, $k = E_f A_f / L_f$ is the fiber stiffness, E_f, A_f, and L_f are the modulus, cross-sectional area, and length of the fiber, respectively. The primes denote spatial derivatives while the overdots are derivatives in time. Here we use $q_1(0,t)=0$, $q_2(0,t)=0$, $q_1'(0,t)=0$, $q_2'(0,t)=0$ as geo-

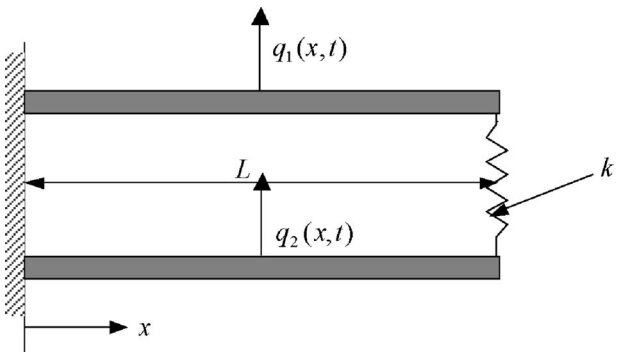

FIG. 1. Schematic of the problem showing two prismatic beams cantilevered at one end and coupled with a nanofiber of stiffness k at the other end.

[a]Electronic mail: jaturner@unl.edu

metric boundary conditions and $q_1''(L,t)=0$, $q_2''(L,t)=0$, $EIq_1'''(L,t)=k[q_1(L,t)-q_2(L,t)]$, $EIq_2'''(L,t)=-k[q_1(L,t)-q_2(L,t)]$ as natural boundary conditions. The shear force in the two cantilevers is balanced by the stiffness of the nanofiber at the coupling point. The values of the dimensionless wave numbers $\gamma=L\lambda(\lambda^4=\rho\omega^2/EI)$ are obtained from the numerical solution of the characteristic equation of the problem,

$$\{\gamma^3(1+\cos\gamma\cosh\gamma)-2C(\cos\gamma\sinh\gamma-\sin\gamma\cosh\gamma)\}\times\{\gamma^3(1+\cos\gamma\cosh\gamma)\}=0, \quad (2)$$

where C is the stiffness ratio given by k/k_c and $k_c=3EI/L^3$ is the stiffness of the beam. If there is no coupling between the cantilevers, the characteristic equation is that for two beams in free vibrations, $[\gamma^3(1+\cos\gamma\cosh\gamma)]^2=0$. If the fiber is very stiff relative to the spring constant of the cantilevers such that $k/k_c\to\infty$, the characteristic equation becomes $\cos\gamma\sinh\gamma-\sin\gamma\cosh\gamma=0-$ that of a beam with a pinned boundary condition. This idealized system was used to select the appropriate cantilevers for the PAN nanofibers of interest. Stiffness curves as a function of frequency increment can be obtained for a particular cantilever type. The difference between the resonant frequency of the beam without the nanofiber and that of the beam with the fiber attached is taken as the frequency increment. If the spring constant of the cantilever and the vibration mode are selected appropriately, the resonance frequency increment for the vibrating cantilever becomes sensitive to the nanofiber stiffness.

Utilization of the described technique requires collection or isolation of a single nanofiber. In this work, a grounded metal tweezers was utilized to "capture" a single nanofiber during electrospinning. The tweezers was placed aside the electrospinning jet instability zone.[1] Capturing the nanofiber in this way ensures that it remains in tension after attachment to the tweezers. By carefully controlling the position and retaining time, a single nanofiber or a few aligned nanofibers were spun across two tips of the tweezers. Commercial PAN dissolved in *N*, *N*-dimethylformamide was used to manufacture the PAN nanofiber. All chemicals used were obtained from Aldrich. The experiment was conducted at 12.5 kV supplied by Gamma High Voltage, UC5-20P, with a 20 cm distance from the tip of the stainless steel tube to the bottom plate. The internal diameter of the tube was 0.76 mm. A Cole Parmer 74900 series micropump and a 5 ml plastic syringe were used to provide a steady supply of polymer solution. The typical feed rate was 0.20–0.25 ml/h. The single PAN nanofiber spun on the tweezers was then transported and suspended between two AFM cantilevers for further mechanical testing. The ends of the suspended nanofibers were wrapped around the cantilevers, thus improving nanofiber attachment.

Resonant frequencies of the AFM cantilever beams were obtained using an Autoprobe CP AFM (Park Scientific Instruments, Sunnyvale, California) operating in noncontact mode. The laser beam was steered such that it reflected from the back of the uppermost cantilever, use being made of the optical view. An optimal amplitude value that yielded good frequency response curves was chosen. The maximum cantilever resonance peaks were recorded for both the free cantilever vibrations (10.0 kHz) and for the case when the cantilever had nanofibers attached (19.4 kHz). Adhesive forces between the fiber and the silicon cantilevers were found to satisfy the assumption that the nanofibers were fixed onto the

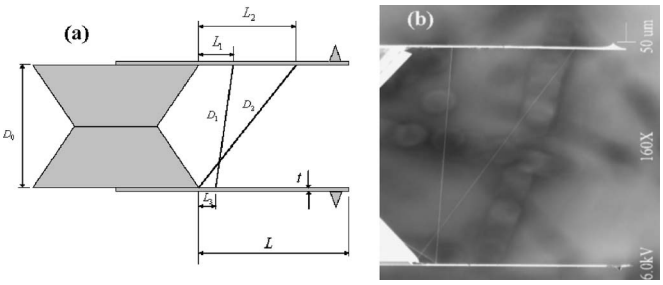

FIG. 2. Nanofibers attached to two similar AFM cantilever probes. (a) Schematic that shows how the nanofibers are attached and the distance from the fixed end of the cantilever. (b) Scanning electron microscope image that shows nanofibers attached to the AFM cantilever probes.

cantilevers since the fiber position did not change after the experiment was performed. Tan and Lim[11] also found that the adhesion force between the fiber and silicon substrate satisfied the assumption of a fixed boundary condition. Figure 2 shows two cantilevers (Veeco Probes, MPP-32100, length of cantilever $L=450$ μm, width=35 μm, thickness =2 μm, spring constant $k_c=0.1$ N/m, $L_1=94.5$ μm, $L_2=342.8$ μm, and $L_3=47.8$ μm) that are connected by two nanofibers of diameter of ~200 nm. The diameter of the nanofibers was calculated from the scanning electron microscope (JOEL JSM–5600LV) images. The images were taken without coating so that the mechanical properties of the fiber were not affected.

Although the simple model of Fig. 1 was used for choosing the appropriate cantilevers, Fig. 2 clearly shows that the nanofiber is not attached at the ends of the cantilevers. Thus, finite element analysis (FEA) was used to analyze the frequency shift of the above problem (ANSYS). The cantilever beam was modeled using 2520 SOLID45 [three-dimensional (3D) eight-node] elements, and the tip mass was represented with MASS21 element as a 3D structural mass without rotary inertia. The modal analysis of the cantilever beam was performed by the subspace iteration method. Considering the aforementioned system, in which two nanofibers connect two parallel cantilever beams on the same sides, the nanofiber can be modeled as a spring with an elastic constant $k=EA/D_0$, where E is the Young's modulus of the nanofiber, A is its cross-sectional area, and D_0 is the distance between the two beams ($D_0=600$ μm). Both nanofibers are assumed to have the same Young's modulus and the same cross-sectional area. Thus, according to the length of each nanofiber, the elastic constant of each nanofiber can be expressed as

$$k_i=\frac{EA}{D_0}\frac{D_0}{D_i}=k\frac{D_0}{D_i} \quad (i=1,2), \quad (3)$$

where $D_1=606.67$ μm and $D_2=691.02$ μm represent the lengths of the nanofibers. Here, COMBIN14 element (3D longitudinal spring damper) was used to simulate the nanofiber. From the FEA model, the first frequency can be made equal to 19.4 kHz, the same as the experimental result, if k is 1.401 N/m. Compared to the results of the free vibrations, the first frequency is enhanced by about 94%, but the second one just rises 2.7%. This result implies that the presence of nanofibers affects the first frequency but higher frequencies are not significantly affected. In addition, the vibration response was dominated by the nanofiber furthest from the cantilevered end. For a nanofiber with a diameter of 200 nm, Young's modulus can be calculated as 26.8 GPa. This value

agrees with other PAN nanofiber measurements.[14]

On the basis of microbeam vibration theory, we have developed a technique for measuring Young's modulus of a single electrospun nanofiber suspended between two AFM microcantilevers. The method utilizes a unique capability of the electrospinning process to produce long, freestanding sections of nanofibers and the possibility to attach these nanofibers to microcantilevers by a combination of adhesion and wrapping. The capabilities of modern AFM systems to excite and detect vibrations in the kilohertz region are also utilized, in conjunction with finite element method modeling. By selecting the spring constant of the cantilever and the vibration mode appropriately, the resonant frequency increment for the vibrating cantilever becomes sensitive to the nanofiber stiffness and can be used to evaluate Young's modulus. This technique can be beneficial to research and development of continuous nanofibers with well-controlled mechanical and functional properties. It is expected that this technique can be automated and used for high-throughput evaluation of nanofibers and quality control.

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