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Size-dependent elastic modulus of single electroactive polymer nanofibers

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The authors report for the first time the size dependency of the elastic modulus of well-aligned single polymeric nanofibers. The nanofibers were fabricated from electroactive polymers (EAPs) and had an ellipsoidal cross section because of impingement between a solid surface and a polymer jet during electrospinning. Although the EAPs had very weak mechanical properties in the bulk, the elastic modulus of single EAP nanofibers increased exponentially as the diameter of the EAP nanofibers decreased to diameters of a few tens of nanometers. The elastic modulus of single nanofibers was measured using three-point bending tests employing an atomic force microscope.
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The relationship between the physical properties of one-dimensional (1D) nanostructures and structural elements such as size and geometry has been actively investigated because of unique properties of 1D nanostructures, which are unattainable in the bulk.[1–6] In the investigations into the size-scale effect of mechanical properties of 1D nanostructures, Lee *et al.* showed that the elastic modulus of multiwalled carbon nanotubes (MWNTs) grown by chemical vapor deposition (CVD) depends strongly on the diameter of MWNTs and suggested that it may result from the development of crystalline structures related to the mechanism of MWNT growth in CVD.[5] Wu *et al.* demonstrated that the average elastic modulus of silver nanowires prepared through the kinetic control of the hydrothermal conditions is higher than that of bulk silver and the controlled grain orientation within the nanowires is responsible for their anomalous mechanical properties.[6] However, a size-scale effect on mechanical properties of polymer nanofibers produced by electrospinning (a typical method used to produce polymer nanostructures for applications such as tissue engineering scaffolds,[7] sensors,[8] and oscillators[9]) has been little investigated although the nanofibers undergo severe structural deformations[10] during electrospinning.

In this letter, we elucidate the size-scale effect between well-aligned single polymer nanofibers and elastic modulus using a three-point bending technique[11–13] employing an atomic force microscope (AFM). Among many polymers, a poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) polymer has its unique character showing very slender and uniform morphology even in a diameter of a few tens of nanometers in electrospinning.[14,15] The PAMPS polymer is well known as an electroactive polymer (EAP) hydrogel that can exhibit a change in volume under an external electric field,[16] which has potential applications as artificial muscles, smart devices, and polyelectrolytes.[16–18] However, such a PAMPS polymer has shown very low elastic modulus of 0.051 MPa in the fully swollen bulk state.[19]

PAMPS with an average molecular weight of 2×10^6 g/mol was used as the polymer material for fabricating nanofibers and was dissolved to a concentration of 15 wt % in water. The PAMPS solution and ethyl alcohol were purchased from the Aldrich Chemical Co. (Milwaukee, WI). The AFM calibration gratings (model TGZ02, step height range=102±2 nm, pitch=3.0 μm) and AFM tips with a triangular shape (radius of curvature ≈35 nm, force constant=0.35 N/m) were purchased from MikroMash (Portland, OR).

The 3.5 wt % PAMPS/water/ethanol solution was prepared by mixing the 15 wt % PAMPS/water/solution and ethanol. To ensure a homogenous mixture, the solution was used after 24 h. Aluminum electrodes were used as the collector to fabricate randomly oriented nanofibers. The PAMPS solution was loaded into a plastic syringe equipped with a stainless steel needle. The polymer solution was fed at a flow rate of 2 μl/min using a syringe pump (KD Scientific, Holliston, MA) located in a horizontal mount. A voltage of 0.67 kV/cm was applied between the syringe needle and the grounded electrodes using a high-voltage power supply (Nano Technics, Korea). To fabricate well-aligned nanofibers, AFM gratings and Si wafers were laid between two parallel metal strips with a 3 cm gap, and all the other experimental parameters were the same as those used for the aluminum electrodes.

From the field-effect scanning electron microscope (SEM, model S4700, Hitachi, Japan) image of Fig. 1(a), it was confirmed that the PAMPS nanofibers were long and uniform and had diameter distributions ranging from ~60 to ~250 nm. To minimize the error that can occur during the measurement of the mechanical properties of single nanofibers employing an AFM (model XE-100, PSIA Inc., Korea), well-aligned PAMPS nanofibers [Fig. 1(c)] were fabricated by placing the AFM grating between two metal strips that generated a split electric field in the electrospinning system.[20,21]

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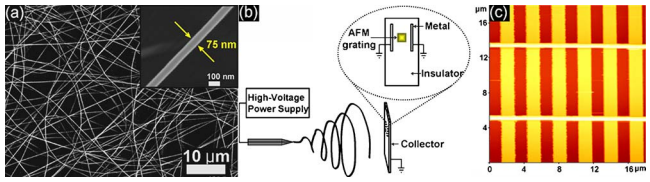

FIG. 1. (Color online) (a) SEM image showing randomly oriented PAMPS nanofibers deposited on an electrode. The inset shows a magnified SEM image of a nanofiber with a diameter of about 75 nm. (b) A schematic diagram of the process used to align a single nanofiber on the AFM calibration grating with 1.5-μm-wide periodic trenches, and (c) an AFM image showing well-aligned PAMPS nanofibers.

The measurement of elastic modulus using the three-point bending theory requires accurate dimensions of a cross section of nanofibers because the elastic modulus is related to diameter to the fourth power.[22] In an electrospinning process accelerating polymeric fluid jets by a high electric field,[23] polymer nanofibers with a noncircular cross section can be produced due to strong impingement with a collector surface. From Fig. 2, we confirmed the ellipsoidal nature of the nanofiber after contact with the collector surface.

It is well known that the AFM produces artifacts when imaging steep steps due to the conical shape of the tip.[24] Similarly, the tip cannot penetrate overhangs as they occur on the underside of the nanofiber. The determination of the fiber geometry must, therefore, include a correction for these limitations of the AFM. In Fig. S1 (supplementary information), we illustrate how the AFM tip traces over the nanofiber and produces a linear side to the image of the nanofiber (as shown in the height profile). To determine the width of the nanofiber, we found points on either side of the nanofiber where the profile changed from curved to linear. The profile between these points was assumed to represent an accurate image of the top surface of the fiber, and the distance between the points was taken as the fiber width. The height of the nanofiber could be accurately determined directly from the AFM image.

Figure 3(a) shows a magnified AFM image of a suspended PAMPS nanofiber that is ready for testing by applying a vertical force from the AFM tip in a three-point bending mode. In Fig. 3(c), the diameter of the nanofiber was determined to be 99.74 nm because the step height of the AFM grating was 102 nm. Comparing Figs. 3(b) and 3(c), it was confirmed that the nanofiber did not droop across the trench. The height profile of the single nanofiber shown in Fig. 3(d) [the black dotted line in Fig. 3(a)] shows that the width of the nanofiber was 184 nm. By considering the curvature of the AFM tip used for imaging the single nanofibers, it was confirmed that the cross sections of the PAMPS nanofibers fabricated using electrospinning were ellipsoidal rather than circular. This may be the result of the strong impingement of the jet ejected from the solution rapidly impacting the AFM grating. On the other hand, since the fiber does not make an impingement contact with the collector surface in the suspended region, it is possible that the fiber attains a circular cross section. If a cross section of the fiber changed across the trench, the AFM image would detect a change in fiber height since the volume of the fiber must remain constant per unit length of fiber (both suspended and in contact with the collector). However, because Figs. 3(a)–3(c) do not almost show any deviation in fiber height in the suspended part, we conclude that the fiber has a constant ellipsoidal cross-sectional shape in the suspended parts.

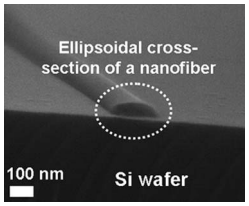

FIG. 2. SEM image showing a cross-sectional shape of a nanofiber cut using a diamond pen without cooling with liquid nitrogen after the nanofiber was aligned on a Si wafer.

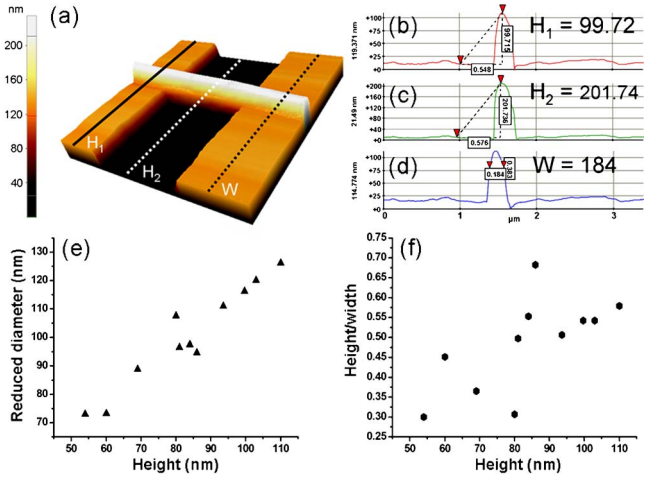

FIG. 3. (Color online) (a) AFM contact mode image showing a single nanofiber magnified for the measurement of elastic modulus, [(b) and (c)] height profiles of the single nanofiber shown in Fig. 3(a) [(b)—black solid line and (c)—white dotted line], (d) a height profile for determining a width of the single nanofiber shown in Fig. 3(a), (e) a diagram showing the relationship between the reduced diameter and the height of the measured nanofibers, and (f) a diagram showing the aspect ratio (height/width) of the measured nanofibers according to the height of the nanofibers.

To minimize the deformation of a nanofiber by the shear stress that can generate during three-point bending tests of a nanofiber, the suspended length to diameter ratio of the measured nanofibers must be >10.[22] Because the nanofiber height was smaller than the nanofiber width due to the impingement effect of nanofibers (like Fig. 2), it could be unreasonable to regard height as a diameter and calculate the suspended length to diameter ratio. Therefore, we used a reduced diameter induced from height and width of nanofibers and only selected nanofibers with the ratio >10. We defined the height as being the short diameter and defined the width as the long diameter when calculating the second moment of the area of a nanofiber (I). The suspended length was 1.5 μm and the reduced diameter was obtained from the following relationship:[22]

$$\frac{\pi d^4}{64}(I_c) = \frac{\pi a^3 b}{64}(I_e), \tag{1}$$

where I_c is the second moment of the circular area, I_e is the second moment of the ellipsoidal area, d is the reduced diameter of the nanofiber, a is the short diameter (height) of the nanofiber, and b is the long diameter (width) of the nanofiber. From Eq. (1), the reduced diameter of the single nanofiber (height=99.74 nm) shown in Fig. 3(a) was 116.24 nm, and the suspended length to reduced diameter ratio was 12.9. Figure 3(e) shows that the reduced diameter generally increased as the height increased. This means that there is a good correlation between these variables (the cor-

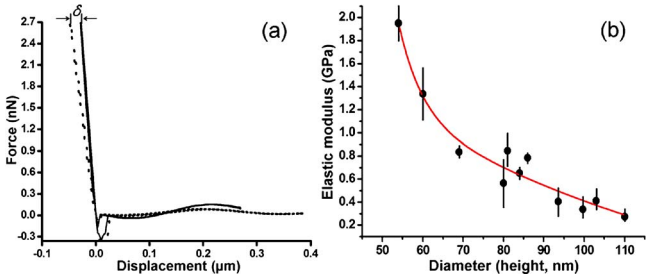

FIG. 4. (Color online) (a) Force-displacement curves obtained by applying a vertical force via an AFM tip to a single PAMPS nanofiber (dotted line) and the surface of an AFM grating as a reference (solid line), and (b) a plot of the size-dependent elastic modulus vs the diameter (height) of PAMPS nanofibers.

relation coefficient was 0.96). In Fig. 3(f), all the measured nanofibers had an ellipsoidal cross section since the nanofibers would have a circular cross section if the aspect ratio (height/width) were unity.

Figure 4(a) shows that the nanofiber underwent elastic deformation under the applied force from the AFM tip because the loading and unloading cycles of the force-displacement curves were linear and coincided with each other. When a maximum force of 2.7 nN was applied at the midpoint of the nanofiber with a loading rate of 0.2 μm/s, the deflection (δ) of the nanofiber was obtained using a literature method[25,26] from the data shown in Fig. 4(a). The elastic modulus was calculated from the three-point bending equation using the following relationship:[22]

$$E = \frac{FL^3}{192\delta I}, \tag{2}$$

where E is the elastic modulus, F is the maximum force, and L is the suspended length of the nanofiber. In Fig. 4(b), as the diameter of the nanofiber decreased, the elastic modulus of the nanofiber increased exponentially at the diameter of about 70 nm. This would result from a transformation of the mechanical properties due to the orientation of polymer molecules inside nanofibers arising from the strong strain forces in polymer jets. In electrospinning, the strain rate of the ejected polymer jets has a magnitude in the order of 10^4/s,[10] and it has been experimentally elucidated that polymer chains of the resultant polymer nanofibers are oriented along the fiber axis due to the high strain rate of polymer jets.[27–30] The decrease in the diameter of the nanofibers under the same experimental conditions means that the strain rate of the nanofibers was very high, and therefore the orientation of the polymer chains could be well developed. As a result, the data shown in Fig. 4(b) reflect the orientation of the polymer molecules in the nanofibers achieved during electrospinning. Moreover, Fig. 4(b) suggests that it is necessary to fabricate polymer nanofibers with diameters of a few tens of nanometers for tough nanofiber assemblies. The modulus values were found to be in the range of 0.3–2.1 GPa, which is low for glassy polymers. It is likely that the PAMPS fibers were plasticized by atmospheric moisture thereby lowering their moduli although relative humidity has been constantly maintained at 28%.

In conclusion, we have found that the elastic modulus of a single EAP nanofiber is size dependent. This effect would play an important role in the engineering of the mechanical properties of a nanofibrous matrix, or of single polymer nanofibers when they are applied to sensors, to scaffolds, or to artificial muscles. Although the size-dependent effect on the mechanical properties of single polymer nanofibers was elucidated through EAP nanofibers, this effect would be applicable to all the other polymer nanofibers generating polymer chain orientation during electrospinning.

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