Crystalline Polyethylene Nanofibers with the Theoretical Limit of Young’s Modulus

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Low-density materials such as polymers usually have low stiffness and strength.[1] In many fields, such as the electronics and space industries, lightweight materials with high strength and stiffness are of great importance in order to enhance reliability and portability. The search for these materials has led to the development of functional polymers that have remarkable mechanical properties.[2–5] Although bulk polymers usually possess low strength and stiffness due to the entanglement of the molecular chains, crystalline polymers with well-packed and aligned molecular chains can theoretically provide a maximum stiffness that is controlled by covalent bond distortions. Over the past few decades, significant efforts have been devoted to enhancing the chain alignment (and thus the stiffness) through fabrication of polymer (e.g., polyethylene (PE)) fibers using methods such as solution/gel-based spinning,[6–9] surface growth,[10–13] and electrospinning.[4,14–17] Commercially-available oriented PE fibers, with diameters ranging from 10 to 30 μm, currently achieve stiffnesses (i.e., Young’s modulus) of ~150 GPa at room temperature,[5,18] and reported values in the literature are generally below 200 GPa.[3,7–9,19,20] The values obtained from these conventional methods are two orders of magnitude higher than the stiffness of bulk PE (~1 GPa).[21] Due to the presence of defects such as voids and entanglements, however, the measured values for PE fibers still fall below the theoretical limit of a single PE molecule or PE single crystals, which is predicted to be as large as 374.5 GPa.[22]

Extensive work has been done to measure or predict the maximum Young’s modulus of PE. In a PE crystal, interchain interactions have a negligible effect on axial stretching because the axial modulus is much higher the radius modulus.[23] As such, the Young’s modulus of a PE crystal (i.e., the maximum Young’s modulus of PE), can be obtained with acceptable accuracy from the response of a single chain.[24] Interpretation of data from Raman spectroscopy and neutron inelastic scattering experiments yielded Young’s modulus values of 358 GPa,[25] and 329 GPa,[25,26] respectively. The Young’s modulus was estimated from X-ray diffraction studies to be 283 GPa.[24] At zero temperature, ab initio calculations predicted a Young’s modulus of 305 ± 30 GPa,[24] and 374.5 GPa,[22] while that from empirical quantum mechanical calculations was reported to be 315–326 GPa.[24] Overall, the predicted maximum Young’s modulus of PE spans a range of 280–380 GPa.

The microstructure of oriented microfibers consists of amorphous regions and nanocrystalline regions that are induced during the drawing process (also referred to as “Shish-Kebab” structures).[27] The flow induced shish-kebab structures have been extensively reviewed.[28] Individual crystallites have been observed to be tens of nanometers in lateral dimension,[18,24,30] In contrast with microfibers, nanofibers have diameters comparable to the dimensions of the nanocrystallites and can thereby be used to minimize the extent of amorphous regions. With identical lengths, the volume of a nanofiber is at least two orders of magnitude smaller than that of a microfiber. The growth of the amorphous regions of the nanofiber is greatly prohibited, thus a substantially lower concentration of defects will exist in a nanofiber than in a microfiber.

In this letter, we fabricate crystalline PE nanofibers by combining a traditional gel-based spinning method with a tip-drawing technique.[13] We demonstrate, for the first time, that the Young’s modulus of PE nanofibers with diameters from 70 nm to 260 nm can be as high as 312 +/- 108 GPa, within the range of the predictions of the theoretical maximum. This value is comparable with the best Young’s modulus of metal alloys, but the density of the PE nanofibers is one order of magnitude smaller. Crystalline nanofibers, which can potentially achieve the ultimate modulus of polymers, thus open up a new route to manufacture light-weight and ultra-strong polymer fibers.

To fabricate a PE nanofiber, we first dissolve PE powder (ultrahigh molecular weight PE; dimensionless relative molecular mass of 3 – 6 x 10^6; Alfa Aesar) in Decalin at 140 °C to prepare a PE gel. The dilute solution has a concentration of 0.8 wt%. The dissolving process is conducted inside a glove box filled with argon gas to avoid molecular degradation. After the white PE powder is completely dissolved, the mixture becomes a transparent viscous fluid and the beaker containing the liquid is immediately put into a cold water bath. When the liquid is cooled down to room temperature, the translucent PE gel is made.

Following the PE gel preparation, a two-stage heating process is implemented to produce highly-crystalline PE nanofibers.[31] A hot plate is used to uniformly heat the air above at 90–100 °C. A 5 mm by 5 mm silicon chip is suspended about 1 cm over the hot plate. A small heater is attached to the back of the chip. The heater and the chip together form a PE gel holder whose temperature can be adjusted to melt the gel in a controllable period of time. The gel is heated at 120 °C on the silicon chip for a few seconds until the translucent gel turns into a clear liquid. A glass tip fixed to a micromanipulator is then used to horizontally pull...
a microfiber with a length of hundreds of microns. The microfiber suspended over the hot plate is heated by the hot air. The microfiber is then slowly drawn so that its size is scaled down to nanometer level, and during this drawing process, the fiber is subject to the second stage heating. A mixed elongational and shear flow is observed during the drawing process.\[^{32,33}\] The pulling velocity is on the order of 50 µm·s\(^{-1}\). The shear rate is estimated to be >1500 s\(^{-1}\). The entire fabrication process is conducted under a dark-field stereo microscope and takes 1–2 minutes. The uniformity of nanofibers can be improved by using a lower pulling velocity. However, with the same shear duration, a higher pulling velocity generally results in a larger shear rate and a smaller diameter of a nanofiber.

The states of the PE molecules at each fabrication step are shown in Figure 1. In the translucent gel (Figure 1a) before the first stage heating, some PE molecular chains are folded locally in the form of small crystallites, usually termed as “lamellae”, that are tens of nanometers in height and several microns in length. While some other molecular chains are randomly entangled and distributed in the gel, the “lamellae” serve as common joints for the entangled PE molecular chains. When the gel is heated above the PE melting temperature (120 °C) during the first stage heating, both lamellae and entangled molecular chains are dissolved in the solvent, resulting in a uniformly clear solution that contains only entangled PE chain networks swollen by the solvent (Figure 1b). When these PE molecular chains are stretched by the fine glass tip in the second stage heating, they solidify and align in a common direction (Figure 1c) because the solvent evaporates to the air.

Through the two drawing steps, the fiber diameter can be reduced from several microns to less than 100 nm. For instance, a 3 µm thick fiber that is drawn into a nanofiber 80 nm in diameter has a draw ratio larger than 1400 (calculated by assuming volume conservation and a cylindrical shape). The large draw ratio enables extreme extension and alignment of the PE chains in the drawing direction due to a large shear rate\[^{28}\] between chains along the nanofiber. The diameters of the final PE fibers are a few hundred nanometers (or even below 100 nm), which is comparable to the core sizes of Shish-Kebab structures.\[^{30}\] In this case, the platelet (i.e., the Kebab) growth is significantly suppressed. The solidification of the PE nanofibers after the solvent evaporation maintains the alignment and orientation of the PE molecules (Figure 1c). As a result, the number of defects and impurities is greatly reduced, compared with a microfiber, which leads to an extremely high crystallinity (>90%). The fabricated PE nanofibers have diameters ranging from 70 to 500 nm. An example of a 80.9 nm diameter nanofiber is shown in Figure 2a. The selected area
trenches are 500 nm in depth with widths ranging from 5 to 10 μm. They are fabricated on a 4-inch silicon wafer using photolithography and reactive ion etching. The silicon wafer is sliced into the aforementioned substrates (3 × 3 mm²) so that a typical nanofiber spans the width of the chip. Under a high precision microscope (Nikon, Eclipse LV 100 DA-U), we use a tungsten tip (tip diameter ∼1 μm) to clamp both ends of the nanofiber across the trenches with super glue (Gorilla Glue Inc., Precision Glue Pen).

We probe and measure the deflection of the PE nanofiber with an AFM (Agilent 5500 SPM). The cantilevers are standard silicon probes (Model: FMV; Bruker AFM Probes) with rectangular shapes. The spring constant of each cantilever is calibrated using the in situ thermal noise method based on the equipartition theorem. In our experiments, the spring constant of the cantilever must be larger than 1 N/m in order to obtain a measurable nanofiber deflection while keeping the bending of the cantilever in the linear region. By scanning the PE fiber using the AFM, we can locate its middle point across the trench. We perform FDS at this middle point to obtain force-deflection (FD) curves. The FD curves show the relationship between a force applied on the cantilever and the vertical displacement of the sample. During the FDS test, the AFM scanner is able to move the tip to approach the sample and retract it from the sample. In a typical FD curve, the force is plotted against deflection for both approach and retraction. In Figure 3c, the approach and retraction curves overlap well.
which indicates that the nanofibers behave linearly with low applied forces (<150 nN).

The FD curve we obtain is a combination of the deflections of both the PE nanofiber (diameter 102 nm, length 5 μm) and the AFM cantilever. In order to isolate the deflection of the PE nanofiber, we also performed FDS measurement on a bare silicon surface to get an FD curve for the cantilever itself. Two FD curves from experiments, i.e., one on a PE nanofiber and the other on a silicon substrate, are shown in Figure 3c, including both approach and retraction curves. When the AFM tip is brought to contact with the rigid silicon substrate, only the AFM cantilever bends, and hence with the same applied force $F$, the deflection $\Delta Z_s$ corresponding to the cantilever bending is smaller than the combined deflection $\Delta Z_p$. The difference between $\Delta Z_p$ and $\Delta Z_s$ is the downward deflection $\delta$ of the PE nanofiber at its midpoint. By analyzing Figure 3c, we can express $\delta$ by the slopes of these two FD curves as:

$$\delta = \Delta Z_p - \Delta Z_s = \frac{F}{k_p} - \frac{F}{k_s} = F \left( \frac{k_s - k_p}{k_s k_p} \right)$$  \hspace{1cm} (1)

where $k_s$ and $k_p$ are the slopes of the FD curves in Figure 3c for a silicon substrate and a PE nanofiber. When a homogeneous beam is fixed at both ends and a concentrated load is applied at its center, the expected maximum deflection at the center is given by:

$$\delta = \frac{FL^3}{192EI}$$  \hspace{1cm} (2)

which is a solution of the Euler-Bernoulli beam equation provided that the longitudinal length of the beam's neutral plane does not change during the bending. In Equation (2), $F$ is the concentrated central load, $L$ is the length of the original beam, and $I$ is the moment of inertia of the beam. Combining Equations (1,2,) and substituting the moment of inertia for a circular cross section, $I = (\pi d^4)/4$, the Young's modulus can be expressed as:

$$E = \frac{k_s k_p L^3}{k_s - k_p} \frac{1}{192I} = \frac{k_s k_p L^3}{k_s - k_p} \frac{1}{3\pi d^4}$$  \hspace{1cm} (3)

where $d$ is the diameter of the nanofiber.

In Figure 3c, under a load of 150 nN at the middle point, the deflection of a PE nanofiber with a diameter of 102 nm is 51 nm after subtracting the cantilever deformation from the combined deflection. We limit the deflections of the PE nanofibers to their diameters to: (1) Ensure that the Euler-Bernoulli beam theory is valid for our measurements, and (2) Avoid damage and breakage of both the AFM cantilever and the PE nanofiber. From Figure 3c, we can also observe that in this small deflection range, the deflections of the cantilever and the PE nanofiber are both in a linear region, indicating that the deformations are elastic. Within the limited range of force and deflection, we also perform FDS tests on nanofibers placed directly on the substrate. The slopes of the FD curves are nearly identical to those obtained from bare silicon substrates. This result confirms that the tip indentation into the nanofiber and deformation of the nanofiber cross section are both negligible.

When applying Equation (3), the Euler-Bernoulli beam theory assumes that the PE nanofiber is an isotropic material. For nanofibers, however, the axial Young’s modulus is much higher than the radial one because the carbon covalent bond along the PE chain is much stronger than chain-chain Van der Waals interactions. In order to identify the impact of the anisotropy of the nanofiber on our FDS measurements, we also performed finite element analysis (FEA) for a nanofiber with the same dimensions (diameter 102 nm, length 5 μm) as the sample that yielded the FDS curves in Figure 3c. In terms of the orthorhombic PE crystal structure (Figure 4a), we assume
that the fiber has an axial (z direction) Young’s modulus of 343 GPa (obtained from Figure 3c) and that the fiber has an axial, x, and y directions are 9 GPa and 9.5 GPa, as obtained from theoretical predictions. \cite{23,47,48} For an anisotropic PE fiber with a center load of 150nN (Figure 4b), the maximum deflection of the middle point is 62 nm, as shown in the FEA simulation result (Figure 4b). For an isotropic PE fiber with the same dimensions, the maximum deflection from the FEA simulation is 54.2 nm (Figure 4c), which agrees well with the analytical solution (54.1 nm) and the experimental result shown in Figure 3c. We note that the anisotropic model gives a deflection 10% higher than the isotropic model and the analytical solution. This result is consistent with another set of FEA simulations for a load of 200 nm on the same nanofiber (See Supporting Information). Since the anisotropic model yields a larger deflection, the derivation in our experiment gives a lower Young’s modulus, which indicates that the real axial Young’s modulus of the PE fiber is slightly higher (12% in this case) than our experimentally derived results. For the reported results, we extract the Young’s modulus using the isotropic model rather than FEA because the isotropic model is much simpler and the moduli in the x and y are difficult to measure experimentally.

Before calculating the Young’s modulus, the clamping conditions of the nanofiber at the edges of the trench should be carefully examined because they determine if Equation (3) is applicable. In our experiments, each FDS test is performed at least five times on the silicon substrate and the PE nanofiber for each sample. For our samples, the slopes of the resulting FD curves on a nanofiber deviate randomly in a very small range (±3–4%). This small deviation confirms that the nanofibers are tightly fixed at both ends and that they don’t slide, lift off from the substrate, or plastically deform. Therefore, the adhesion from the glue and the Van der Waals force between the PE nanofiber and the silicon substrate validate the fixed ends approximation made in Equation (2). In addition, as mentioned in previous reports, the ratio between the suspended length of the nanofiber and its outer diameter should be at least 16 in order to eliminate the shear deformation of the nanofibers during the FDS test.\cite{32} In our experiments, this ratio is larger than 40 for all measured samples. We can thus properly assume that there exist only elastic tensile and compressive deformations.

Young’s moduli have been calculated and are plotted in Figure 5 for 47 PE samples with diameters from 70 nm to 260 nm. The average Young’s modulus is 312 GPa with a standard deviation of 108 GPa. This result is significantly higher than the previous experiment results, which all fall below 200 GPa.\cite{3,19,20} We attribute the exceptionally high Young’s modulus to the nearly 100% crystallinity created by the ultra-high drawing process, as shown in Figure 2b. Besides the high Young’s modulus, we notice that there is a large variation among the measurements. Even at a large draw ratio or shear rate, however, some of the folded or entangled chains cannot be completely eliminated and thus remain in the fiber as defects. Those defects can significantly reduce the Young’s modulus of nanofibers. Hence, some nanofibers have a smaller Young’s modulus around 200 GPa. We believe that there are two potential causes: real variation of different PE nanofibers and the experimental uncertainty. During the fabrication process, when the diameter of the PE fibers reaches nanometer scale, especially for the fibers below 100 nm, it is very difficult to precisely control the quality of each nanofiber due to the variation of local temperature, shear force, and evaporation rate of solvent. These parameters are crucial for the formation of the crystallized nanofibers and lead to the variation of Young’s modulus between the samples with the same fiber diameter, especially in the nanometer level.

In the FDS method, the measured Young’s modulus depends on the characterizations of the PE fiber sizes and AFM cantilever spring constants, which are the dominant sources of errors. The suspended length can be precisely measured by AFM to be within 5% uncertainty. Given that the nanofiber diameter appears to the fourth power in Equation (3), an ~8% uncertainty is expected when the diameters are below 100 nm. Accounting for uncertainties in the cantilever and nanofiber dimensions, together with the photodiode sensitivity, the maximum relative error in the nanofiber modulus is estimated to be less than 40% (see Supporting Information). Our experimental uncertainties are consistent with previous measurements based on FDS.\cite{32}

In conclusion, our experimental results demonstrate a practical method to achieve the ultimate Young’s modulus of polymers using nanofibers. With the ultra-drawing technique, we have obtained PE nanofibers with diameters in a range of 70 to 260 nm. The PE nanofibers in our experiments possess extremely high crystallinity (i.e., a lower concentration of defects), which leads to the enhanced Young’s modulus. The high Young’s modulus of 312 GPa of the PE nanofibers can significantly expand the use of PE in various applications which require high strength but low density (below 1000 kg m$^{-3}$). Our fabrication method and mechanical characterization technique may be extended to other polymeric materials, such as poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN), and thus pave the way to understand and harness the high strength of polymers.
Experimental Section

The experimental section is available in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

P. L. and S. S. acknowledge support from NSF grant CMMI 1334630. J. H. M. and L. H. acknowledge support from NSF grant CBET 0933510. The authors would like to thank Ting Tan for useful discussions.

Received: August 15, 2013
Revised: September 23, 2013
Published online:  