MECHANICAL PROPERTIES OF NANOSCALE TUBULAR OBJECTS

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Introduction

Nanoscience is a rapidly developing set of disciplines which will allow the next wave of miniaturization. However, manipulating and studying objects with a typical size of 1nm (10^{-9} m) is difficult and requires the development of new methods and approaches. Measuring the mechanical properties of nanoscale objects, for example the Young's modulus, is one of these new approaches that will help us gain more insight into their structure.

Young's modulus

The Young's modulus is the property of a material which describes its resistance to deformation. A homogeneous cylinder, like the one on Fig. 1, with a length L, will elongate by dL when it is subjected to a force F, acting along its axis.

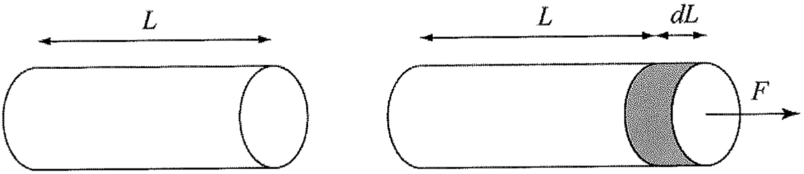


Figure 1. Elongation of a cylindrical bar of initial length L subjected to an axial loading force F.

The ratio of the force F and the tube's cross-sectional area A is the stress σ:

$$\sigma = \frac{F}{A} \tag{1}$$

On the other hand, the consequence of applying the stress σ will be the strain ε which the relative elongation of the cylinder:

$$\varepsilon = \frac{dL}{L} \tag{2}$$

A law formulated by 17th century scientist and philosopher Robert Hooke states that stress and strain are proportional:

$$\sigma = E_{Youg}\varepsilon \tag{3}$$

with E_{Young} being the Young's modulus.
The material with the highest known value of the Young's modulus is diamond with E_{Young} =1TPa. Other values for some materials from our everyday lives are given in table 1.

Material	Young's modulus E
Diamond	1000 GPa=1TPa
Steel	210 GPa
Aluminum	70 GPa
Plastic (Plexiglas)	1GPa = 1000 MPa

Table 1. Comparison of the Young moduli of some materials

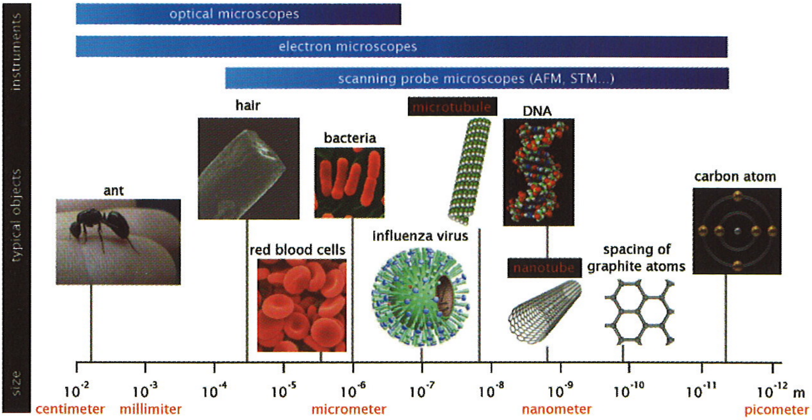


Figure 2. Typical objects with dimensions ranging from a couple of centimeters down to a couple of picometers, together with instruments used to visualize them.

Although Hooke's law had been formulated in the 17th century, it can still help answer fundamental questions in physics of nanoscale structures where it requires the use of latest technology (Fig. 2.). Using simple and intuitive terms it can provide valuable insight into the structure of nanoscale objects, give sufficient incentive for their practical application and also, in the case of biological nanostructures, deepen our knowledge on the functioning of living matter.

Carbon Nanotubes

Carbon nanotubes are the most recently discovered form of carbon (Fig. 3). From our everyday lives, we are familiar with diamonds and graphite. Thanks to the strong sp^3 bond between carbon atoms, diamond is the strongest material known to us. On the other hand, graphite is soft and greasy to touch and we use it for writing with pencils. Atoms in graphite are strongly bound within sheets that are held together by the weak, van der Waals interaction.

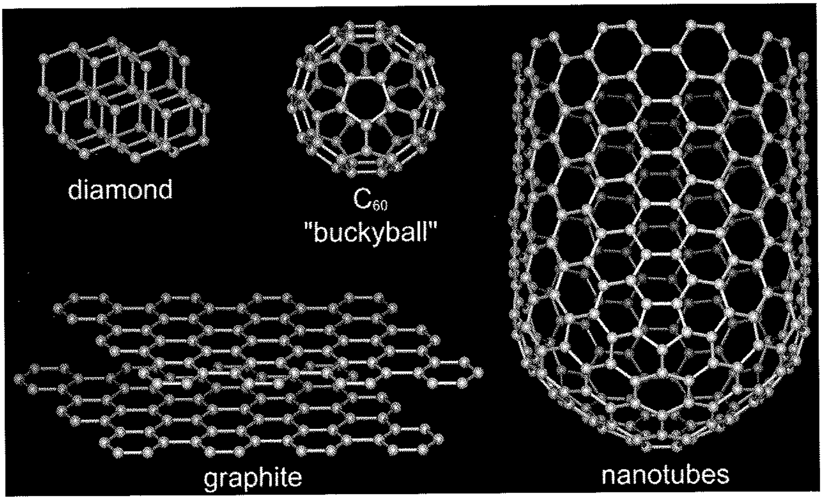


Figure 3. (a) Crystalline forms of carbon [1].

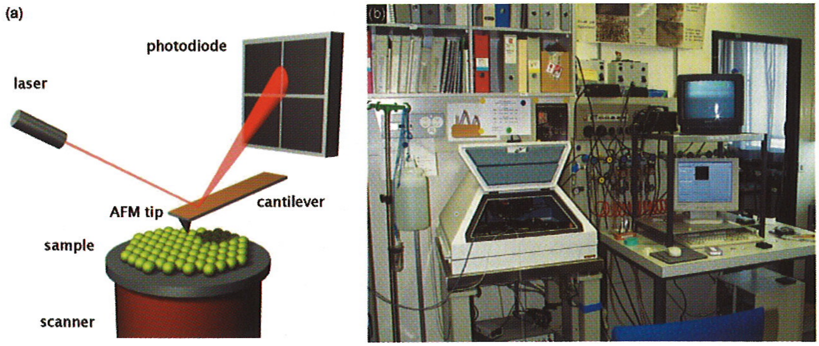
Fullerenes are a recently discovered class of spherical and ellipsoidal molecules, with C_{60} their most known representative. They were named after R. Buckminster Fuller, an architect famous for the invention of geodesic dome. Carbon nanotubes can be thought of as single sheets of graphite wrapped into the form of a cylinder and sometimes capped with a fullerene.

Atoms in graphite are arranged into sheets and connected via sp^2 bonds. Each of these sheets is as strong as the diamond. However, there are no chemical bonds between the sheets – only the weak van der Waals force is keeping them together, so it's very easy to slide these sheets apart. This is why we perceive graphite as weak and are able to use it for writing. Carbon nanotubes, which are in fact single sheets of graphite wrapped up into the form of a cylinder, have the same problem. Every nanotube is as strong as diamond, but they have very smooth surfaces and easily slide apart when assembled together.

The obvious solution to this problem is to introduce chemical links between neighboring nanotubes and the best way of proving the appearance of these links is by measuring their mechanical properties.

This can be achieved by using an instrument developed in 1986, the atomic force microscope (AFM) [2]. AFM forms an image of a sample by detecting the force acting between a very sharp tip and atoms on the sample's surface (Fig. 4). The AFM tip is located at the end of a flexible cantilever which bends due to the force between the tip and the sample. This bending is most easily observed by shining a laser on the cantilever and detecting the reflected beam using a photodiode. The sample is raster scanned by means of a piezo scanner and the image is composed pixel by pixel from the deflection of the cantilever.

Figure 4. (a) Schematic of an atomic force microscope (AFM) setup based on the laser beam deflection method for detecting cantilever deflection. (b) AFM used in this work.



The AFM used during this work is shown on Fig. 4b. It is floating on 4 four pneumatic "legs" that isolate it from building vibrations. The white hood protects it from acoustic vibrations.

The AFM tip exerts force on the sample during imaging. With a judicious choice of the sample this will allow measurements of the mechanical properties of nanotubes. This can be achieved by depositing carbon nanotubes on a porous substrate and deforming them during AFM imaging (Fig. 5a). By measuring the nanotube deformation and the applied force, we can calculate tube's resistance to bending, the bending modulus. Fig. 5b is an electron microscope image of a human hair. Next to it is an atomic force microscope cantilever with a sharp tip at its end which is used to deform the nanotube, which is at least 10000 times thinner than the hair shown in this image.

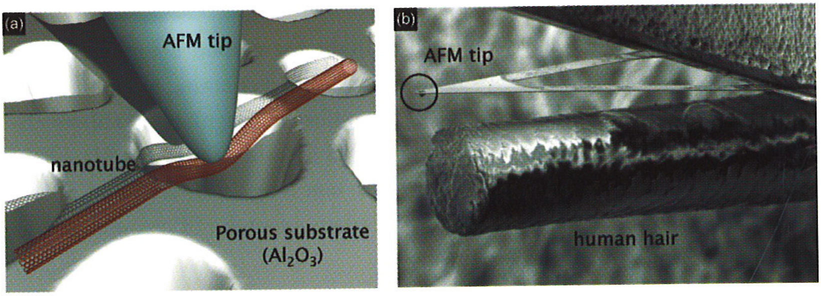


Figure 5. (a) Schematic drawing of a nanotube deposited on a porous substrate. During imaging, the tube is deformed by the AFM tip. This deformation is recorded as local height in the corresponding AFM image. (b) Scanning electron microscope image of an AFM cantilever and tip, compared with human hair.

Even though they are extremely thin, carbon nanotubes can be assembled into large scale structures - ribbons and cables like the ones shown on Fig. 6 [3]. Due to the weak van der Waals interaction between the tubes, these structures can easily slide apart [4]. This is one of the main problems in potential applications of carbon nanotubes. Even though individual nanotubes have mechanical properties comparable to diamond, the weak interaction between the tubes will cause macroscopic structures to fall apart. The solution would be to introduce links between neighboring nanotubes.

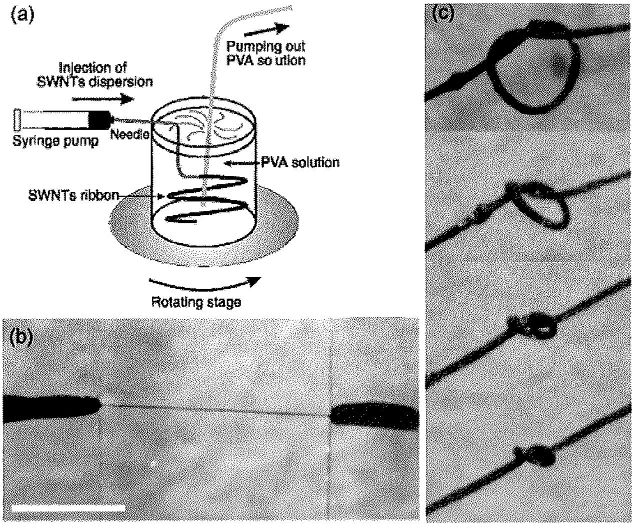


Figure 6. (a) Schematic of the setup for producing carbon nanotube fibers. Suspension of purified nanotubes is introduced into a spinning beaker containing polyvinyl alcohol, which causes the nanotubes to coagulate into fibers aligned with the flow direction. (b) Photograph of a carbon nanotube fiber held between two glass slides. The scale bar is 1 mm long. (c) A series of photographs showing that knots can be tied on carbon nanotube fibers, demonstrating their flexibility and durability [3].

During this research, we have discovered that carbon nanotubes can be linked together when exposed to an electron beam in a transmission electron microscope. The transmission electron microscope (TEM), developed in 1932 by Knoll and Ruska in Germany is the first scientific instrument to rely on the wavelike nature of matter (electrons) for its operation. The underlying design of a TEM has a lot in common with light microscopes or even slide projectors (Fig. 7) encompassing a source of "light" (electrons), condenser and objective lenses. High resolution is achieved by using matter waves for imaging. Electrons are focused and deflected using magnetic lenses. In classical light microscopy, the image contrast results from different parts of the specimen absorbing light differently. In TEM, electron absorption is minimal and image contrast is due to electron scattering. Bright-field TEM images are composed of direct, unscattered electrons while dark-field images and diffraction patterns are formed by scattered electrons.

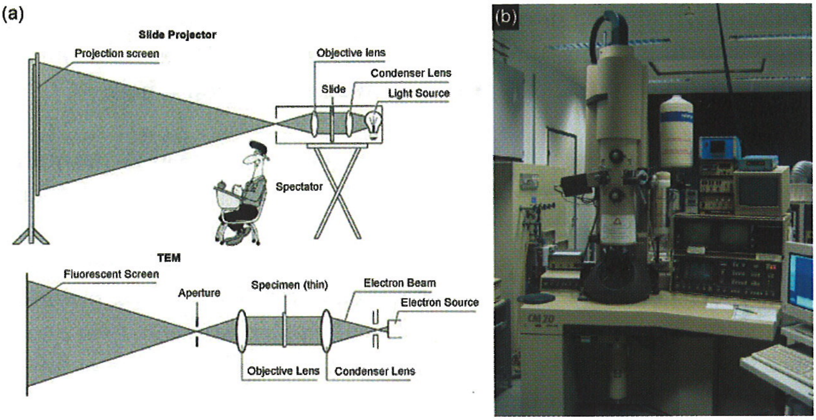


Figure 7. (a) A cartoon comparing the operation of a transmission electron microscope with a slide projector. Reproduced from [5]. (b) Philips CM20 electron microscope on which this work had been carried out at CIME, EPFL.

In order to prove that electron beams lead to creation of stable links between nanotubes, a very thin silicon-nitride substrate was used into which holes have been cut using focused ion beams. Bundles, consisting of several hundred nanotubes are deposited on these substrates, imaged and located using the atomic force microscope, Fig. 8. At the same time, mechanical properties of the bundle are measured. After that, the substrate is placed into a transmission electron microscope where the same bundle is located. In the electron microscope, the fine structure of the bundle can be observed. In the same time, the nanotube can be irradiated with electrons.

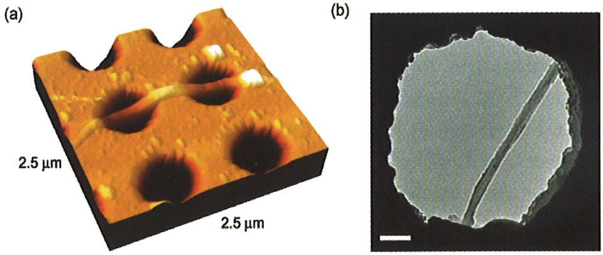


Figure 8. (a) 3D rendering based on the AFM image of a carbon nanotube rope spanning two holes. Measurements were performed on the right-side hole. (b) TEM image of the same nanotube. The scale bar on the TEM image is 100 nm long.

Following irradiation during a couple of minutes, the sample is placed back into the atomic force microscope and the change of bending modulus is measured. This process is repeated several times.

Measurements of the bending modulus show that pristine nanotube bundles are easily bent because nanotubes can easily slide apart. However, even an exposure to a small dose of irradiation can increase their bending modulus by a factor of 30. As the exposure is increased, the bundle gradually becomes amorphous, and the bending modulus decreases. The dramatic increase of the bending modulus upon exposure to electrons is very promising and shows a possible way of fabricating fibers that could be as strong as the diamond.

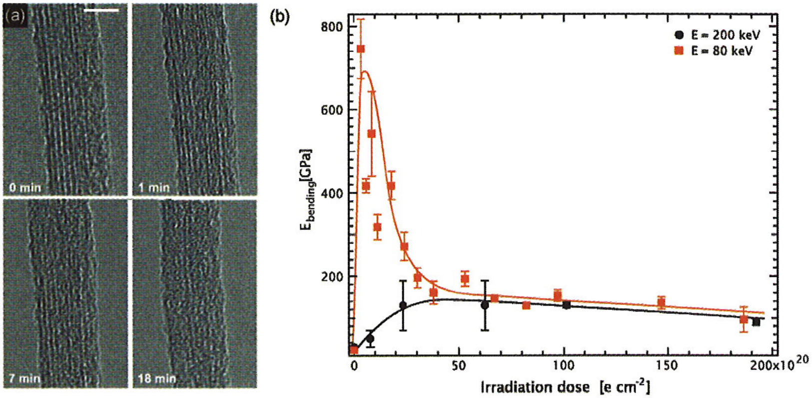


Figure 9. (a) A series of TEM images of a carbon nanotube bundle. The bundle becomes increasingly amorphous as the exposure to electrons is increased. The scale bar is 10nm long. (b) Behavior of the bending modulus $E_{bending}$ of different carbon nanotube ropes as a function of received dose for two incident electron energies. The bending modulus increases on short exposures due to crosslinking and degrades at higher exposures because of structural damage. The rope irradiated with 80keV electrons shows a much stronger and sharper increase of the bending modulus [6].

The method itself, consisting of depositing nanotubes on porous and thereby electron-transparent membranes could enable a host of experiments in which AFM, TEM and SEM measurements could be combined on the same nanoscale object.

Microtubules

Microtubules are biological objects similar in size to carbon nanotubes. They are cylindrically shaped protein polymers that form networks inside living cells. These networks perform various vital functions: they provide mechanical stability to cells and act as a transport network. Microtubules also pull apart chromosomes during cell division and form bundles that move cells. Sperm cells are one of the examples.
In order to explain these vital physiological functions of microtubules, it is important to accurately measure their mechanical properties.

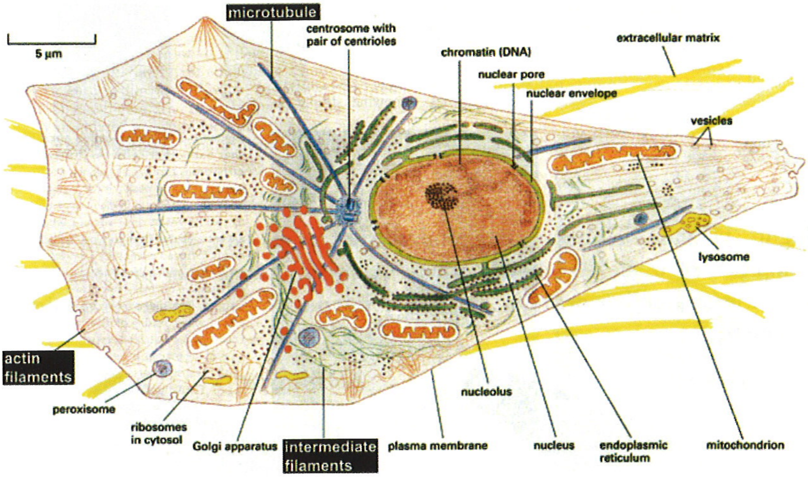


Figure 10. Major features of a typical animal eukaryotic cell [7]. Components of the cytoskeleton – microtubules, actin and intermediate filaments are highlighted.

The basic building block of microtubules is the αβ-tubulin dimer. These dimers associate head-to-tail to form a linear chain, the protofilament (Fig. 11). Protofilaments bind laterally, forming a hollow cylinder with a typical diameter of 25nm. In the most usual case, microtubules have 13 protofilaments. Their length inside living cells is constantly fluctuating. Microtubules can both grow and shrink depending on factors like temperature and monomer concentration.

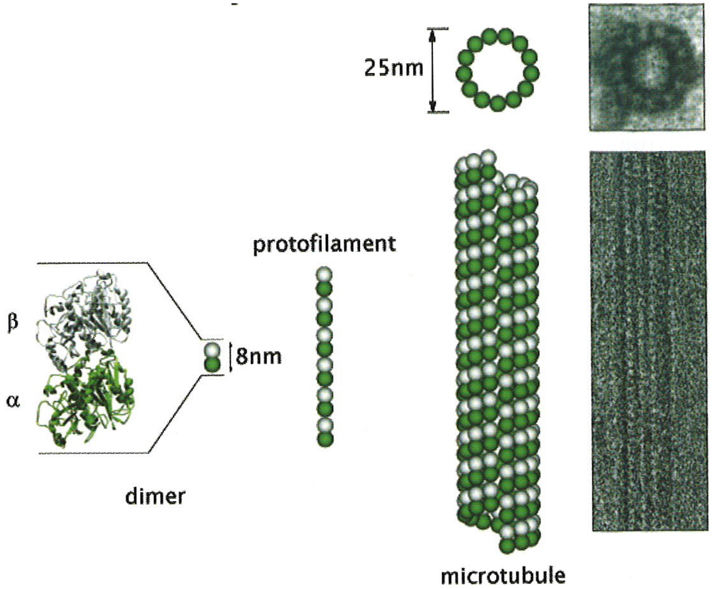


Figure 11. (a) structure of a microtubule and its subunit, the tubulin dimer, composed of α and β-tubulin. Tubulin dimers arrange into protofilaments which form a hollow cylinder – the microtubule. (b) TEM image of a microtubule [8].

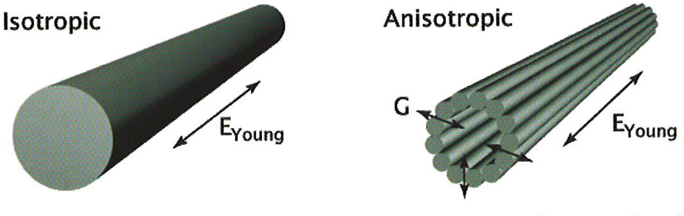


Figure 12. The resistance of a mechanically isotropic object to bending is characterized by its Young's modulus. The mechanical behavior of anisotropic objects is more complicated and is governed by the shear modulus G and Young's modulus as given by Eq. 5 [9].

Microtubules have been traditionally described as mechanically isotropic, similar to for example metal bars. The most important property of such objects is that their characteristic resistance to bending $E_{bending}$ is equal to the Young's modulus:

$$E_{bending} = E_{Youg}$$

and independent of their dimensions. However, we know that microtubules are composed of weakly connected protofilaments. An anisotropic model (Fig. 12), with a Young's modulus E_{Young} describing the resistance of protofilaments to stretching and a shear modulus G describing weak connections between the protofilaments is therefore much more appropriate. The most important characteristic of this model is that the bending modulus will depend on microtubule's length L and diameter D:

$$\frac{1}{E_{bending}} = \frac{1}{E_{Young}} + \frac{1}{G}\frac{10}{3}\frac{D^2}{L^2}$$

In order to prove our model, we deposited microtubules on an engineered substrate into which slits with different widths have been introduced using electron beam lithography, Fig. 13.

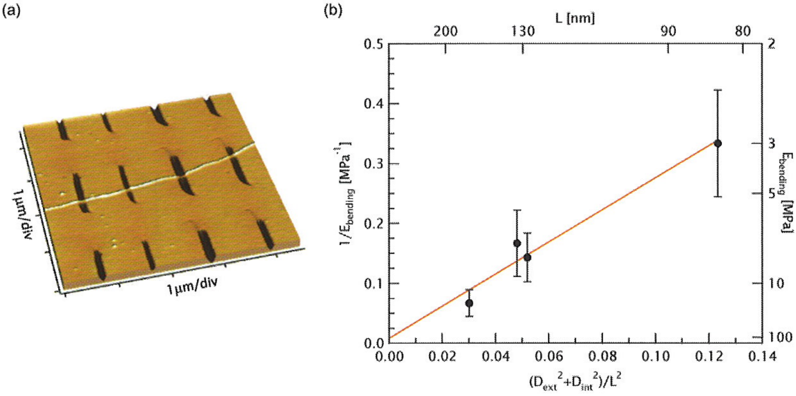


Figure 13. (a) Pseudo-3D rendering based on the AFM image of a microtubule deposited on a lithographically tailored substrate. (b) Variation of $E_{bending}$ as a function of suspended length for the microtubule shown in (a). Red line is a fit to Eq. 5, with shear modulus corresponding to the inverse slope and Young's to the inverse segment on the abscissa [10]

On the left hand side is an atomic force microscope image of a single microtubule deposited on the substrate. By chance, the microtubule spanned four slits with different widths. The mechanical response of segments with different suspension lengths was measured using an atomic force microscope. The data, shown on the right hand side clearly demonstrates that the bending modulus depends on length. If microtubules were mechanically isotropic, all the data points on Fig. 13b would have fallen on a horizontal line.

From the slope of the fit to data on Fig. 13b, we were able to extract the shear modulus:

$$G = (1.5 \pm 0.3)\ \mathrm{MPa}$$

while from the segment on the y-axis, we could estimate the Young's modulus:

$$E_{Young} > 130\ \mathrm{MPa}$$

The mechanically anisotropic model is therefore more suitable for modeling microtubules. It can also discriminate interactions between neighboring subunits in the longitudinal direction (determining the Young's modulus) and in the lateral direction (determining the shear modulus). Lateral interactions between protofilaments are biologically very interesting because they are modified by changes in microtubule's environment and could help explain how microtubules react to temperature, pH or exposure to drugs.

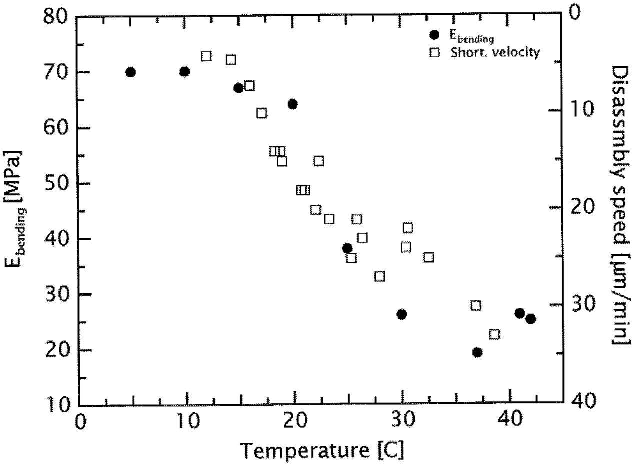


Figure 14. Comparison of the temperature behavior of $E_{bending}$ with the disassembly speed of microtubules from [11].

The temperature, for example, has a profound effect on the elasticity of microtubules. As the temperature is lowered, microtubules become more rigid because the interaction between the protofilaments becomes stronger. By comparing our measurements with previously published data on the growth and shortening velocity of microtubules [11], we were able to conclude that the dynamic behavior of microtubules is strongly influenced by their mechanical properties.

Conclusions

Mechanical measurements on a series of nanoscale tubular objects have been performed. In the case of carbon nanotubes, a nanoscale “engineering” problem was addressed – how to connect carbon nanotubes together? The measurement method was extended using substrates compatible with imaging inside a transmission electron microscope. This enabled observations of nanotube structure and AFM measurements on the same nanotube, with repeatable and accurate repositioning of the sample both inside the TEM and AFM. Nanotube bundles irradiated with electrons inside a TEM show a dramatical increase of the bending modulus, indicating the onset of crosslinking. Further irradiation decreases the bending modulus. TEM imaging confirmed that this decrease corresponds to structure amorphization. Apart from the academic significance, these findings could also have a profound influence on applying nanotubes as reinforcing fibers as they show the way to connecting carbon nanotubes with the goal of producing strong fibers. Furthermore, the method of depositing nanotubes on fabricated, patterned membranes could enable a host of related experiments in which TEM, SEM and AFM observations on nanotubes and nanowires could be combined.

Mechanical measurements on the biological equivalent of nanotubes, the microtubules, have revealed new facets of their already fascinating properties. Measurements of the bending modulus on the same microtubule have shown that they behave as a mechanically anisotropic cylinder, in strong contrast to a 20 year old belief that they can be modeled as mechanically isotropic objects. In fact, microtubules have a shear modulus that is at least hundred times lower than their Young’s modulus, indicating that the tubulin molecules are more strongly bound in the longitudinal than in the lateral direction. These measurements are also the first example where these two mechanical properties have been determined simultaneously on a single mesoscopic object. The temperature dependence of the shear modulus shows good correlation with the dynamic properties of microtubules, the assembly and disassembly speed, indicating that the dynamic behavior of microtubules is strongly influenced by their mechanical properties. The mechanical measurements performed on microtubules are an introduction to a future systematic study in the field of cellular biophysics. The same method could also be applied to the study of other cytoskeletal components: actin and intermediate filaments.

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