Size Effect on the Elastic Modulus of Nanomaterials as Measured by Resonant Contact Atomic Force Microscopy

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ABSTRACT

The elastic modulus of metallic (Ag and Pb) nanowires and polymer (polypyrrole, PPy) nanotubes was measured using a novel method, resonant contact atomic force microscopy (resonant C-AFM). The cantilever vibration is excited with an electric field applied between the sample holder and the AFM head. The resonance frequency of the cantilever in contact with the sample shifts to higher values compared to the free resonance frequency. Its value depends on the stiffness of the tip-sample contact.

It is shown that this method enables to quantitatively measure the Young's modulus of nanotubes or nanowires. The obtained results are discussed in terms of an effect of the reduced size on the measured elastic modulus.

Keywords: Atomic Force Microscopy, polymer nanotubes, metallic nanowires, elastic modulus.

1 INTRODUCTION

Presently, materials with nanoscopic dimensions are of fundamental interest because their properties can change in the regime of transition between the bulk and the molecular scales. Due to these properties, they have a lot of potential technological applications in different areas. This work take place into a more general study concerning the effect of low dimensionality on the physical properties of polymer nanotubes and metallic nanowires and the first aim is the study of the mechanical properties of these nanostructures using Atomic Force Microscopy (AFM)

Indeed, AFM is widely used to study materials mechanical properties. Dynamic methods such as Tapping Mode (TM) or Force Modulation (FM) allow mapping the mechanical properties of samples with high resolution but present drawbacks and limitations. Non-linear behavior of TM complicates the analysis of the data in terms of quantitative surface mechanical properties. In direct FM, generally realized by modulating the height of the sample or of the cantilever holder, induces shearing stress of the contact. Friction properties are often mixed in the data. Direct FM was obtained using magnetic force but necessitates magnetic cantilevers [1,2].

A new method that does not present these drawbacks was developed. The direct application of a normal load to the contact is obtained using a sinusoidal electric field applied between the sample holder and the microscope head that induces the cantilever vibration. This enables to measure the resonance frequencies of the cantilever-sample system, which shift to higher values relatively to the resonance frequencies of the free cantilever. From resonance frequency measurement, it is then possible to determine the contact stiffness [3].

It will be shown that this method enables the quantitative measurement of the elastic modulus of polymer nanotubes or metallic nanowires. The obtained results will be discussed in terms of an effect of the reduced size on the measured elastic modulus.

2 EXPERIMENTAL

The metallic nanowires and polymer nanotubes were synthesized using a template-based method within the pores of polycarbonate track-etched membranes [4]. Silver and lead nanowires were electrochemically synthesized from solutions containing respectively $AgNO_3$ and $Pb(BF_4)_2$. Nanotubes of a conductive polymer (polypyrrole, PPy) were electrochemically synthesized using the procedure extensively described elsewhere [5]. The template polycarbonate (PC) membranes were 20 µm thick and had a pore density of 10^9 cm^{-2}. In order to obtain nanomaterials with different outer diameters, PC membranes with pore size ranging between 30 and 250 nm were used. After synthesis, the membrane was dissolved by immersion in a dichloromethane solution containing dodecyl sulfate as surfactant and the suspension was placed in an ultrasonic bath during one hour to separate the nanostructures from the gold film previously evaporated on the backside of the PC membrane. An oxidation layer, more or less important according to the metal nature, necessarily covers the metallic nanowires surface after their extraction from the PC membrane. The thickness of this oxide layer is difficult to determine but will modify the value of the surface energy with respect to the value obtained for pure metals.

The suspensions were then filtered through poly(ethylene terephthalate) (PET) membranes with pore diameters ranging between 0.8 and 3 µm. In order to remove any contaminant from the nanomaterials surface the samples were thoroughly rinsed with dichloromethane. To minimize shear deformations in the experiment, the ratio between the suspended length of the tube or beam, L, and its outer diameter, D_{out}, should be higher than 16 [6]. To achieve this, each series of nanowires or nanotubes

synthesized in a template membrane with a specific pore diameter was dispersed on a PET membrane with a pore diameter satisfying this criterion.

All the AFM experiments were performed with an Autoprobe® CP microscope (Thermomicroscopes) operated in air with a 100 µm scanner equipped with ScanMaster® detectors correcting for drift, non-linearity and hysteresis effects. The cantilevers were standard Si_3N_4 Microlevers™ with integrated pyramidal tips (typical apex radius of curvature between 30 and 50 nm). The spring constant of each cantilever was calibrated by deflecting it against a reference cantilever of known spring constant [7]. Values ranging between 0.3 and 0.5 $N.m^{-1}$ were obtained for all the cantilevers used in the experiments. Geometrical characterization of the cantilever was realized by high resolution scanning electron microscopy. Obtained data were used for the description of the dynamical behavior of the cantilever using the Rayleigh-Ritz approximation [8]. The modulated electric field was applied between the sample holder and the AFM head using a function generator (Agilent Technologies, model 33120A). In order to avoid tip displacement on the sample surface and to keep resonance peak symmetrical, resonance spectra were recorded without polarization offset and with small excitation amplitude. The cantilever deflection signal was measured using a lock-in amplifier (EG&G Princeton Applied Research, model S302). The signal generator command and the data collection from the lock-in were computerized and data analysis was realized using routines developed under Igor Pro software (Wavemetrics).

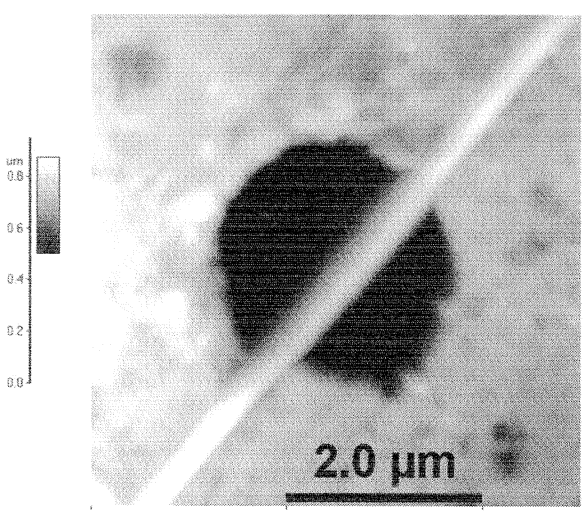

Figure 1: C-AFM image of a 70 nm thick polymer nanotube crossing a pore.

After dispersion of the nanotubes on a PET membrane, large-scale images were first acquired in order to select nanomaterials suspended over pores that could be used to measure their mechanical properties. Once a suspended nanostructure was located, an image of it at lower scale was then realized to precisely determine its dimensions, i.e. its suspended length, L, and its outer diameter, D_{out} (Fig. 1). The outer diameter is determined by the measurement of its height with respect to the supporting membrane to avoid tip artifacts. For the nanotubes, the inner diameter, D_{in}, was estimated using a previously established calibration curve relating the outer and the inner diameters [5].

The tip was then located at the mid-point of the suspended length of the nanotube or nanowire. The resonance spectrum of the cantilever in contact with the nanostructure was then measured.

3 RESULTS AND DISCUSSION

In a typical spectrum, three peaks are present with two of them corresponding to flexural cantilever vibrations (F_1 & F_2) and the third one being due to torsional vibrations (T_1) (Fig. 2). The two first flexural frequencies of a cantilever with the tip resting on a spring were calculated using the Rayleigh-Ritz method, and compared to the experimental data for different nanotubes and nanowires configuration (suspended length and outer diameter). A very good agreement between the theoretical prediction and the measured experimental data was observed (Fig. 3). This proved that the polymer nanotubes or the metallic nanowires behave as pure springs and that their inertia can be neglected. This is in accordance with the fact that the natural frequency of the suspended nanotubes is much higher than that of the cantilever. From the shift of the cantilever resonance frequency with respect to its free resonance frequency, the model enables to deduce the nanotube or nanowires stiffness.

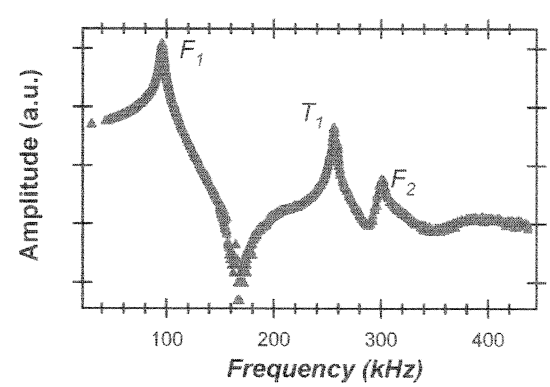

Figure 2: Typical resonance spectrum of a cantilever in contact with a polymer nanotube.

The technique also enables to determine the model describing the physical configuration and the mechanical characteristics of the system [9]. In the present case, it was demonstrated that the suspended nanostructures behave as clamped beams resting on deformable supports. The elastic modulus of the nanostructures can then be calculated from the stiffness.

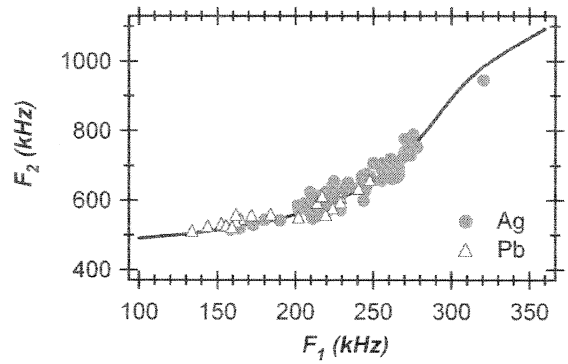

Figure 3: Relation between the frequencies of the first two flexural vibration modes of a cantilever in contact with Ag and Pb nanowires compared to the theoretical curve for a cantilever on a spring (solid curve).

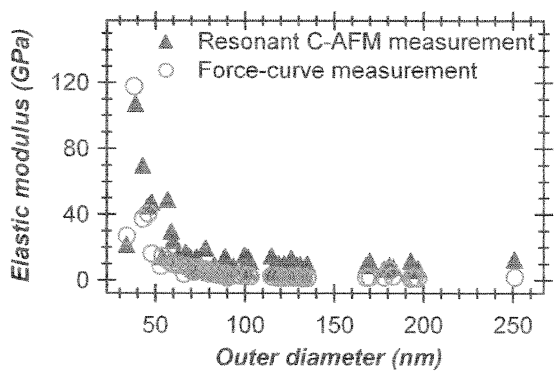

Figure 4: Variation of the elastic modulus of PPy nanotubes as a function of their outer diameter.

Materials	Tensile elastic modulus (GPa)	
	Literature values	Experimental values
Ag	76[a]	78.0 ± 5.6
Pb	16[a]	17.0 ± 1.9

[a] from ref. [10]

Table 1: Comparison between the values of the Young's modulus of Ag and Pb reported in the literature with the average values measured on 30 Ag and 18 Pb nanowires.

In figure 4, the elastic modulus measured on the PPy nanotubes with the resonant C-AFM method is compared to that previously measured using a nanoscopic three points bending test [5]. A very good agreement is observed for both the qualitative point (dependence on the outer diameter) and the quantitative point. In table 1, the average experimental values measured on 30 Ag and 18 Pb nanowires are compared with the values of the elastic tensile modulus of Ag and Pb reported in the literature [10]. A good quantitative agreement is also observed. These observations prove that resonant C-AFM is a powerful technique that enables the quantitative measurement of the mechanical properties of nanostructures like polymer nanotubes and metallic nanowires.

As it can be observed in figure 4 and 5, the measured elastic modulus increases with decreasing outer diameter for both the PPy nanotubes and the Ag and Pb nanowires. The effect is more pronounced for the PPy nanotubes (Fig. 4) than for the metallic nanowires (Fig. 5).

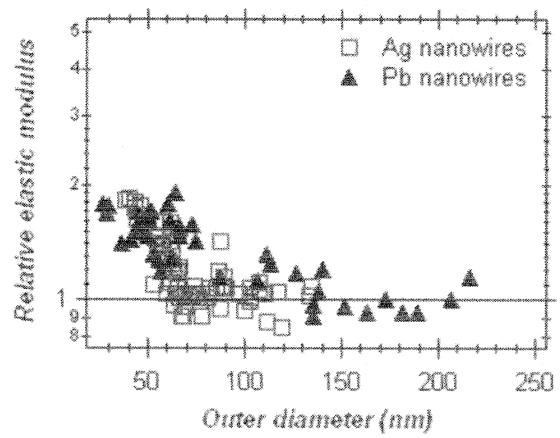

Figure 5: Variation of the elastic modulus normalized to the value of the bulk modulus as a function of the outer diameter for the metallic nanowires.

In order to explain this increase, two assumptions can be advanced. The first one is that, because the physical properties such as the elastic modulus are directly related to the material structural perfection, the degree of order of the nanostructures could increase with decreasing diameter. The second one is that surface energy effects become more important for nanowires or nanotubes with smaller diameter because the surface to volume ratio increases when the diameter decreases. The second hypothesis can be verified by considering that the work of the applied force on the nanostructures is not only used to elastically deform the material but also to create surface. The total energy, U, of a bent beam is then given by

$$U = -F\delta + \frac{1}{2}k_t\delta^2 + \Phi\Delta L\gamma \qquad (1)$$

where F and δ are respectively the applied load and the beam deflection at the mid-suspended length, k_t is the beam stiffness, Φ is the contour length of its section, ΔL the length increase and γ is the surface energy of the material. Assuming small deformations of clamped beams, the length increase can be evaluated. The introduction of a surface related term leads to the following expressions for the measured elastic tensile modulus, E_{app}, for nanowires

$$E_{app} = E + \frac{8}{5}\gamma\frac{L^2}{D^3} \qquad (2)$$

and for nanotubes

$$E_{app} = E + \frac{8}{5}\gamma L^2 \frac{D_{out} + D_{in}}{D_{out}^4 - D_{in}^4} \quad (3)$$

where E is the pure elastic modulus of the material. Reporting the apparent modulus as a function of L^2/D^3 or $L^2(D_{out} + D_{in})/(D_{out}^4 - D_{in}^4)$ should give linear relations where the intercept with the ordinate axis should be equal to the bulk or real elastic modulus of the material and the slope is related to the material surface energy.

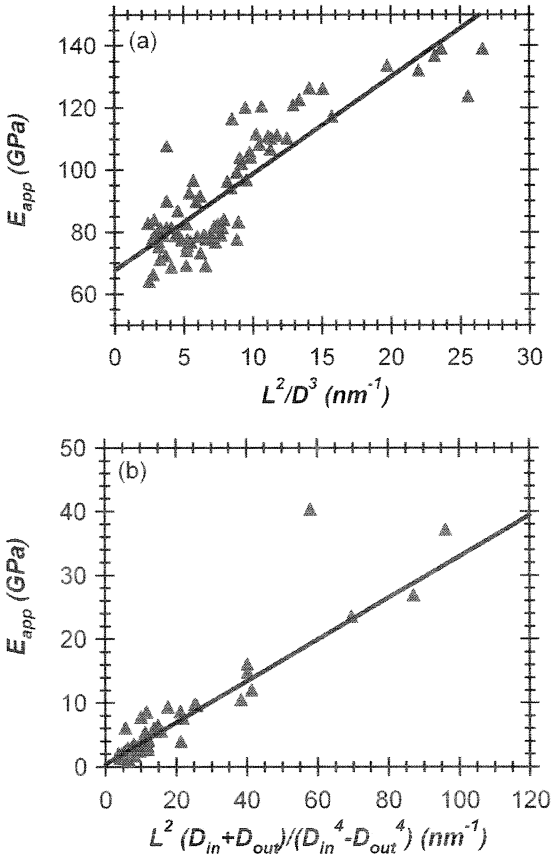

Figure 6: Comparison between the fits using relations (2) and (3) and the experimental data, respectively for (a) the Ag nanowires and (b) the PPy nanotubes.

The results of these fits are illustrated in figure 6 for the Ag nanowires and the PPy nanotubes and are given in table 2. The values obtained for the tensile elastic modulus, E, are in very good agreement with those reported in the literature for bulk materials. The values of the surface energy, γ, are also in agreement either to the value reported in the literature for Ag or to values that could be expected for lead oxide or for a conductive polymer. These observations tend to prove that the apparent increase of the elastic modulus observed on the smallest metallic nanowires or polymer nanotubes is mainly due to surface effects. In other words, the reduced size of these nanostructures leads to an increase of the surface to volume ratio and the work of the applied load is not only used to elastically deform the structure but also to create additional surface.

Materials	E (GPa)	γ (J.m^{-2})
PPy	0.6 ± 0.3	0.20 ± 0.01
Ag	67.5 ± 2.1	1.95 ± 0.21
Pb	16.9 ± 0.8	0.57 ± 0.12

Table 2: Young's modulus, E, and surface energy, γ, for the polymer nanotubes and metallic nanowires obtained from the fit of the experimental data with relations (2) or (3).

4 CONCLUSIONS

A new method of resonant C-AFM based on the electrostatic excitation of the cantilever vibration and the measurement of the resonance frequency shift when the tip contacts the sample was developed to measure the elastic properties of surfaces and nanomaterials. It was shown that this method enables the quantitative determination of the Young's modulus of nanostructures like metallic nanowires or polymer nanotubes.

For both the Ag and Pb nanowires and the PPy nanotubes, an apparent increase of the tensile modulus is observed when the diameter decreases. Taking into account the surface modification during the deformation, it was shown that this effect of reduced size might be mainly explained by an increase of the surface to volume ratio in these nanostructures.

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