# **REVIEWS OF TOPICAL PROBLEMS**

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# Mechanical properties of carbon nanostructures and related materials

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<u>Abstract.</u> The current status of research on the mechanical properties of carbon nanotubes (CNTs) and composites containing them is reviewed. The structural features of CNTs determining their mechanical characteristics are considered. The applicability of the concepts of classical mechanics for describing the behavior of nanometer-sized objects is analyzed. The results of experimental investigations into the mechanical characteristics of CNTs and macroscopic objects containing nanotubes are discussed. The problem of reinforcement of polymer materials as a result of inserting carbon nanostructures is reviewed. Examples showing the effective operation of nanoelectromechanical systems (NEMSs) are analyzed.

# 1. Introduction

At the end of the 20th century, a new class of closed surface carbon structures, which are closed surfaces consisting of hexagons and pentagons with carbon atoms in their vertices, was discovered. This marked the beginning of one of the fields in nanotechnology, related to research on and the development of nanomaterials on the basis of such structures. Interest in investigations of such structures stems, on the one hand, from their unique physical and chemical characteristics and, on the other hand, from the considerable potential for applications. Fullerenes and carbon nanotubes are the most interesting examples of such new carbon structures. Thus, the surface of fullerenes has a closed spherical or spheroidal form [1-3], including not only regular hexagons whose number

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Received 2 August 2006, revised 4 September 2006 Uspekhi Fizicheskikh Nauk 177 (3) 233–274 (2007) Translated by A V Eletskii; edited by A Radzig depends on the size of the fullerene molecule, but also 12 pentagons arranged in a regular manner over the spherical surface. The discovery of fullerenes was awarded the Nobel Prize in Chemistry for 1996 [4–6].

Another class of surface carbon nanostructures includes carbon nanotubes (CNTs) [7] which are elongated cylindrical structures ranging from one to several dozen nanometers in diameter and reaching up to several micrometers in length. Such tubes consist of one or several graphite layers scrolled into a cylinder and usually terminating in a semispherical cap which can be considered as half a fullerene molecule.

The most general way to synthesize both fullerenes and CNTs is based on using an arc discharge with graphite electrodes, which utilizes He or Ar as a buffer gas. Carbon atoms liberated as a result of the thermal evaporation of a graphite anode condense under certain conditions to form soot. Depending on the buffer gas pressure this soot contains either fullerenes [2] (at pressures of 100-200 Torr) or multiwalled nanotubes (at pressures close to atmospheric pressure). Other methods of CNT production are based on the evaporation of a graphite surface under the action of high-intense laser radiation (laser ablation method), as well as on the process of the thermocatalytic decomposition of a carbon-containing gas on the surface of metal particles playing the role of catalyst [chemical vapor deposition (CVD) method].

The research field related to the synthesis, investigation, and application of CNTs comprises one of the branches of nanotechnology. Two stimuli motivating the development of such investigations can be noted. On the one hand, this is a fundamental aspect caused by the miniature size and unique physical and chemical properties of nanotubes. On the other hand, due to such properties CNTs possess considerable potential in practical applications, which attracts interest from researchers and engineers dealing with new technologies and developing new types of devices and materials. The electronic properties of a nanotube, such as number density and mobility of carriers, energy gap width, and electrical conductivity, are determined by its geometry, the main parameters of which are its diameter and chirality, i.e., the angle of orientation of the graphite plane with respect to the nanotube axis [8-10]. Thus, nanotubes represent a class of miniature objects with variable electronic characteristics. Such objects are considered as possible elements for future nanoelectronics.

Nanotubes possess extraordinary emission characteristics that are resulted from their high aspect ratio and high conductivity. Such properties give CNTs potential in effective applications as the basis of electron field emitters [11 - 13]. Monitors, X-ray sources, and lighting equipped with such emitters are distinguished by their miniature size and notably lower supply voltage compared to standard electron field emitters.

The unique sorption properties of CNTs are caused by a record value of the specific surface area, which reaches  $2600 \text{ m}^2 \text{ g}^{-1}$ . Due to this property and also because of a natural cavity existing inside a nanotube, the latter is able to absorb both gaseous and condensed substances. Since the diameter of the inner channel inside a CNT exceeds the characteristic size of a molecule by only 2 to 3 times, the capillary properties of a nanotube, enabling it to absorb liquid substances like a pipette [14], manifest themselves on the nanometer scale.

Experiments showed that CNTs possess an extraordinarily high Young modulus (around a TPa) [15-18]. This is determined by their structural perfection and the interaction force between the carbon atoms constituting the nanotube. The high strength characteristics of CNTs are of keen interest from the viewpoint of creating new materials and objects with enhanced mechanical properties. Thus, methods have been developed for obtaining superhard filaments [19], yarns [20], and ribbons [21] from nanotubes. These products go beyond comparison to any similar materials in their mechanical characteristics. Nowadays, the efforts of many researchers are geared to producing composite materials that are polymers doped with CNTs [22-24]. If the problem of conjugation between the surfaces of a polymer and a CNT, providing the effective transfer of loading from the polymer matrix to the CNT, is resolved, such materials combining the plasticity and low cost of polymers with the good electrical conductivity and high strength of nanotubes will become a unique tool for overcoming many problems of materials technology. Atomic force microscopes where CNTs are utilized as a sensitive probe have proved themselves quite well [25-27]. The high strength, low diameter, and high aspect ratio enable increasing considerably the resolving power of such devices compared to standard ones based on the use of silicon-capped probes.

One of the important features of nanotubes is the interconnection between their electronic characteristics and mechanical deformations [28-30]. Such important characteristics as the forbidden band width, the number density of the carriers, and the phonon spectrum change as a result of deformation of a nanotube. In turn, this is reflected in the CNT conductivity. Therefore, a nanotube is a quite effective transformer of a mechanical motion into an electrical signal, which makes it a unique element of nanoelectromechanical systems (NEMSs).

Due to the above-listed extraordinary physical and chemical properties and because of a considerable potential of their practical applications, CNTs are the object of research in many laboratories all the world over. The results of such research are published in hundreds of articles a year, so that the total number of publications in this field has reached the tens of thousands. Detailed reviews of these publications have been presented particularly in the articles [13, 14, 31-33], as well as in monographs [8-10, 34-36]. The present article overviews the current status of investigations into the mechanical properties of CNTs and related applications. While this subject is rather badly reflected in the abovecited review literature, the basic and applied interest in this problem comprises one of the main priorities of modern scientific development. The article discusses the basics of modern approach to describing the mechanical properties of elongated cylindrical objects. The methods and results of measuring the mechanical characteristics of individual nanotubes, as well as the relevant bundles, filaments and related materials, have been analyzed. Experiments on devices whose action depends on the extraordinary mechanical characteristics of CNTs are described. Possible ways of applying such devices in technologies of new materials and mechanisms are considered.

# 2. Elastic properties of carbon nanotubes

# 2.1 Elastic moduli

A carbon nanotube in its structure can be presented as a single-layer or multilayer cylindrical shell ranging between one and several dozen nanometers in diameter, and between one-tenth and several dozen microns in length. From the viewpoint of the analysis of elastic properties, a single-walled nanotube seems to be the simplest object. Figure 1 portrays various structures of single-walled nanotubes differing from each other in the chirality angle — that is, the angle of orientation of the graphite plane with respect to the nanotube's axis. The chirality of a nanotube has a determining impact upon its electronic characteristics, such as the energy gap width, carrier number density and some others. However, there are no indications of the existence of some perceptible dependence of the mechanical characteristics of a nanotube on its chirality. The absence of such dependences is confirmed by the results of the model calculations that are



**Figure 1.** The structure of single-walled CNTs of various chirality: (a) *armchair* configuration where the graphite surface is oriented at a  $30^{\circ}$  angle with respect to the axis of the nanotube; (b) *zigzag* configuration where the orientation angle is  $0^{\circ}$ , and (c) the structure with chirality indices (10, 5) and orientation angle of about  $41^{\circ}$ .



**Figure 2.** The main types of deformation of a nanotube: (a) axial strain; (b) axial compression (diameter buckling); (c) symmetrical bending; (d) radial compression; (e) elastic deviation, and (f) Euler deformation (shell buckling).

given below. Therefore, one can believe that the mechanical behavior of CNTs does not depend on their chirality and this dependence will not be taken into account later in the discussion.

As a subject of the theory of elasticity, a single-walled nanotube can be represented by a thin cylindrical shell [37, 38]. In doing so it is hard to expect total similarity in the behavior of a carbon nanotube and a macroscopic object of a similar geometry. Indeed, a CNT, as distinct from a macroscopic system, does not have a continuous wall and is one atom thick. Therefore, it is of a great basic interest to clarify to what degree the classical notion about the mechanics and elastic properties of cylindrical shells is applicable to such an exotic object as a CNT. This question, as well as other similar ones, can be answered on the basis of the comparative analysis of experimental data obtained recently and taking into account the results of model calculations performed on the atomic and molecular level with the use of the classical concepts of the theory of elasticity. The results of such an analysis will be presented below.

The elastic mechanical properties of an elongated cylindrical shell are characterized by a set of parameters (elastic moduli) that are the coefficients of proportionality between a stress and the deformation of the shell in a specific direction. The elastic moduli are defined under conditions of a light load when the deformation has an elastic reversible character. The most important types of deformation of a single-walled nanotube are presented in Fig. 2. Along with the deformation types shown, the torsion of a shell with respect to its axis should also be mentioned.

The main parameter characterizing its tensile strength (Fig. 2a) is the longitudinal Young modulus E, defined by the expression

$$E = \frac{\sigma}{\varepsilon} = \frac{N}{2\pi R h\varepsilon} \,. \tag{1}$$

Here,  $\sigma$  is the longitudinal stress representing the ratio of the longitudinal tensile force N applied to a nanotube to its cross section area,  $\varepsilon$  is the relative tension (change in the length) of

the nanotube due to the action of the force, R is the radius of the nanotube, and h is the thickness of its shell. Expression (1) constitutes one of the specific formulations of the Hook law. The tension of a cylindrical shell is usually accompanied by a lowering of its lateral dimension. This property is characterized by the Poisson coefficient v that is defined as the ratio of the relative transversal constriction  $\varepsilon'$  to the relative longitudinal tension  $\varepsilon$ :

$$v = \frac{\varepsilon'}{\varepsilon} \,. \tag{2}$$

Analysis shows that the magnitude of the parameter v cannot exceed 0.5.

The elastic modulus corresponding to the axial compression of a nanotube (Fig. 2b) is defined in a similar manner. The elastic tension and compression of a nanotube have a common atomic origin related to the character of the dependence of the interaction potential of carbon atoms on the internuclear distance. For this reason, the elastic moduli corresponding to the axial tension and compression are expressed through the second derivative of this dependence at the minimum point and are practically equal to each other. However, the symmetry between the tension and compression of a nanotube takes place only at infinitesimal stresses that do not disrupt its structure. A very high compressive force results in a sharp change in the structure of a shell, called buckling (Fig. 2f). This form of compression, accompanied by a structural change, is called 'Euler deformation' and has the character of instability. The threshold of this instability is characterized by the magnitude of critical compressive force.

The elastic moduli corresponding to lateral (bending) deformations of an elongated cylindrical shell (Fig. 2d-f) are expressed through the above-defined Young modulus *E* and the Poisson coefficient *v*. This is caused by the bending deformation of a shell being accompanied by a tension of its outer surface and compression of its inner surface, which promotes the relevant local stresses proportional to the magnitude of the local tension (compression). Thus, in accordance with the classical theory [37, 38], the bending rigidity of a hollow cylinder, which is defined as the energy expended in bending a tube by the unit angle (Fig. 2e), is given by the following relationship

$$D = \frac{Eh^3}{12(1-v^2)},$$
(3)

where h is the thickness of the wall. The ability of such a cylinder to withstand a lateral stress is characterized by the parameter

$$C = Eh. (4)$$

One more parameter characterizing the mechanical properties of a material is the bulk elastic modulus B that is defined by the relationship

$$p = -B \, \frac{\Delta V}{V} \,. \tag{5}$$

Here, p is the uniform pressure acting on an object, and  $\Delta V/V$  is the relative change in the volume that is promoted by this action. In the case of isotropic materials, the following equation interconnects the bulk elastic modulus and Young

modulus:

$$B = \frac{E}{3(1-2\nu)} \,. \tag{6}$$

Departures from this dependence imply the presence of space anisotropy in the structure of a shell.

The elastic modulus of a single-walled nanotube can be estimated on the basis of the microscopic approach taking into account the interaction between carbon atoms comprising the hexagonal surface. In doing so, we shall assume that the carbon atoms entering into the nanotube reside along filaments that are parallel to its axis and interact with each other according to the model Morse potential

$$U(R) = U_0 [1 - \exp(-2\beta\xi)]^2,$$
(7)

where  $U_0$  is the potential well depth for carbon atoms,  $\xi = (R - R_0)/R_0$  is the dimensionless internuclear distance,  $R_0$  is the equilibrium internuclear distance, and  $\beta \sim 1$  is the dimensionless parameter characterizing the degree of sharpness of the interaction potential. In this case, assuming the CNT tension to be small ( $\xi \leq 1$ ), one obtains the following estimate for the Young modulus of the system under consideration:

$$E = \frac{\partial^2 U}{\partial R^2}(R_0) \frac{nR_0}{n\pi r_0^2} = \frac{8U_0\beta^2}{\pi r_0^2 R_0} \,. \tag{8}$$

Here, *n* is the effective number of filaments, which is proportional to the diameter of the nanotube, and  $r_0$  is a quantity of the order of radius of a single carbon atom. Inserting the characteristic magnitudes  $r_0 \sim 0.5 \times 10^{-8}$  cm,  $R_0 \sim 1.5 \times 10^{-8}$  cm,  $U_0 \sim 6$  eV, and  $\beta = 1$  into formula (8) one obtains the estimate for  $E \sim 6 \times 10^{12}$  Pa.

The result of the qualitative estimation performed shows that while the Young modulus of an elongated cylindrical shell does not depend on its diameter, it does depend drastically on the thickness  $2r_0$  of the wall. The uncertainty in the magnitude of this parameter, which is of the order of the atomic size, is the main factor determining the error in such a kind of estimation. As will be seen later, the estimated magnitude of the Young modulus (8) is in qualitative agreement with the results of direct measurements. Let us compare this magnitude with that of the majority of metals having high tensile strength (steel, molybdenum, copper, etc.) ranging within the interval of 10-30 GPa. Therefore, the tensile strength of CNTs exceeds the relevant parameter for all known materials by as much as about two orders of magnitude. Such a difference is caused mainly by the presence of defects in the crystal structure of macroscopic materials. The tensile strength of macroscopic specimens of materials is determined by defects whose occurrence lowers drastically the magnitude of the interaction energy for neighboring atoms, compared to the characteristic value  $U_0$ used in the above-performed estimation. The structure of CNTs is frequently defect-free; therefore, their tensile strength reaches the maximum possible magnitude (8).

The above estimation shows that the Young modulus for single-walled and multiwalled nanotubes should be of the same order of magnitude, assuming the structure of both to be defectless and the tensile force is distributed homogeneously over all the shells of the multiwalled CNT. Indeed, in this case the above estimate contains in both the numerator and the denominator not only the effective number of filaments n but also the number of nanotube layers m that is to be cancelled in the same manner as n.

The elastic properties of CNTs are the subject of numerous detailed calculations. Two general approaches to the calculation of mechanical characteristics of CNTs can be highlighted. The first is based on the modern-day methods of quantum chemistry and molecular dynamics, taking into account the real arrangement of carbon atoms over the cylindrical surface of a nanotube and their interaction potential. In this case, the change in the potential energy of carbon atoms arranged in a regular manner over the cylindrical surface is calculated ab initio for various deformations of this surface (see Fig. 2). Such an approach seems to be most consistent; however, due to the large number of atoms involved and the considerable uncertainty in the interaction potential between atoms in the presence of surrounding particles, the results obtained have a rather qualitative character. Therewith, qualitative calculated results obtained by various authors using different model assumptions can notably differ from each other [39-50]. However, this approach permits one to establish the dependences of the mechanical characteristics of CNTs on their structural features, such as chirality and the presence of defects.

Another approach to the analysis of CNT mechanical properties is based on the modern-day mechanics of continuous media and the theory of elasticity. In this case, the nanotube surface made up from carbon atoms is substituted with a continuous shell whose mechanical characteristics are determined on the basis of measurement data or comprehensive calculation results. Such an approach, like any empirical method, is not exactly fully justified; however, at the moment it is the only tool to analyze more complicated tasks, for example, those related to establishing the mechanical characteristics of multiwalled nanotubes. Comparison of the results obtained by using the two above-described approaches, as well as experimental data, permits one to infer to what degree taking into account the atomic structure of a CNT affects the mechanical properties of this object.

One of the first successful examples of the detailed calculation of the elastic characteristics of single-walled CNTs is the paper [39] guided by the empirical forceconstant model. According to this model, the interaction potential of atoms is approximated by the sum of pair potentials of the harmonic type. The force constants are determined empirically by matching the calculated and experimental magnitudes of elastic constants and phonon frequencies. The calculated results for single-walled CNTs are summarized in Table 1. Here,  $(n_1, n_2)$  are the chirality indices of a nanotube, R is its radius, B is the bulk modulus, E is the Young modulus, M is the shear modulus (torsion relating to the nanotube axis), and v is the Poisson coefficient. As can be seen, the calculated values of the elastic moduli of a CNT are rather weakly sensitive to its geometry (diameter and chirality). The error of calculations relates to the uncertainty in the thickness of the nanotube wall and is estimated by several dozen percent. The three to four significant figures in the data of the table do not correspond to this uncertainty and are shown only to illustrate the weak character of the qualitative moduli-geometry dependence.

The calculation data presented in Table 1 imply that the elastic moduli of a nanotube do not practically depend on its diameter or chirality indices. Such a conclusion seems to be natural for calculations performed within the framework of

$(n_1, n_2)$	<i>R</i> , nm	$C_{11}$	$C_{33}$	<i>В</i> , ТРа	E, TPa	M, TPa	v
(5,5)(6,4)(7,3)(8,2)(9,1)(10,0)(10,10)(50,50)(100,100)	0.34 0.34 0.35 0.36 0.37 0.39 0.68 3.39 6.78	0.397 0.397 0.397 0.396 0.396 0.396 0.398 0.399 0.399	1.054 1.054 1.055 1.057 1.058 1.058 1.054 1.054 1.054	0.191 0.191 0.190 0.190 0.191 0.190 0.191 0.192 0.192	0.971 0.972 0.973 0.974 0.974 0.975 0.972 0.972 0.972	0.436 0.437 0.454 0.452 0.465 0.451 0.457 0.458 0.462	0.280 0.280 0.280 0.280 0.280 0.280 0.280 0.278 0.277 0.277
(200, 200)	13.5	0.399	1.054	0.192	0.972	0.478	0.277
Graphite, along the hexagonal plane		1.06		0.0083	1.02	0.44	0.16
Graphite, perpendicular to the hexagonal plane			0.036	0.0083	0.0365	0.004	0.012
Diamond, along t	the cubic axis	1.07	1.07	0.442	1.063	0.5758	0.10415

Table 1. Parameters of single-walled carbon nanotubes of various structure, calculated on the basis of the empirical force-constant model [39].

the empirical force-constant model. In this case, the mechanical properties of a solid shell modeling a real carbon nanotube depend only slightly on the angle between the direction of an external action and the orientation of the graphite plane. The absolute magnitude of the Young modulus accounts for an order of TPa that corresponds to the above-performed estimate (8). The values of the Young modulus and shear modulus are comparable with those for a diamond and graphite layer. However, these materials do not have an elongated structure and therefore cannot be considered as objects possessing extraordinary tensile strength. Calculations imply that the rigidities of CNTs in the axial and radial directions are close to each other.

As was noted above, the results of the determination of elastic moduli are quite sensitive to the accepted value of the thickness of the cylindrical shell modeling the object under investigation [see formula (3)]. Such sensitivity is the reason for considerable discrepancy between the data obtained by various authors using different assumptions about the magnitude of this parameter. Thus, substituting the magnitude of h = t = 0.34 nm corresponding to the effective thickness of the graphite layer into equation (3) that interconnects the Young modulus and bending rigidity of a cylindrical shell results in a highly overestimated magnitude of the bending rigidity of a nanotube [40, 42]. The molecular dynamics calculations [40] performed assuming a nanotube wall thickness t = 0.066 nm and a Poisson coefficient v = 0.19resulted in a Young modulus of 5.5 TPa, effective bending rigidity of 0.85 eV, and lateral deformation strength C = Et = 360 J m<sup>-2</sup>. The five-fold difference between this result and the Young modulus data of Table 1 [39] that has been confirmed by further measurements is caused by the violation on the atomic scale of one of the main principles of the mechanics of rigid body in accordance with which an elastic substance should be homogeneous.

The above-noted difficulties that arise in calculations of the Young modulus of single-walled nanotubes on the basis of the continuous shell model and relate to the uncertainty in the magnitude of the nanotube's thickness h are managed to avoid using instead of expression (1) the alternative definition of the Young modulus [46]

$$E = -\frac{1}{V_0} \left. \frac{\partial^2 W}{\partial \varepsilon^2} \right|_{\varepsilon = 0}.$$
(9)

Here,  $V_0$  is the equilibrium volume, and W is the tension energy. In such a definition of the Young modulus, the problem related to uncertainty in the nanotube's wall thickness can be avoided. The results of the relevant calculations performed by the molecular orbital method using the tight binding formalism are shown in Table 2. These data differ by about 30% from those of Table 1 obtained using the elastic shell model, which characterizes the possibilities of modern-day approaches to modeling the mechanical properties of CNTs. In spite of a considerable error in the determination of the absolute magnitudes of the Young modulus, the qualitative conclusion of both research teams relating to the slight sensitivity of this parameter to the diameter and the chirality of a nanotube holds true.

 Table 2. Parameters of single-walled CNTs of various chirality and diameter as calculated in Ref. [46].

Chirality indices $(n,m)$	(10,0)	(6,6)	(10, 5)	(10, 10)	(20, 0)	(15, 15)
Diameter, nm	0.791	0.820	1.034	1.360	1.571	2.034
v	0.275	0.247	0.265	0.256	0.270	0.256
E, TPa	1.22	1.22	1.25	1.24	1.26	1.25

Scrolling the graphite plane into the cylindrical surface of a nanotube necessitates the expenditure of energy, depending on the radius of the nanotube and, generally speaking, on its chirality indices. These dependences calculated using the pseudo-potential and density functional theory (DFT) methods are presented in Fig. 3 [41]. As can be seen, the stress energy is slightly dependent on the chirality of a CNT but rises quite sharply as the nanotube's radius decreases. It should also be noted that the typical radius of single-walled CNTs produced by standard methods ranges between 0.6 and 0.8 nm. The stress energy of such nanotubes is relatively low and amounts to about 0.05 eV. For this reason, the mechanical properties of single-walled nanotubes are very close to the relevant parameters of a graphite plane (see Table 1).

While the number of experiments addressed to establishing the mechanical characteristics of CNTs and related materials is quite large [15-18, 51-80], the set of reliable quantitative data in this field is rather limited, which is explained by the obvious technical difficulties in manipulat-



Figure 3. Dependences of the stress energy on the radius of a single-walled nanotube, calculated for nanotubes of various chirality through the DFT method [41]. The inset shows the same dependences on a logarithmic scale. The linear shape indicates a power-like dependence with the power index of  $-2.05 \pm 0.02$ .

ing objects a nanometer in size. As is shown above, the Young modulus of single-walled and multiwalled nanotubes should be close to each other in the absence of structural defects. However, manipulating multiwalled CNTs is simpler from the technical viewpoint. For this reason, either multiwalled nanotubes or bundles containing some quite large number of single-walled nanotubes have been used as the subjects of investigation in the majority of experiments. Early publications on this subject have been reviewed by Salvetat et al. [51].

One of the first experimental examinations of the Young modulus of single-walled CNTs was performed in Ref. [52] on the basis of the results of measurements of the vibrational frequency of a nanotube of a certain geometry using the transmission electron microscope (TEM). The nanotubes were produced by the laser ablation method. Twenty-seven individual nanotubes shorter than 100 nm, having various lengths and diameters without visible contaminations, were selected. Statistical processing the measured data resulted in a room-temperature Young modulus  $E = 1.3 \pm 0.45$  TPa, which is in good agreement with the results of the abovecited calculations [46] and measurements by other authors, as well. Due to the large uncertainty in measured data that is caused by the difficulty in exactly determining the nanotube's length, these data do not permit one to conclude what the ratio between the Young modulus of a single-walled nanotube and that of graphite (1.06 TPa) is [53].

Another approach to the measurement of elastic moduli of CNTs has been developed in Refs [15, 16, 51]. Nanotubes were deposited onto a well-polished alumina membrane that is usually used for ultrafiltration. Some nanotubes are found on such a surface lying over pores as bridges. The load on a nanotube bridging a pore is transferred through an Si<sub>3</sub>N<sub>4</sub> tip of an atomic force microscope (AFM). Processing the set of microimages obtained at various loads permits one to determine the diameter of the nanotube, the distance *L* between the clamped points, and the deflection *d* caused by the load *F*. The interconnection between the deflection of a clamped hollow cylinder and the force has the following



Figure 4. Characteristic dependence of nanotube deformation on the stress, as measured in Refs [15, 16, 51].

form [54]

$$d = \frac{FL^3}{aEI},\tag{10}$$

where E is the Young modulus,  $I = \pi (R_0^4 - R_1^4)/4$  is the moment of the inertia of the cylinder,  $R_0$ ,  $R_1$  are its inner and outer radii, respectively, and the numerical factor a = 192. It is assumed that the nanotube's ends are firmly secured on the membrane surface, so that its bending does not promote their motion over the surface. The dependence of the nanotube deflection on the applied force is shown in Fig. 4. The linear and reversible shape of this dependence confirms the elastic character of the deformation. The slope of the linear function provides the Young modulus, given the magnitudes of L and  $R_0$ . The statistical processing of data for 11 nanotubes according to Eqn (10) has resulted in a mean value of the Young modulus of  $0.81 \pm 0.41$  TPa. This magnitude is comparable with that calculated for graphite (along the hexagonal plane) (1.06 TPa) [53], as well as with the result (1.28  $\pm$  0.59 TPa) of the statistical processing of the experimental data [55] obtained for 6 multiwalled CNTs between 26 and 76 nm in diameter and with one end clamped. The Young modulus for a bundle of single-walled nanotubes, estimated on the basis of measurements [15, 16, 51], has a close magnitude ( $\sim 1$  TPa).

One more method for the measurement of the Young modulus of CNTs has been developed by Enomoto et al. [68], who used a nanomanipulator designed specially for this aim and presented schematically in Fig. 5. It contains a stationary stage and a piezo-driving stage. The device permits one to apply a compressing or bending load to an individual nanotube, as well as an electrical voltage between two stages. Each CNT bundle was fixed on the tip of an aluminum wire that was attached to a stationary stage with a silver paste.

A cantilever characterized by a force constant of  $0.03 \text{ N m}^{-1}$  is connected to a piezo-driving stage. The bending load was applied onto the nanotube through the cantilever in incremental steps. Therewith, the deflection of the nanotube's tip was determined with a TEM operating at an electron energy of 200 keV. The Young modulus was evaluated using the measured interconnection between the applied load and the deflection, modeling the nanotube by a cylindrical beam of constant cross section, whose mechanical parameters did not depend on the load. Five types of



**Figure 5.** Schematic illustration of the action of a nanomanipulator designed for determining the mechanical characteristics of nanotubes [68]: (a) nanoprobe equipped with a cantilever, and (b) magnified image of the cantilever and nanotubes to be measured.

multiwalled nanotubes were subjected to the measurements, and their parameters are listed in Table 3.

The Young modulus  $E_a$  (MPa) was evaluated by the formula  $E_a = Pl^3/3yI$ , where P (N) is the bending load applied to the nanotube tip; l (mm) is the length of the nanotube reckoned from the clamping point; y (mm) is the deflection of the nanotube tip, and I (mm<sup>4</sup>) is the crosssectional moment of inertia of the nanotube. The parameter  $E_a$  determined in the above-described manner is designated as 'the apparent Young modulus' because it is defined without taking into account the distortion in the nanotube's structure from its bending. The measurements show that a force of 6.6 nN acting on the tip of a nanotube 20 nm in diameter produced by the electric arc method promotes the deflection

**Table 4.** CNT Young modulus measured by various authors.

Table 3. Parameters of CNTs studied in experiment [68].

Number of the sample	Diameter of a CNT, nm	CNT production method
1	10 - 20	Electric arc
2	10	Chemical vapor deposition (CVD)
		in the presence of a catalyst
3	50	CVD followed by thermal treatment
		at 3000 K
4	80	CVD followed by thermal treatment
		at 3000 K
5	100	CVD in the presence of a catalyst

of 88 nm, which corresponds to the apparent Young modulus of 3.3 TPa. Measurements performed for other types of CNTs reveal the effect of lowering the Young modulus as the degree of crystallinity of their structure decreases, which is characterized by the ratio of the intensity of the Raman peak at 1350 cm<sup>-1</sup> to that of 1580 cm<sup>-1</sup>. Table 4 collates the magnitudes of the Young modulus measured by various authors.

As can be seen these data are in general agreement with the above-presented calculated results (see Tables 1, 2) and with the qualitative estimate of this parameter,  $E \sim 1$  TPa, as well. Therefore, nanotubes represent the material possessing the record magnitude of the Young modulus. The magnitudes of the Young modulus of CNTs synthesized by the CVD method [15, 16, 51, 72] are beyond the majority of the data. This is explained mainly by a considerable content of structural defects in such nanotubes, which determines both the elastic and strength characteristics of the material.

The results of numerous experiments (see, for example, Refs [15, 68]) imply a critical dependence of the Young modulus of multiwalled CNTs on the degree of layer ordering. Therewith, the extraordinarily high magnitudes of the Young modulus  $E \sim 1$  TPa are inherent only in nanotubes synthesized by either the electric arc or the laser ablation methods, providing relatively low defect content. However, these methods are characterized by a rather low productivity (at a level of  $\sim 1$  g h<sup>-1</sup>), so it is hard to expect their practical

No.	E, TPa	References	Object	Measuring method	Remarks
1	$1.3\pm0.45$	[52]	Single-walled CNTs	Vibrational frequency	
2	$0.81\pm0.41$	[15, 16, 51]	Multiwalled CNTs synthesized by the electric arc method	Elastic deformation	
3	0.027	[15, 16, 51]	Multiwalled CNTs synthesized by the CVD method	Elastic deformation	Highly disordered structure
4	$1.8\pm0.9$	[53]	Multiwalled CNTs	Thermal vibrations	$300 \leqslant T \leqslant 1100$ K; <i>E</i> is noted to tend to increase as the nanotube's diameter decreases
5	$1.28\pm0.59$	[55]	Multiwalled CNTs between 26 and 76 nm in diameter	Vibrational frequency	
6	1 - 1.2	[56]	Multiwalled CNTs		
7	$0.45\pm0.23$	[57]	Bundles 2 mm in length and 10 µm in diameter containing multiwalled CNTs 12 nm in inner diameter and 30 nm in outer diameter	Direct measurements	
8	3.5	[68]	Multiwalled CNTs between 10 and 100 nm in diameter	Processing the data of bending deformation measurements	<i>E</i> is noted to tend to increase as the degree of crystallinity rises
9	0.01	[72]	Single-walled CNTs grown by the CVD method		
10	$1.23\pm0.09$	[73]	Multiwalled CNTs 3.2 nm in inner diameter and 14.3 nm in outer diameter synthesized by the CVD method		

realization proceeded exclusively from their extraordinary strength properties. The CVD method is characterized by a considerably higher productivity and technological simplicity, usually yielding multiwalled CNTs of large diameter and high defect density. For this reason, such nanotubes possess a notably lower Young modulus  $E \sim 30-100$  GPa [15]. Reducing the defect content as the diameter of a multiwalled CNT decreases suggests an idea for the selective production of multiwalled nanotubes of relatively small diameter as a possibility for the purposeful high-productivity synthesis of high-strength nanotubes by the CVD method.

Such a possibility has been demonstrated by the authors of Ref. [70], who modified to this end the standard CVD method of production of multiwalled CNTs with a small outer diameter and few layers. Two types of samples containing such nanotubes were produced. The samples of the first type (1) were synthesized as described in Ref. [81], by passing the  $H_2 + CH_4$  mixture in the ratio 82:18 over cobalt nanoparticles at a temperature of 1000 °C. The catalyst particles were prepared by selectively reducing a solid suspension  $Mg_{1-x}Co_xO$  (x ranges between 0.01 and 0.1). The CNTs obtained were annealed in an oven at 600 °C under an Ar flow of 3 1 min<sup>-1</sup>. The samples of the second type (2) were synthesized as described in Ref. [82] through the thermal catalytic decomposition of acetylene at 700 °C using the zeolite Fe-Mo/NaY as a catalyst. TEM observations showed that the sample 1 contained nanotubes between 1.1 and 3.5 nm in outer diameter, and between 0.65 and 2 nm in inner diameter. More than 70% of the nanotubes had two layers, while the rest of them were single-walled or threewalled. Sample 2 contained nanotubes between 2 and 16 nm in outer diameter, so that 50% of them were two-layered with the outer diameter between 1.6 and 4.0 nm, 25% were threelayered with the outer diameter between 3 and 12 nm, and 25% were four-layered with the outer diameter between 4 and 16 nm. All the nanotubes were bound into bundles. The mechanical properties of the CNTs synthesized were measured by the direct method [15] using an AFM. In accordance with this method, a nanotube bundle is arranged across a pore formed on a porous alumina membrane. The Young modulus is determined on the basis of the known inter-relation between the applied load and the relevant deflection of the bundle. The apparent Young modulus  $E_{\rm b}$  obtained on the basis of the measurements is expressed through the true Young modulus E by the relationship

$$\frac{1}{E_{\rm b}} = \frac{1}{E} + \frac{10}{3G} \frac{D^2}{L^2} \,,$$

where *D* is the diameter of the bundle, *L* is its length, and *G* is the shear modulus. The second term on the right-hand side of this equation relates to the mutual displacement of nanotubes entering the bundle. Since the characteristic magnitude of *G* is of order GPa, while  $E \sim 1$  TPa, the contribution from the second term is notable in the case of short CNTs (D/L > 0.01). The measured data imply a strong dependence of the apparent Young modulus  $E_b$  on the nanotube diameter. For nanotube bundles with a diameter less than or of the order of 5 nm, belonging to any above-listed types, the magnitude of this parameter ranges between 0.8 and 1.2 GPa. For bundles with a diameter of 7 nm or more, the magnitude of the apparent Young modulus does not exceed 100 GPa and in some cases descends to 10 GPa. The high magnitude of the Young modulus, characterizing small-diameter bundles, indicates a low defect content in nanotubes constituting such bundles.

Along with the Young tension modulus, the tensile strength is also an important parameter of a nanotube. This parameter is defined as the tension stress (per unit area) over which the nanotube's structure undergoes irreversible changes. The magnitude of this parameter determines the maximum relative strain of a sample in elastic deformation conditions. As follows from the above definition, the magnitude of the tensile strength does not depend on the number of nanotubes used for the measurement. Therefore, by utilizing bundles consisting of a large number of singlewalled nanotubes one can avoid the problems arising in manipulations of very miniature samples of individual CNTs. Such an approach has been demonstrated by the authors of Ref. [61], who managed to exclude the role of subordinate factors, for example, related to the effect of the substrate. Single-walled nanotubes bound into bundles were grown by the standard laser evaporation method with the use of catalysts. Each of the bundles was several micrometers in length and contained from dozens to hundreds of nanotubes bound to each other by van der Waals attractive forces. These bundles were inserted into N, N-dimethylformamide to give a suspension. A silicon surface coated with an oxide film was immersed into the suspension, and after letting the solvent dry the nanotube bundles were arranged freely on the surface. This surface was then covered with Cr and Au layers of 2 and 20-50 nm, respectively, which was followed by an etching procedure. As a result of this procedure, the nanotube bundles were found to be hanging between two metal pads. The distance between the hanging points was 4  $\mu$ m, while the depth of the trench formed was about 2  $\mu$ m. The bundle was loaded through the tip of an AFM. The measurements resulted in establishing a link between the lateral loading on the bundle and the deflection of the tip. This link has a cubic form that is intrinsic to a string. Processing the measurement data obtained with 4 objects results in the maximum magnitude of elastic strain reaching  $5.8 \pm 0.9\%$ . This is followed by a magnitude of tensile strength of the nanotube bundle running to  $45 \pm 7$  GPa, which exceeds by about 20 times that of high-strength steels.

Multiwalled nanotubes grown on an Fe-Si substrate using the catalytic pyrolysis of acetylene possess a considerably lower tensile strength. This follows from the experiment [57] where a very long bundle (more than 10  $\mu$ m in diameter, and about 2 mm in length) containing tens of thousands of multiwalled CNTs of 12 nm in inner diameter and 30 nm in outer diameter aligned perpendicular to the substrate and spaced, on the average, at about 100 nm was used as the subject of investigation. The bundle was fixed by two ends in a measuring device aiming to evaluate its strain vs. an applied load. The measurements resulted in an average Young modulus of  $0.45 \pm 0.23$  TPa in the samples under investigation, while the tensile strength was  $1.72 \pm 0.64$  GPa. This magnitude is several times lower than the characteristic values of the Young modulus given in Table 4, and an order of magnitude lower than the result of the above estimate (8) ( $\sim 6$  TPa). The measured magnitude of the tensile strength is also an order of magnitude lower than the result (45 GPa) of the above-cited work [61], where the nanotubes synthesized by the laser ablation method were studied. The discrepancy noted implies radical differences between the mechanical properties of CNTs produced by the CVD method and those synthesized by the conventional electric arc method.

As noted above, these differences manifest themselves mainly in a larger number of defects in nanotubes produced by the CVD method, which is followed by their lower strength characteristics. Moreover, in manipulations with bundles containing a large number of multiwalled nanotubes there arises a problem related to the transfer of the load applied directly to the nanotubes in contact with the clamping devices to the total massif of nanotubes. Due to a weak van der Waals interaction between neighboring nanotubes, as well as between neighboring layers of a common multilayer nanotube, the load transfer is not always full. For this reason, measured mechanical characteristics can turn out notably lower than those of an individual nanotube or a small bundle, even if the defect content is not high.

The extraordinarily high plasticity of CNTs has been demonstrated recently by Huang et al. [50]. It has been shown that the magnitude of tensile strain of single-walled CNTs at elevated temperatures (about 2000 K) can reach hundreds of percent, which is accompanied by a considerable decrease in the diameter of the nanotube. The initial nanotube of 24 nm in length was synthesized as a result of the electric breakdown of a multiwalled CNT that was inserted into the chamber of a high-resolution TEM equipped with a piezomanipulator which was used for applying the axial load to the nanotube. At tensile failure, the nanotube length reached 91 nm, which corresponds to a tensile elongation of 280%. The tensile elongation of the nanotube was accompanied by a 15-fold decrease in its diameter, from 12 to 0.8 nm. The effect of the extraordinarily high plasticity of CNTs at elevated temperatures can be used in producing new composite materials.

#### 2.2 Bending rigidity and strength of nanotubes

In accordance with the measurements [55], the bending strength of multiwalled CNTs is equal to  $14.2 \pm 0.8$  GPa, which exceeds by about 15 times the relevant magnitude  $(\sim 1 \text{ GPa})$  for graphite fibers [56]. Such a high magnitude of bending strength of CNTs relates to their enhanced flexibility. The bending rigidity of CNTs was measured in detail in Ref. [71] where aligned multiwalled CNTs having a bamboo-like structure 20 nm in diameter and up to 10 µm in length were studied. These nanotubes were produced as a result of the pyrolysis of iron (II) phtalocyanine, PcFe, under the flow of  $Ar + H_2$ . The bending modulus was measured by applying alternating voltage of varied frequencies to a nanotube clamped at one end in order to determine the resonance vibrational frequency. In accordance with the classical theory of elasticity, the resonance frequency of a shell is expressed through its parameters as follows:

$$v_i = \frac{\beta_i^2}{8\pi} \frac{1}{L^2} \sqrt{\frac{(D^2 + D_1^2)E_d}{\rho}}.$$
 (11)

Here, D,  $D_1$  are the outer and inner diameter of the nanotube, respectively, L is its length,  $\rho$  is its density,  $E_d$  is the deformation modulus, and  $\beta_i = 1.875$  and 4.694 are the numerical factors for the first and second harmonics, respectively. The measurements of the resonance frequency, performed for 6 nanotubes, resulted in values of ~ 1 MHz with the width of the resonance amounting to  $\Delta v/v \sim 0.01$ . Processing these measurement data provided the bending moduli that are presented in Table 5. The values given are about an order of magnitude lower than the estimated result (200 GPa) obtained in Ref. [28] for nanotubes over 30 nm in

 Table 5. Resonance frequencies and bending moduli of nanotubes evaluated in Ref. [71].

No. of the sample	Outer diameter D, nm	Inner diameter D <sub>1</sub> , nm	Length <i>L</i> , μm	Resonance frequency v, MHz	Bending modulus <i>E</i> <sub>d</sub> , GPa
1 2 3 4 5 6	33 39 39 45.8 50 64	18.8 19.4 13.8 16.7 27.1 27.8	5.5 5.7 5.3 4.6 5.7	0.658 0.644 0.791 0.908 1.420 0.968	$\begin{array}{c} 32 \pm 3.6 \\ 26.5 \pm 3.1 \\ 26.3 \pm 3.1 \\ 31.5 \pm 3.5 \\ 32.1 \pm 3.5 \\ 23 \pm 2.7 \end{array}$

diameter produced by the electric arc method. Such a discrepancy is caused by the bamboo-like structure and high content of point defects in the nanotubes utilized in Ref. [71].

Since the resonance frequency of a nanotube depends on its mass, joining some particle of a specific mass to a nanotube changes its resonance frequency. Therefore, such an oscillator can be used as the tool for weighing the mass on the femtogram level  $(10^{-15} \text{ g})$ . Thus, the authors of Ref. [71] evaluated the mass of a nanotube attached to another nanotube by measuring the change in the resonance vibrational frequency. The result of the evaluation (23 fg) is comparable with an independent estimation of this quantity (17 fg).

The high sensitivity of the resonance vibrational frequency of nanotubes to the presence of foreign inclusions has manifested itself in studies of so-called 'peapods' which are single-walled nanotubes filled with fullerene molecules. Basic interest in investigating such structures stems from the unique possibility of obtaining and establishing the physical and chemical properties of 1D chains consisting of fullerene molecules [14]. The mechanical behavior of such systems was examined by the authors of Ref. [78]. Single-walled nanotubes produced by the laser ablation method were purified in the standard way including treatment in nitric and hydrochloric acids, hydrogen peroxide, alkali NaOH, toluene, and distilled deionized water, as well as filtration and ultrasonication. The paper-like material produced containing single-walled nanotubes bound into bundles was used as a reference sample. As a result of the above-described treatment, the nanotubes opened their caps, facilitating filling them with fullerene  $C_{60}$ molecules. In doing so, the paper-like sample was kept for 3 h in a sealed capsule together with powdered  $C_{60}$  at 650 °C in a vacuum of 10<sup>-6</sup> Torr. This resulted in the CNTs filling with fullerenes. In order to close the nanotube caps and remove chemical adducts from their walls, both filled and reference samples were kept at 800 °C in a vacuum for 1 h. Such a treatment also promotes the elimination of structural defects in CNTs and the recovery of the regular crystalline structure of bundles. The degree of filling the nanotubes with fullerene molecules was determined through X-ray diffraction measurements, as well as using TEM observations. The measured data showed the existence inside the nanotubes of quite homogeneous lengthwise 1D chains of C<sub>60</sub> molecules spaced, on the average, 0.997 nm apart.

Mechanical resonance characteristics of both filled and reference nanotubes were determined with a scanning probe microscope. A paper-like sample of the purified CNTs was attached by means of a silver paint to the microscope tip. A CNT bundle was moved with the help of a nanometric device in the direction of the grounded contra-electrode. Then, an alternating voltage was applied across the tip and contraelectrode, and the resonance frequency and amplitude of

	Bundles comprising unfilled nanotubes				Bundles comprising filled nanotubes				
D, nm	L, nm	f, MHz	$(E_{\rm d}/\rho)^{1/2},{ m m~s^{-1}}$	D, nm	L, nm	f, MHz	$(E_{\rm d}/\rho)^{1/2}$ , m s <sup>-1</sup>		
16	1635	12.46	15,069	14	1693	13.2	19,465		
16	2354	6.82	16,572	16	2405	7.96	20,962		
17	1705	14.94	17,842	18	2616	8.04	22,603		
17	1819	9.84	13,452	19	1556	21.56	19,847		
19	2429	6.6	14,649	20	2682	6.32	16,607		
23	1653	17.44	15,071	20	2733	7.66	20,766		
24	3004	5.16	13,754	21	3442	4.56	18,215		
27	2006	11.52	12,318	23	5916	1.52	16,796		
53	7027	1.42	9391	35	6831	1.64	15,757		
67	10,273	0.9	10,046						
68	11,615	0.52	7372						
Average value			13,230		Average value				
Standard deviation			3187		Standard deviation	1	2307		

Table 6. Resonance frequency of various CNT bundles measured in Ref. [78].

vibrations of the bundle, depending on its size, were measured. For the *i*th harmonic, the resonance vibrational frequency  $f_i$  of a solid cylinder L in length and D in diameter clamped at one end is expressed through its parameters by the relationship

$$f_i = \frac{B_i^2}{8\pi L^2} D \sqrt{\frac{E_{\rm d}}{\rho}} \,.$$

Here,  $B_1 = 1.875$  and  $B_2 = 4.694$  are the numerical factors for the first and second harmonics, respectively,  $E_d$  is the effective bending modulus, and  $\rho$  is the density of the material of the cylinder.

Table 6 presents the magnitudes of the resonance frequency measured for various bundles. The values of  $(E_{\rm d}/\rho)^{1/2}$ , evaluated from the measured data using the above formula, are also shown. The bundle dimensions were determined with the aid of TEM observations. As is seen, for unfilled CNTs the average magnitude equals  $(E_d/\rho)^{1/2}$  =  $13,230 \pm 3187$  m s<sup>-1</sup>, while for the 'peapods'  $(E_d/\rho)^{1/2} =$  19,002 ± 2307 m s<sup>-1</sup>. Processing these data taking into account the change in the density of the nanotubes as a result of their filling implies that filling of single-walled CNTs with fullerene molecules promotes an increase in the average bending modulus  $E_d$  from 240 ± 105 up to 650 ± 156 GPa. Attention should be drawn to the lowering of the bending modulus of filled bundles as their diameter rises, which is obviously caused by the mutual sliding of the nanotubes constituting the bundle at their bending. This tendency has also been noted by the authors of Ref. [79], who studied single-walled nanotubes bound into bundles.

#### 2.3 Radial stiffness

The radial stiffness of nanotubes is considerably lower than in the case of tension or compression. One should note that a distortion of the ideal cylindrical structure of nanotubes can be caused not only by external mechanical loading but also by their van der Waals interaction with the substrate or neighboring nanotubes. It seems obvious that the magnitude of such a distortion rises as the diameter of the nanotube and the diameter of its inner cavity increase. These intuitive considerations are confirmed by the calculated results obtained using the molecular dynamics methods and are shown in Fig. 6 [63].

Distortion of the cylindrical structure of nanotubes under radial loading was observed with the aid of an AFM [63]. Multiwalled CNTs dispersed in methylene chloride were deposited onto an Si(100) surface and subjected to loading, periodically alternating within the range of 0.16-0.24 N m<sup>-1</sup> at a frequency of 25–30 kHz. Treatment of the obtained dependences of the deformation on the loading provides an estimate of the binding energy ~ 10 eV nm<sup>-1</sup> for a nanotube 9 nm in diameter.

The dependence of the radial rigidity of CNTs on the nanotube radius has been demonstrated experimentally by the authors of Ref. [65], who used an AFM operating in the tapping mode. Nanotubes between 2 and 50 nm in diameter were synthesized by the electric arc method. The suspension of CNTs in 2-butanone was prepared through ultrasonication. An Si plate coated with an SiO<sub>2</sub> layer was used as a substrate. The substrate was subjected to electron beam lithography and plasma etching. Parallel trenches of 70 nm in width and 17 nm in depth spaced 500 nm apart were formed on the substrate surface as a result of the treatment. A drop of suspension containing nanotubes was deposited onto the substrate surface and dried at room temperature. Then the sample was studied by a silicon-tipped AFM operating in the tapping mode. The relative radial deformation of various sections of a long bent multiwalled CNT was measured vs. the radial load. The measured dependence is close to linear,



**Figure 6.** The results of calculations of the deformation of nanotubes, taking account of their van der Waals interaction with the substrate [63]: (a) the deformation increases as the nanotube diameter rises, and (b) the deformation of multiwalled nanotubes decreases as the number of inner layers increases.

however, the slope of this linear dependence (radial rigidity of the CNT) is different for various sections of the nanotube, ranging between 11 and 44 N m<sup>-1</sup>. This corresponds to the radial Young modulus within the range between 3 and 40 GPa. This rather low magnitude of the radial Young modulus is caused by the large diameter of the nanotube and by the presence of an inner cavity inside it.

In analyzing experiments aimed at evaluating the radial deformability of CNTs, one should take into consideration the character of the interaction between a nanotube and the substrate surface. Thus, experiments [64] performed with multiwalled nanotubes implied that the interaction is determined not only by the properties of the nanotubes but also by the type of a substrate surface. Nanotubes produced through the standard electric arc method were drenched with ethanol. Then, the graphite or mica substrate was coated with the suspension obtained and dried. Individual CNTs were positioned with a nanomanipulator comprising the silicon tip of an AFM that provided simultaneous recording of the load applied. As follows from such recordings, the nanotube either rotates around its central point or moves as a whole or rolls over the substrate, rotating around its axis, depending on the load application point. It was found that the behavior of nanotubes on the graphite and mica surfaces is different. A nanotube on the mica substrate turns in the substrate surface and moves as a whole, so that the ratio between the turning and displacement depends on the specific load application point. In the case of the graphite substrate, a nanotube does not turn and only its displacement as a whole in the direction of the applied load occurs. The measurements showed that the value of the load applied depends in a periodical manner on the distance passed by the nanotube in the plane. The period of this dependence  $(85 \pm 2 \text{ nm})$  coincides with the circumference  $(83 \pm 3 \text{ nm})$  of the nanotube under investigation (of 13.3 nm radius), which implies that the nanotube rolls over the graphite substrate surface. The fact that under some conditions the rolling of nanotubes over the substrate surface is observable, while the load of 4 nN necessary for the sliding of a nanotube 590 nm in length is much lower than that necessary for rolling (800 nN), is one of the paradoxical conclusions derived from the experimental data [64]. This paradox can be explained supposing a strong inhomogeneity of the interaction between the nanotube and substrate along the length of the nanotube.

The possibility of irreversibly compressing bundles consisting of a multitude of single-walled nanotubes permits one to consider this material as an energy storage device. Possible types of deformation of nanotubes under such compression are displayed in Fig. 7 [83]. This deformation was studied for bundles comprising single-walled nanotubes about 1.36 nm in diameter and spaced 0.34 nm apart. The nanotubes were produced by the double laser ablation method. A typical bundle more than 10 nm in diameter and over 10 µm in length contained hundreds of closely packed nanotubes. A cylinder 7 mm in inner diameter was filled with such bundles and subjected to a load up to 20 tons through a piston. This provided a pressure up to 29 kbar in the sample. The change in the volume of the sample vs the load applied was measured at room temperature. Reproducible compression of the sample in accordance with its volume compressibility at atmospheric pressure,  $2.77 \times 10^{-3}$  kbar<sup>-1</sup>, was observed repeatedly. This magnitude is in agreement with the above-performed estimations. The measurements showed that the density of the sample under a pressure of 29 kbar increases more than by



**Figure 7.** Possible images of the cross section of a nanotube bundle under compression [83]: (a) initial configuration, with the distance between neighboring nanotubes being 0.34 nm; (b) configuration corresponding to homogeneous compression of the bundle, with the distance between neighboring nanotubes being 0.32 nm; (c) configuration corresponding to the formation of edges, and (d) configuration corresponding to the elliptical deformation of the nanotube.

50%, reaching 2.1 g cm<sup>-3</sup>. Therewith, the cross section of the nanotubes changes from circular to elliptical (Fig. 7d) with the ellipse axes of 2 and 0.5 nm. Such a reversible compression of nanotubes points to accumulation of mechanical energy in the bundles, so that the specific energy storage is estimated as 0.18 eV/atom C. This offers the possibility of using nanotubes as the base of composite materials that are able to store considerable mechanical energy in a reversible manner.

#### 2.4 Torsion elastic modulus

While the elastic properties of nanotubes in relation to both tensile and bending loads have been quite well studied, their torsion rigidity has been explored to a notably less degree. This property determines, specifically, the behavior of nanotubes engaged in nanoelectromechanical systems (NEMSs), the operation of which is described in forthcoming chapters of this article. The torsion elastic modulus of CNTs has been measured directly by the authors of Ref. [77], who used as an object of investigation single-walled nanotubes 0.97 nm in average diameter grown by the CVD method on a silicon substrate with an oxide layer 1 µm in thickness. Two metal anchors  $4 \times 4 \,\mu m$  in size spaced 1  $\mu m$  apart and covered with a layer of chromium 10 nm in depth and a layer of gold 75 nm in depth were placed along the length of the nanotube. A paddle about  $10^{-13}$  g in mass and about  $10^{-23}$  g cm<sup>2</sup> in moment of inertia was affixed to the nanotube. Applying a voltage between the gate electrode and the paddle promotes the rotation of the latter, so that the applied voltage of about 2-4 V causes turning through 90°. The angle of the plate deflection proportional to the magnitude of the applied voltage was determined by an SEM. Upon removal of the applied voltage, the paddle returned to its initial position. Therefore, the behavior of a nanotube is similar to that of a torsion spring. Processing the measured dependences of the deflection angle of the paddle on the rotating moment permitted determining the torsion modulus of CNTs as  $0.41 \pm 0.36$  TPa. The main source of the uncertainty in this measurement is related to the difficulty in precisely determining the diameter of a nanotube.

# 2.5 Axial compressing and Euler instability

Axial compression of a nanotube considered as a thin cylindrical shell promotes an increase in its diameter (buckling, see Fig. 2b). At low loading, the axial compression has an elastic reversible character, so that the relevant elastic modulus coincides with the Young modulus defined for the tension. Upon exceeding some critical stress, so-called Euler instability occurs, which is accompanied by an abrupt lowering of the elastic modulus and irreversible distortion of the nanotube's structure. The nanotube's surface is thereby subjected to shell buckling (Fig. 2f).

The simplest way to establish the critical conditions of irreversible distortion of the cylindrical structure of a CNT as a result of its axial compression is based on the consideration of the nanotube as a rigid cylindrical shell. The standard approach to describing the behavior of such a shell [43, 44] results in the following relation for the critical pressure:

$$p_{\rm c} = 0.32E \left(\frac{h}{R}\right)^3,\tag{12}$$

where *E* is the Young modulus, *h* is the thickness of the nanotube wall, and *R* is its radius. Taking  $E = 5.5 \times 10^7$  atm, h = 0.15 nm, and R = 0.65 nm one obtains from this equation  $p_c \sim 10$  GPa. This magnitude is in a qualitative agreement with the data of the above-cited experiments [74, 75, 84, 85] in accordance with which the value of  $p_c$  ranges between 1.5 and 1.9 GPa.

The Euler instability arising upon axial compression of nanotubes has been studied in detail experimentally by the authors of Ref. [58], who have proposed and realized a simple method for the exploration of shell buckling in an individual multiwalled CNT under compression. Nanotubes were synthesized through acetylene pyrolysis with the cobalt catalyst present. A highly porous anodized aluminum foil was used as a substrate, so that its vertical pores were filled with cobalt particles with the use of the electrodeposition method. This resulted in the synthesis of vertically aligned highly ordered nanotubes 50 nm in outer diameter and 40 nm in inner diameter spaced about 100 nm apart. The height of the nanotubes over the substrate was either 50 or 100 nm. The deformation of the CNTs under the axial load was studied in accordance with the scheme depicted in Fig. 8a. The axial compression of the nanotubes was performed by an indenter having a conic tip 100 nm in radius. Therewith, both the load and the deflection of the indenter were recorded.

The measured dependences of the load on the vertical displacement consist of three parts that correspond to three stages of deformation upon compressing nanotubes. The first part, corresponding to relatively low loads, demonstrates practically linear dependence. Upon exceeding some critical load this dependence is saturated, which is interpreted as the Euler instability. The second part is characterized by a rather flat dependence of the load on the displacement. This part reflects the irreversible character of the nanotube's deformation, as is illustrated in Fig. 8b. Upon further increase in the load (the third part), the dependence becomes similar to that for the first part. This means that the indenter comes into contact with other nanotubes that are still in the linear elastic deformation mode. Multiple measurements show that the critical load corresponding to the Euler deformation of nanotubes ranges between 2 and 2.5 µN. As follows from the estimations performed, this corresponds to the critical pressure equal to  $p_c \sim 1$  GPa.



**Figure 8.** (a) Schematic of the experiment addressed to study the Euler deformation of nanotubes under an axial compression [58], and (b) the character of deformation of a nanotube at the Euler instability.

The images of buckled CNTs were obtained by compressing a large number of vertically oriented nanotubes simultaneously using an indenter 10  $\mu$ m in radius. Such an indenter is practically flat for the majority of the nanotubes. The SEM image of deformed nanotubes is in agreement with the concept of Euler deformation (Fig. 8b).

As follows from the classic consideration [38, 86], the critical stress  $\sigma_c$  and compression  $\varepsilon_c$  of a thin cylindrical shell of radius *R* and thickness *h*, corresponding to the Euler deformation, are expressed by the following equations:

$$\sigma_{\rm c} = \frac{Eh}{R\sqrt{3(1-v^2)}}, \quad \varepsilon_{\rm c} = \frac{h}{R\sqrt{3(1-v^2)}},$$
 (13)

where *E* is the modulus of elasticity in axial compression, and v is the Poisson ratio for the material under consideration. This is followed by the expression for the critical axial load

$$f_{\rm c} = 2\pi R h \sigma_{\rm c} = \frac{2\pi E h^2}{\sqrt{3(1-v^2)}} \,. \tag{14}$$

Estimation of the critical load on the basis of formula (14) for the conditions of the above-described experiment (h = 0.15 nm, E = 1 TPa, v = 0.26, and the number of layers in the nanotube n = 30) results in  $f_c = 2.53 \mu\text{N}$ , which practically coincides with the measured quantity  $(2-2.5 \mu\text{N})$  given above.

Expressions (13), (14) imply that the conditions of the Euler deformation do not depend on the height of a cylindrical shell, as distinct from those for bending deformation. These expressions can be utilized for the case of multiwalled CNTs on neglecting a weak van der Waals interaction between layers. Therewith, the Euler deformation of layers in a multiwalled CNT proceeds sequentially beginning from the outer layer for which the ratio h/R is at a minimum. The same magnitude of critical load resulting in the Euler deformation of a CNT (between 2.26 and 2.63  $\mu$ N) was reported in Ref. [59], where the deformation of CNTs under an axial load was studied using a diamond stamp 2  $\mu$ m



**Figure 9.** Illustration of the vertical compression of a massif of nanotubes [80]. When the load is removed, the height of the nanotubes is restored practically totally.

in diameter providing an axial load for 360 CNTs simultaneously. Euler deformation of nanotubes was observed also in Ref. [60] using a rather complicated apparatus combined with an SEM. However, in this work the main focus was on the development of the nanomanipulation technique, not on the investigation of the mechanism of Euler deformation, so that no quantitative data concerning the conditions of occurrence of Euler instability were obtained.

The ability of vertically standing nanotubes to undergo axial Euler deformation accompanied by a notable lowering in their height imparts extraordinary properties to this material. Thus, the authors of Ref. [80] have found that vertically aligned nanotube film is similar to a foam-like material that is able to change its density repeatedly in a reversible manner under the action of a load. Vertically oriented multiwalled CNTs up to 1 mm in height were grown on a surface up to 2 cm<sup>2</sup> in area by the CVD method using ferrocene and xylene as precursors. The samples were subjected repeatedly to vertical compression, as shown in Fig. 9. Measurements reveal that the nanotube film compressed to a thickness of about 15% of the initial one recovers practically fully its original thickness at the end of each cycle. Thus, after 1000 cycles the thickness of the film was lowered from 860 to 720 µm. The velocity of the reverse movement of CNT caps after removing the load is about 120 mm min<sup>-1</sup> or 2000  $\mu$ m s<sup>-1</sup>. This exceeds considerably the characteristic magnitude of the velocity inherent in conventional polymer foam structures. Microimages of compressed CNT films contain discernible wave-like bends whose wavelengths depend on the initial thickness of the film. Thus, for a layer 860  $\mu$ m in thickness, the wavelength is 12  $\mu$ m, while for a layer 1.2 mm in thickness the wavelength is  $25 \mu \text{m}$ . The closer to the base of a CNT, the more pronounced the bends. This implies a change in mechanical characteristics along the nanotube. Figure 10 presents a typical dependence of the load on the compression of a CNT film. The shapes of these dependences imply the existence of three stages in the course of the compression. The first one, corresponding to a relative compression  $\varepsilon < 22\%$ , is appropriate to the elastic modulus exceeding 50 MPa. At the second stage (plateau), the parameter  $\varepsilon$  ranges between 22% and 79%, which conforms to an elastic modulus of about 12 MPa. The third stage corresponds to an abrupt increase in the load and the maximum degree of compression of the film ( $\varepsilon = 85\%$ ). The existence of a hysteresis points to the pronounced effect of the



Figure 10. Hysteresis character of the dependence of the relative axial compression of a massif of nanotubes on the stress [80].

absorption of energy upon compression that is seemingly caused by the mutual friction of the nanotubes, as well as the compression of air stored in pores. Since the proper volume of nanotubes is about 13% of the total volume of the film, the real loading exceeds by about 7.8 times the nominal one. This gives for the elastic modulus corresponding to the critical loading the value of 12 MPa  $\times$ 7.8 = 93.6 MPa. On the other hand, in accordance with the Euler theory, the maximum compression load, exceeding which promotes irreversible structural changes in a CNT, is given by the relationship

$$\sigma_{\rm c} = E \left( \frac{\pi R}{L} \right)^2,$$

where *E* is the Young modulus of the nanotube, *R* is its radius, and *L* is half of the wavelength of the bend. Substituting the values of E = 1 TPa, R = 12 nm, and  $L = 12 \mu m$  into this relationship results in  $\sigma_c = 110$  MPa, which is in good agreement with the measured data.

# 2.6 Elecromechanical properties of carbon nanotubes

The mechanical deformation of a nanotube is accompanied not only by the occurrence of inner stresses but also by changes in its electronic structure. This is reflected in the electronic characteristics of a nanotube, such as electrical resistance, energy gap width, carrier number density and some others. Therefore, a mechanical action upon a nanotube being an element of an electronic circuit can change its parameters. This property of CNTs can be used as the basis for extra-miniature devices transforming a mechanical action into an electric signal and, conversely, an electric signal into mechanical motion. Such NEMS devices now constitute the subject matter of intense research and development.

The influence of structural distortions upon the electrical and electronic properties of single-walled nanotubes of an *armchair* structure possessing metallic conduction has been established on the basis of electronic structure calculations [87]. The calculations imply that the resistance of CNTs rises as the bending angle increases. In addition, it was revealed that the torsion twisting of a nanotube promotes the appearance of a forbidden band whose width rises linearly as the twisting angle increases.

As an example of the detailed experimental studies on the electromechanical properties of CNTs, the series of works [28] can be cited. These studies dealt with individual multiwalled 238

nanotubes produced by the standard electric arc method. A nanotube was attached to a thin gold wire to which an electrical potential could be applied. A contra-electrode oriented at some angle in relation to the nanotube was placed at a distance of  $5-20 \,\mu\text{m}$  from its end. Upon applying an outer voltage to the nanotube it was attracted to the contraelectrode and bent by some angle. This can be considered as manifestation of the electromechanical behavior of CNTs, i.e., its ability to transform mechanical energy into an electric signal and vice versa. This property gives rise to expectations for the development of a new class of electronic transformers of mechanical energy into electromagnetic signals, based on CNTs. Microphone represents a simplest device of this sort, in which the CNT-based transformer is utilized as an active element. In a device of another sort that is a superminiature analogue of the loudspeaker, the reverse transformation of an electromagnetic signal into sound vibrations occurs. The practical achievability of such an opportunity follows from the results of investigations of frequency characteristics of CNT-based transformers that were performed in the work cited. Besides investigating the electromechanical characteristics, the procedure developed have permitted the measurement of the Young modulus of multiwalled nanotubes of various diameters. The measurements are based on the dependence of the resonance oscillation frequency of a CNT on the square root of the Young modulus. An abrupt lowering of the Young modulus has been found as the diameter of the nanotubes exceeds 10 nm.

One of the important features determining the possibility of practically using devices on the basis of the electromechanical properties of CNTs is the frequency characteristic of such a device. The higher the response frequency of such a device, the higher the rate of information processing and, therefore, the higher its efficiency. The acoustoelectric effect in CNTs has been investigated in detail in Ref. [29] at various frequencies of a signal applied to a nonotube. Single-walled CNTs of about 1.2 nm in diameter produced by the standard electric arc method using cobalt as the catalyst have been studied. The nanotubes were bound into bundles, each containing about 100 nanotubes. Two samples of bundles were examined, one of which (I) was 1.7 µm in length, had a room temperature resistance of 65  $\Omega$ , and consisted of about 200 CNTs, while the second one (II) was 0.6 µm in length, had a room temperature resistance of 10 k $\Omega$ , and consisted of about 100 CNTs. The first sample was connected to superconducting Au/Re contacts and exhibited superconductive properties for T < 1.2 K. Both samples demonstrated high sensitivity to the presence of a high-frequency (HF) electromagnetic field whose amplitude was estimated as  $\sim 1 \text{ V cm}^{-1}$ . Therewith, the frequency dependence of the voltage drop across the sample I, measured at a current of 2.7  $\mu$ A and a temperature of T = 120 mK, had a clearly defined resonant character revealed in abrupt peaks of voltage at frequency multiples of 330 MHz. A similar dependence was observed for the sample II, which showed semiconducting properties within the whole temperature range. The results obtained are treated as a manifestation of the acoustoelectric effect due to which the CNT sample is subjected to mechanical vibrations under the action of an HF field, so that the frequencies of the vibrations are multiples of their proper resonance vibrational frequency. This assumption was confirmed by the calculation of the resonance vibrational frequency of the sample under consideration, which is in agreement with the observed magnitudes.

The dependence of the conductivity of a single-walled nanotube on the applied mechanical load was measured directly in Ref. [30]. In this experiment, the nanotubes were clamped on a silicon nitride membrane 1035  $\mu$ m<sup>2</sup> in area. The electrical contact was provided by Pd electrodes deposited from both ends of the nanotubes. The membrane was subjected to an outer pressure up to 1.5 atm. The currentvoltage characteristics of the nanotubes were measured vs. mechanical load at the bias voltage of 10 mV. The measurements revealed that all 12 nanotubes exhibited semiconducting properties, while eight of them were characterized by a narrow energy gap width. The measured resistance ranged between 7 and 25 k $\Omega$ , which is comparable with the magnitude of quantum resistance equal to 6.5 k $\Omega$ . The results of measurements indicate a notable dependence of the electrical resistance on the mechanical load. Both increasing and decreasing dependences of the resistance on the load were observed. Such a feature of CNTs offers an opportunity to create a superminiature pressure sensing element with a threshold sensitivity on the level of 0.1 atm. The authors [30] explained the observed dependence of electronic characteristics of CNTs on the applied load by a change in the energy gap width under deformation.

Along with single-walled and multiwalled nanotubes, two-layer nanotubes also show a dependence of electronic characteristics on external mechanical action [88]. Such nanotubes, ranging between 2 and 6.5 nm in diameter, are more appropriate for such manipulations compared to single-walled and multiwalled CNTs due to their higher rigidity. The nanotubes were grown on the edge of a silicon substrate coated with a platinum layer to ensure electrical contact. The substrate with a protruded nanotube was placed into the chamber of a TEM. A silicon tip coated with a platinum layer was used as a probe. Moving this tip toward the individual nanotube promoted its bending. It was stated that the reversible deformation angle exceeded 50°. Applying a voltage between the probe and the nanotube promoted the passage of current through the straight or bent nanotube. At a low magnitude of applied voltage, the current was proportional to the voltage. A subsequent increase in the applied voltage resulted in smoothing the current-voltage characteristic which finally saturated at some magnitude of the applied voltage. A further increase in the voltage was accompanied by a stepwise decrease in the current and the sequential destruction of the nanotube's walls, beginning from the outer one. In the case of a twolayer nanotube 2 nm in outer diameter, the saturation was observed at a voltage of 3.4 V and a current of 13.0  $\mu$ A. The decomposition of the outer wall of the nanotube was accompanied by a decrease in the current to 9.7  $\mu$ A, while the destruction of the inner wall was naturally followed by a decrease in the current to zero. Passage of an electric current through an elastically bent nanotube promotes the partial transfer of the elastic deformation into a plastic one. Therewith, the deformation angle decreases slightly after removing the load but does not reach zero. The typical magnitude of the permanent angle amounts to  $20^{\circ} - 30^{\circ}$ . Therefore, the passage of an electric current through an elastically bent nanotube fixes the bend, which can be considered as an information recording about the passage of current. Measurements show that upon increasing the nanotube's diameter from 2 to 2.8 nm, the critical magnitude of the current corresponding to the transfer of the elastic deformation into the plastic one lowers by 39%, while a further increase in the nanotube's diameter up to 6.5 nm causes a decrease in the critical current by further 9%.

It should be noted that the results of experiments aimed at establishing the dependence of the electronic properties of CNTs on the applied mechanical load can be distorted due to the possible influence of such a load not only on the nanotube but on the contacts providing the passage of the electric current as well. In particular, this follows from the experimental work [89] whose authors paid special attention to the behavior of contacts under the action of a mechanical load. Two methods were used for the preparation of the samples subjected to measurements: electron beam lithography, and AFM-based lithography. In both cases, the methanol suspension of multiwalled CNTs, rotating at a rate of 4000 rpm, was deposited onto a silicon oxide substrate. Two contacts were supplied to both ends of each nanotube. These contacts attached the nanotube to the substrate, preventing the displacement of the former. The CNT was subjected to a dosing load with the aid of an AFM tip.

Measurements revealed that in the absence of a load a nanotube 19 nm in diameter connected with contact wires 16 nm in diameter had a resistance of 85 k $\Omega$ . Application of a load resulting in the relative deformation of  $R_{\rm c}/R_{\rm t} = 7\%$  ( $R_{\rm c}$ is the radius of curvature of the bent nanotube, and  $R_t$  is its radius) promotes an increase in this quantity up to 220 k $\Omega$ , which is unchanged after releasing the load. A further load results in a relative deformation of 11% and promotes a decrease in the resistance to 120 k $\Omega$ , which obviously relates to lowering the contact resistance as the mechanical load increases. In order to avoid the effect of the change in the contact resistance under the load, it was decided to apply the load to the nanotube tip perpendicular to the surface of the substrate. In doing so, a load of 800 nN applied to a nanotube 20 nm in diameter promoted its deformation on the level of 5 nm but did not result in any notable change in the resistance (less than 1%). The resistance of a nanotube 24 nm in diameter connected by Au/Pd contact wires 50 nm in diameter was measured without a load as 135 k $\Omega$ . Applying a load promoted a jump in the resistance up to 400 k $\Omega$ . A further increase in the load gave rise to breaking the circuit, considered to be the result of the decomposition of the nanotube.

The mechanical characteristics of a CNT can change not only as a result of the passage of an electric current but also under external irradiation. Thus, Ref. [90] reports on the effect of a change in the electrical resistance and Young modulus of single-walled nanotubes bound into bundles as a result of UV irradiation. CNT bundles about 50 µm in diameter were extracted by electrophoresis from a suspension based on dimethylformamide. A sample 5 mm in length was cut from a long bundle, placed onto a mica substrate, and brought into contact with four gold electrodes by using a gold-based paint. This permitted the measurement of the resistence of the sample under UV irradiation using the four-probe method. A commercial lamp with  $\lambda = 365$  nm was utilized as the source of UV irradiation, which provided an irradiation intensity on the level of 3.5 W  $\rm cm^{-2}$  at the focus. Measurements revealed that during the first two minutes of irradiation the resistivity of the sample decreased from the initial value of  $\sim 0.2 \Omega$  cm by about 90%, whereupon it remained unchanged for an hour, while the irradiation continued. Note that the effect of decreasing the resistence of a bundle as a result of weak electron beam irradiation reported in the earlier work [91] was four times lower, which points to the higher efficiency of UV irradiation.

The elastic properties of a CNT bundle were evaluated on the basis of measurements of the resonance vibrational frequency. For this purpose, samples 10-15 mm in length cut from a long bundle were suspended at one end of a membrane of a loudspeaker, while the other end was attached to a ferromagnetic ball that was suspended above a transmitter device detecting the movement of the ball. The bundle was subjected to the action of a random noise signal that was recorded together with the response of the sample. The longitudinal vibrations of the bundle resulted in its periodic lengthenings and shortenings, which were detected by a recording device and used as the basis for determining the Young modulus *E* according to the equation

$$E = \frac{4\pi^2 f^2 l_0 m}{A} \; ,$$

where f is the response frequency,  $l_0$  is the initial length of the sample, *m* is its mass, and *A* is its cross section area. Thus, the bundle is assumed to be a homogeneous filament. Measurements imply that the irradiation of the sample for 60 s causes an increase in the resonance vibrational frequency from 487 to 950 Hz, which in accordance with the above relationship corresponds to an increase in the Young modulus from  $5.3 \pm 0.5$  GPa to  $20 \pm 0.5$  GPa. Further irradiation did not change mechanical characteristics of the sample under investigation. It should be noted that for a bundle structure consisting of a number of nanotubes bound to each other by relatively weak van der Waals forces, the response to a periodic lengthening is determined by both the magnitude of the Young modulus E and the modulus of shear G between neighboring nanotubes. Therefore, the strengthening of a sample under the action of UV irradiation corresponds to a nominal increase in the Young modulus, while this effect actually relates to an increase in the shear modulus G. TEM observations reveal that UV irradiation for an hour does not promote visible structural changes in the sample. The authors [90] explain the observed phenomenon of modification of electrical and mechanical characteristics of a CNT bundle by the formation of chemical bonds between nanotubes, with the possible participation of dimethylformamide.

Optical irradiation of an individual nanotube affects its electronic structure, which is accompanied by both a change in its conductivity and mechanical deformations. This follows specifically from experimental findings [92]. Long entangled bundles of single-walled CNTs produced by the laser ablation of a graphite target in the presence of Ar, using Ni and Co at a concentration of 1.2 at.% as a catalyst, have been studied. Net-like filaments ranging between 20 and 50 nm in diameter and consisting of a plethora of CNT bundles were deposited onto a collector at the output of the chamber. While the main part of the bundles was aligned along the axis of the filament, a few of them were entangled. Each of the bundles making up the filament contained from several up to several dozen individual single-walled CNTs. Along with CNTs, the samples also contained metal catalyst particles and amorphous graphite particles attached to the filaments. These samples were irradiated with a halogen lamp of 150 W in output power or an He–Ne laser ( $\lambda = 632.8$  nm) of 10 mW in output power. A light-induced movement of nanotubes, as well as the passage of the electric current through the sample, were observed. The movement combined the tension, bending, and mutual repulsing of individual nanotubes. Upon terminating the irradiation, the nanotubes were reset into the initial state, implying an elastic character to the changes observed. In so doing, the manner of the movement depends on both the type of filaments and their surroundings. Indeed, the direction of movement of shorter and thinner filaments does not depend on the direction of the irradiation, while longer and thicker filaments show a tendency to move towards the light beam. Observations performed using various spectral filters indicate that the character of movement of the filaments is determined by the irradiation intensity and does not practically depend on the wavelength if it corresponds to the visible spectral range. The lightinduced current observed along with the movement is of the same origin in the authors' opinion. As a mechanism of the phenomena observed, the authors considered the effect of a

light-induced transfer of the charge from metallic to semi-

conducting nanotubes, which is followed by their structural

changes. Along with UV and visible irradiation, electron beam irradiation can also promote a modification of the mechanical characteristics of a nanotube bundle. Thus, the papers [91, 93] reported that even a small dose of electron beam irradiation resulted in a 75-fold increase in the shear modulus of a CNT bundle. After 18 min of irradiation with electrons at an energy of 200 keV and flux of  $1.35 \times 10^{19}$  cm<sup>-2</sup> s<sup>-1</sup>, the disordering of the graphite structure of CNTs was observed. Thus, a modification of the mechanical characteristics of the CNT bundle was accompanied by an increase in the electrical conductivity of the sample (the resistivity was lowered as a result of electron beam irradiation to a magnitude of about  $60\,\Omega\,\mathrm{cm}$ , which exceeded by about four times that had reached in Ref. [90] as a result of UV irradiation. The above-described effects indicate a close interconnection between the electrical characteristics and mechanical properties of nanotubes, which in turn is caused by a mutual dependence between their geometrical and electronic structures. UV or weak electron beam irradiation promotes the formation of chemical bonds between the individual nanotubes making up the bundle. On the one hand, this enhances the rigidity of the bundle as a whole, and, on the other hand, it facilitates the passage of the electric current through the bundle whose both transversal and longitudinal dimensions exceed considerably those of an individual nanotube.

# 3. CNT-based materials and composites

#### 3.1 Materials produced from nanotubes

Carbon nanotubes are very thin filaments from which can be produced cloth in much the same manner as cloth is made from silk, wool, cotton, flax, and other kinds of filaments. Producing cloth from CNTs is a multistage procedure, the first stage of which is manufacturing a yarn from individual nanotubes or bundles containing about hundred such tubes. The production of a yarn from carbon nanotubes is similar to the standard procedure that is used in the textile industry. A massif of nanotubes is subjected to a spinning procedure which results in a fiber of macroscopic length. The mechanical properties of such a fiber, first produced in Ref. [94], were studied in detail by the authors of the later publication [19] who used the spin coagulation procedure for producing yarns on the basis of single-walled CNTs. Following this procedure, a water suspension of single-walled CNTs with the addition of surfactants is mixed with a water solution of polyvinyl alcohol in a hydrodynamic flow. This promotes the alignment of nanotubes along the flow and the formation of ribbons which pull out and twist into fibers of high density. These fibers, which easily stretch, bend, and even make knots, contain a ramified network of polymer chains with incorporated singlewalled CNTs.

The complex structure of CNT-based fibers implies possible high sorption characteristics of this material, which, combined with the good mechanical properties, gives promise to new interesting applications. The physical and chemical properties of such fibers were studied in detail by the authors of Ref. [95], who utilized filaments 10-50 µm in diameter produced by ultrasonication of a water suspension (1 wt.%) of single-walled CNTs supplemented with 1 wt.% sodium dodecyl sulfate (SDS). This suspension was injected into a rotating cavity filled with a polyvinylacrylate (PVA) solution. The injection rate was 50 ml h<sup>-1</sup> at a flow velocity of 12.5 m min<sup>-1</sup>. The fibers produced were washed out in pure water in order to remove the remaining SDS and PVA, whereupon they were subjected to annealing in air at a temperature of 320 °C for 3 h. This allowed the removal of up to 95% of the organic admixtures, while the filaments remained intact.

TEM observations indicated that fibers  $10-50 \ \mu\text{m}$  in diameter consisted of hair-like filaments  $0.2-2 \ \mu\text{m}$  in diameter bound into dense bundles. In turn, these filaments consisted of bundles  $10-30 \ \text{nm}$  in diameter containing single-walled nanotubes  $1-2 \ \text{nm}$  in diameter. By this means the outer peripheral region of a fiber  $1-5 \ \mu\text{m}$  in thickness looks much denser compared to the central, axial region. The degree of orientation of the nanotubes in a fiber also decreases moving toward the axis (from 75% at the periphery to 35% near the axis).

The sorption properties of the fibers produced were compared to those of a cloth-like material 25 µm in thickness containing single-walled CNTs and produced by the electric arc method. Determination of the sorption properties was performed on the basis of measurements of absorption isotherms of nitrogen at T = 77.4 K. The absorption – desorption isotherms are characterized by the hysteresis that is inherent in mesoporous materials. Measurements showed that the specific surface area of single-walled CNT-based fibers was 160 m<sup>2</sup> g<sup>-1</sup>, which is comparable to that for a paper-like material containing single-walled CNTs. The specific volume of nanopores evaluated on the basis of experimental data is about 0.2 cm<sup>3</sup> g<sup>-1</sup>, while the size distribution of the pores extends from 1.5 to 20 nm, reaching a maximum at 8 nm. Another method of studying the structure of pores relies on measuring the absorption kinetics of drops of a moistening liquid. According to this method, a drop of a moistening liquid is placed onto the fiber, so that changes in its shape and size are controlled using high-speed photography. The kinetics of penetration of a liquid into a wettable material is governed by its porous structure, therefore the results of measurements yield information about the characteristic size of the pores determining the absorption of the drops. Processing these measured data provided a characteristic pore size of 8 nm, which is in good agreement with the results of absorption measurements.

Along with single-walled nanotubes, multiwalled CNTs can also be used effectively for producing yarns. Such nanotubes are synthesized in macroscopic quantities quite easily using the CVD method [13], so that the synthesis

provides a massif of vertically aligned nanotubes situated in a regular manner like grass on a specially prepared substrate. As is shown by the authors of Ref. [96], such a massif is quite suitable for usage in the standard procedure of yarn production. The yarn fabrication process is very similar to the procedure (reeling) for producing silk filaments from a silkworm cocoon. A matrix of freely standing multiwalled CNTs about 10 nm in diameter and approximately 100 µm in height is twisted into a yarn 30 cm in length and 200 µm in width. Estimates imply that a matrix of  $1 \text{ cm}^2$  in surface area yields a yarn up to 10 m in length. SEM images showed that the yarn consists of parallel filaments several hundred nanometers in diameter. In order to demonstrate the possibility of applied usage of the yarn produced, a filament of the incandescent lamp was fabricated from it. The filament being suspended between two metallic electrodes emits rather intense light when a d.c. voltage up to 70 V is applied in a vacuum of 10<sup>-4</sup> Torr. However, after 3 h of operation at a voltage of 70 V the conductivity of the filament increases by 13%, while the stress increases from 1 to 6.4 mN. This is caused by an imperfection in the contact between the filament and electrodes, which promotes its resistive heating in the contact points.

The above-described yarn possesses an ability to polarize optical radiation, so that only the photons whose direction of polarization is parallel to the nanotube's axis pass through. Measurements showed that for radiation with the wavelength  $\lambda = 325$  nm the degree of polarization reached by utilizing such a system was 0.92. Far UV radiation can be polarized using CNTs about 10 nm in diameter.

The physical and chemical properties of yarns fabricated on the basis of multiwalled CNTs were investigated in detail by the authors of Ref. [97], who studied nanotubes about 10 nm in diameter and 100  $\mu$ m in length grown by the CVD method perpendicular to the surface of a silicon substrate as a broad massif resembling a forest. An iron film 5 nm in thickness was used as a catalyst, and acetylene (C<sub>2</sub>H<sub>2</sub>) diluted in He at a content of 5 mol.% was used as a carboncontaining substance. The synthesis was performed at a temperature of 680 °C for 10 min.

The process of fabricating yarn from CNTs consisted of several stages, as in the classical textile industry. In the first stage, a fiber of about 1 µm in diameter was twisted from a CNT massif about 200 µm in diameter. Thus, about 1 cm<sup>2</sup> of a substrate filled with nanotubes yields up to 50 m of such a fiber. In subsequent stages this fiber is used for the production of thicker yarns with the diameter of a fiber being about 20 and 50  $\mu$ m. Estimates imply that a fiber 5  $\mu$ m in diameter contains up to 100,000 individual nanotubes, which exceeds by 3-4 orders of magnitude the number of elementary filaments in wool or cotton yarns. The linear mass density of an initial filament 1 µm in diameter is estimated as  $\sim 10 \ \mu g \ m^{-1}$  — that is, thousands times lower than that for typical wool and cotton filaments. The density of a twisted yarn is about  $0.8 \text{ g cm}^{-3}$ . The breaking strength of elementary filaments ranges between 150 and 300 MPa. The breaking strength of yarn consisting of two twisted elementary filaments equals 250-460 MPa. Polyvinylalcohol wetting increases the breaking strength by a factor of 3-4.

The distinctive feature of filaments spun from CNTs lies in their ability to retain their torsion angle after release of a load and even after cutting the filament. This feature is caused by the action of friction forces between nanotubes composing the filament, which prevent untwisting of individual nanotubes. In addition, it has been established that CNT-based filaments can be knotted without losing their strength. Wetting CNT-based filaments with polyvinylalcohol imparts them high electrical characteristics. Thus, filaments between 2 and 10  $\mu$ m in diameter possess a resistivity of about 0.003  $\Omega$  cm at room temperature, which is characterized in this temperature range by a negative temperature dependence with a factor of -0.1% K<sup>-1</sup>.

The results of the above-described investigations indicate the good prospects for using yarns and textiles based on CNTs for developing conducting fabric, powering artificial muscles, and in other fields requiring material possessing high specific strength in combination with plasticity and electrical conduction.

The first 2D material fabricated on the basis of nanotubes was a soft paper-like or cloth-like layer containing, along with single-walled nanotubes, a large quantity (usually more than 50%) of amorphous carbon particles, as well as particles of a metal catalyst enclosed in a multilayer graphite shell. Such a material, sometimes called Bucky-paper [97-101], is produced in particular as a result of the synthesis of single-walled CNTs in an arc discharge with graphite electrodes, with the addition of some quantity of a metal (Fe, Ni, Co, Y, etc.) that plays the role of a catalyst. The material containing nanotubes is deposited on the cooled walls of a gas discharge chamber, forming a cloth-like layer, the thickness of which is proportional to the duration of discharge burning. The electrical properties of such a layer were studied by the authors of Ref. [98], who reached a conclusion on the transition from the metallic to nonmetallic behavior as a result of vacuum annealing, based on the results of measurements of the electrical resistance of a sample. In spite of the absence of nanotube ordering in Bucky-paper, the measured elastic modulus of this material was 1.2 TPa [99], which is close to that for individual CNTs. Another approach to producing CNT-based 2D material is demonstrated by the authors of Ref. [100], who fabricated a soft cloth-like material by processing pure CNTs through hot pressing at T = 2273 K and an Ar pressure of 2.5 atm for an hour. The roomtemperature electrical resistivity of the material is  $(2-3)\times 10^{-4}\,\Omega$  cm and shows a descending temperature dependence.

The next step on the way to creating the technology for producing CNT-based materials is the development of the process of textile fabrication. The conventional method of fabrication of cloth from CNTs uses the age-old experience of paper production and includes a week's procedure of filtration of CNTs dispersed in water, followed by drying the layer removed from the filter [102, 103]. The further development of this approach [104] has resulted in the elaboration of a highly productive method of fabrication of broad transparent linen from CNTs. Highly oriented multilayer nanotubes about 10 nm in diameter and between 70 and 300 µm in length synthesized through the thermocatalytic decomposition of acetylene were used as the initial material. The nanotube massif 245 µm in height and resembling grass was drawn out by hand by means of a sticky tape at a rate of about 1 m min<sup>-1</sup> into a sheet about 500  $\text{cm}^2$  in area and 2.7  $\mu$ g cm<sup>-2</sup> in surface density, corresponding to a mass density of the material equal to  $0.0015 \text{ g cm}^{-3}$ . Therewith, a nanotube massif 1  $cm^2$  in area yields linen 3 m in length and 5 cm in width. Using mechanical devices allowed increasing the rate of drawing out the nanotube massif into linen to  $10 \text{ m min}^{-1}$ . The thickness of the linen is determined by the



**Figure 11.** SEM image of a 2D hardened structure fabricated by superimposing four layers of CNT-textile at an angle of 45° [103].

height of the nanotubes in the massif; for nanotubes 245  $\mu$ m in height, the thickness is 18  $\mu$ m. Two pieces of linen joined together easily hold a water drop whose mass exceeds by a factor of 50,000 that of the material in contact with the drop. Some properties of such linen can be inferred from Fig. 11 presenting the SEM image of a 2D strengthened structure produced by mutually superimposing four layers of CNT linen at an angle of 45°.

An essential increase in the mass density of the linen is reached as a result of its densification which is performed by immersing the material into a liquid (e.g., ethanol) followed by drying. Subsequent evaporation of the liquid results in the constriction of the linen, due to the action of the surface tension, to a thickness of about 50 nm, which corresponds to a density of 0.5 g cm<sup>-3</sup>. The densification is accompanied by a lowering in the degree of orientation of the nanotubes. The room-temperature resistivity of such a linen amounts to about 10 k $\Omega$  cm<sup>-2</sup>. Figure 12a presents the temperature dependence of this parameter.

Measurements showed that the densified CNT linen possesses high transparency for visible and IR radiation, which increases as the wavelength rises, reaching 90% for  $\lambda > 1 \,\mu m$  (see Fig. 12b). The radiation passing through the linen becomes polarized, with the degree of polarization amounting to 0.71 for  $\lambda = 500$  nm, and 0.74 for  $\lambda = 780$  nm. The electrical conduction of the linen is characterized by a high anisotropy, so that for nondensified samples the conductivity measured in the direction from which it is drawn out is 50-70 times as large as that in the perpendicular direction. After densification resulting in lowering the degree of ordering this ratio decreases to a value of 10-20. Along with high optical and electrical properties, the CNT linen shows record mechanical characteristics. Thus, the specific tensile strength of a linen consisting of 18 CNT layers reaches the magnitude of 465 MPa  $(g/cm^3)^{-1}$ . This exceeds considerably the relevant magnitudes for highstrength steels [125 MPa (g/cm<sup>3</sup>)<sup>-1</sup>] and aluminum alloys [about 250 MPa  $(g/cm^3)^{-1}$ ]. The combination of high transparency and high electrical conduction with outstanding strength properties makes this linen potentially good material for applications in monitors, videorecorders, solar cells, solid light sources, etc.

One more effective approach to the problem of manufacturing CNT-based materials includes using the effect of alignment of CNTs under the action of an external magnetic field [106, 107]. In practice, the alignment of nanotubes is performed through an external magnetic field that is applied to a suspension containing CNTs. Calculations imply that both CNTs with metallic conductivity and paramagnetic properties and CNTs possessing semiconductive properties that are diamagnetic with the negative magnetic susceptibility tend to align along the magnetic field. According to the estimates covering alignment of nanotubes involved in a suspension at room temperature it is sufficient to apply the magnetic field of an order of 10 T.

For the realization of the above-described approach [105], single-walled CNTs between 100 and 500 nm in length synthesized through the laser ablation method and purified by the standard way were immersed in dimethylformamide and ultrasonicated until a homogeneous suspension was formed. Three ml of this suspension were injected into the



**Figure 12.** (a) Temperature dependences of the reduced resistance of a nonprocessed textile produced from multiwalled (circles) and single-walled (triangles) CNTs [104]. The inset shows the temperature dependences for the textile before (upper data points) and after (lower data points) densification. (b) Spectral transparency of the textile produced from multiwalled CNTs: (1) polarization of light is perpendicular to the direction of extension, the sample was not densified; (2) polarization of light is parallel to the direction of extension, the sample was not densified; (3) polarization of light is parallel to the direction of extension, the sample was not densified; (5) polarized light, the sample was densified.

cavity of an electromagnet providing a magnetic field intensity up to 19 T. The degree of alignment of the CNTs was controlled by means of a polarized laser beam that passed through the suspension at various magnetic field strengths and at various polarization angles. The oscillating dependence of the transmittance of the linen on the polarization angle, as well as the increase in the amplitude of this oscillating dependence as the magnetic field strength increases, indicated the alignment effect. Estimates imply that at the magnetic field strength of 19 T the alignment energy exceeds the magnitude kT by a factor of  $28 \pm 3$ , so that more than 90% of the nanotubes have an axial orientation angle less than  $17^{\circ}$ .

CNT samples aligned by means of a 25-T magnetic field were used to fabricate membranes. For this purpose, the suspension containing 20-40 mg l<sup>-1</sup> of CNTs aligned by means of a magnetic field of 25 T in the Triton-X solvent was forced by a syringe at a pressure of about 1.5 atm through a filter having the form of a nylon membrane 25 mm in diameter with pores 0.2 µm in size. A black film deposited onto the membrane is characterized by a higher reflection coefficient compared to the standard cloth-like structure produced without the magnetic field. The film is separated easily into long ribbons directed along the magnetic field. Measurements showed that the package density of CNTs in the membrane amounts to about 50% of the maximum reachable value for CNTs with the chirality indices (10, 10). The membranes produced possess extraordinary optical characteristics. Thus, the diffusion reflection coefficient for polarized radiation depends on the orientation of the polarization angle relative to the magnetic field.

Along with the above-cited publications, Refs [108–112] also report on the production and investigation of a dense flexible material involving nanotubes. Reference [108] reports on the fabrication of films from single-walled doped CNTs that have high transparency and are 20 times higher in electrical conductivity than that in Ref. [104]. For this reason, the deposition of CNT aerogel [110], Langmuir–Blodgett deposition [111], and sulfuric acid moulding [112] were used.

We should note one more modification of a flexible 2D material produced from CNTs: a network being formed from single-walled CNTs already during synthesis [113]. Samples of such a material were prepared through the CVD method in a three-section quartz tube placed into a two-section furnace. A finely dispersed mixture of ferrocene and sulfur in a molar ratio of 16:1 was used as a catalyst. This mixture was inserted into the first section of the furnace kept at a temperature of 55 °C, through which argon at atmospheric pressure with a small admixture (at a level of 0.1%) of acetylene flowed. This gas, together with some quantity of sublimed catalyst, was supplied through a narrow connecting tube to the reaction chamber that was placed in the second section of the furnace and kept at a temperature of about 1100 °C. Thermocatalytic decomposition of acetylene on the catalyst surface promoted the formation of a 2D network consisting of single-walled nanotubes on the silicon substrate placed at the reaction chamber output. Observations performed using a highresolution TEM and an AFM indicated that the network involved single-walled CNTs between 0.7 and 3 nm in diameter. It is important that the nanotubes composing the network were not bound into bundles. One more distinctive feature was the smooth character of nanotube bending in the practically total absence of elbow-like and spiral-like bends.

Moreover, the possibility of controlling the density of the networks produced, which, on the one hand, depends on the position of the point on the substrate and, on the other hand, under optimal conditions is proportional to the duration of the synthesis process, was apparent.

As follows from general considerations, such characteristics as the strength and rigidity of a bulk material fabricated from CNTs should be lower than those measured for an individual nanotube. This lowering can be caused by both inevitable structural defects which determine the breaking strength of the material, the number of which increases naturally as the size of the sample rises, and rather weak van der Waals interaction between the nanotubes composing the material. The lowering of the strength characteristics of a CNT-based bulk material was indicated, in particular, by the results of measuring the strength characteristics of ribbons produced from multiwalled nanotubes [114]. Such ribbons, 10 cm in length,  $4-40 \ \mu m$  in thickness, and  $50-140 \ \mu m$  in width, were fabricated by the acid processing of CNTs at 100 °C, as described in Ref. [115]. Parts of the ribbon were subjected to graphitization in argon at 2200 °C and a pressure of 5 atm for 2 h. This procedure resulted in an increase in the density of the ribbon from 1.1 to  $1.5 \text{ g cm}^{-3}$ , and in the Young modulus from 2.4 to 6 GPa. The electrical resistivity of the ribbons was measured by the four-probe method within the temperature range from 4 up to 300 K. The room-temperature magnitude of this parameter measured for various samples of unprocessed ribbons ranges between  $4.4 \times 10^{-4}$ and  $12.6 \times 10^{-4} \Omega$  cm. For most of the ribbons, the temperature dependence of the resistivity is of a falling nature, which indicates their semiconductive properties. However, for one such ribbon the dependence has a minimum at T = 260 K, which points to its metallic behavior in a high-temperature region, and nonmetallic properties for T < 260 K.

#### **3.2 CNT-based polymers and composite materials**

The problem of manufacturing and using composite materials combining polymer and some quantity of carbon nanostructures (fullerenes or CNTs) became topical just after the discovery of such structures. These structures contain double carbon bonds, which allows the addition of various radicals, chemical compounds, and polymer chains to them. Therefore, inserting a carbon nanostructure into a polymer can promote lengthening of polymer chains and thereby an enhancement of the mechanical characteristics of such a composite material. Furthermore, insertion of carbon nanotubes having extraordinary mechanical characteristics into a polymer can under some conditions result in a considerable enhancement of the strength properties of the material. Taking into account the relatively low density of carbon nanostructures and their high plasticity and thermal stability, one can expect that the development of composite materials based on carbon nanostructures will have a striking influence on materials science.

The number of publications related to the fabrication and study of composite materials with the addition of CNTs is quite large (see, e.g., Refs [23, 24, 116–144]). These works are distinguished from each other by the type of polymer material used as a matrix, by the characteristics, degree of purity, and content of the nanotubes inserted into the polymer, and by the character of research performed with the material produced. The following have been used as a polymer matrix: epoxy resins [116, 120, 124, 137]; oil resins [117]; polyhydroxyami-

noether (PHAE) [118]; polydimethylsiloxane rubber (PDMS) [119]; three-component thermoplastic elastomer styreneisopren-styrene (SIS) [119]; elastomers based on a nematic liquid crystal (LCE) in monodomen and polydomen forms [119]; polyurethane/diacryl [121]; poly(methyl methacrylate) (PMMA) [122, 126]; polyvinyl alcohol (PVA) [123]; poly(3octylthiophen) (P3OT) [128, 135]; poly(*p*-phenylene vinylene) (PPV) [129, 130, 133]; polyimide resin [134]; polypyrrol [23, 144]; polyaniline [144]; polyacrylnitryl (PAN) [138, 139]; dimethylformamide (DMF) [140]; poly-(biphenol-*A*)carbonate [141]; polycarbonates of various kinds [136, 142], and polydimethylsiloxane [143]. Polymer materials have been doped with both multiwalled and single-walled nanotubes synthesized through the electric arc, laser ablation, or CVD methods.

The main problem arising in attempting to enhance the mechanical characteristics of a polymer through the addition of CNTs relates to the necessity of ensuring the transfer of a load from the polymer matrix to the nanotubes incorporated inside it. If the interaction between the nanotube surface and the polymer molecules has a van der Waals origin, a nanotube incorporated into the polymer moves practically freely through the polymer volume under loading or, figuratively speaking, it behaves like a hair in a pie. In this case, inserting nanotubes into a polymer material impacts rather weakly the mechanical properties of the material and can even deteriorate them. A real improvement in the mechanical parameters of a polymer material as a result of inserting CNTs can be reached if the nanotube's surface is bound with the polymer molecules through a chemical interaction, the characteristic energy of which is dozens of times higher than that of a van der Waals interaction. Therefore, the problem of enhancing the strength properties of composite materials by inserting CNTs is reduced to the chemical problem of conjugation of the surface of a CNT with the polymer molecules to ensure the most effective chemical interaction between them.

One should note one more problem arising from the use of multiwalled CNTs for hardening composite materials. This problem concerns the relatively weak van der Waals interaction between neighboring layers of nanotubes. Due to this factor, the real hardening of a material is reached only due to the outer layer of the multiwalled nanotube, under the condition of a quite strong interaction between the nanotube's surface and the polymer matrix. Therefore, the hardening effect due to inserting multiwalled nanotubes is *N* times lower than that for single-walled CNTs (*N* is the number of layers in the nanotube).

The mechanism of load transfer during tension and compression of CNT-containing composites was first investigated in detail in Ref. [116] where an epoxy resin was utilized as an initial matrix. Multiwalled CNTs in the content of 5 wt.% were dispersed in epoxy resin by using ultrasonication. Then, the composites were cured with a triethylene tetraamine hardener. SEM images of samples indicate that the majority of the nanotubes entering into the composite are curved or interwoven. Cylindrical samples of a composite 25 mm in length and 12.5 mm in diameter were investigated in terms of their mechanical properties. The tension of CNTs was determined by the second harmonic of the Raman scattering peak (2700 cm<sup>-1</sup>). Measurements showed that inserting 5% CNTs into the epoxy resin increased the Young modulus from  $3.1 \pm 0.2$  to  $3.71 \pm 0.5$  GPa, while the compression modulus was increased from  $3.63 \pm 0.25$  to  $4.5 \pm 1.5$  GPa. The difference between the Raman peak



Figure 13. Schematic of a device for producing CNT-based polymer filaments [117].

shifts under tension and compression can be ascribed to the better load transfer under compression than under tension. As can be seen, the material hardening effect due to the insertion of multiwalled CNTs is rather moderate, which is apparently caused by a weak interaction between nanotube layers, so that only the outer layer is subjected to the load.

Usage of single-walled CNTs for enhancing the strength characteristics of composite materials is more effective than using multiwalled nanotubes. This has been demonstrated already in one of the earliest works in the field [117], where single-walled CNTs were inserted into petroleum pitch in an effort to enhance the mechanical characteristics of the relevant fibers. Commercial samples of nanotubes were purified in the standard manner using repeatable washing in distilled water and hydrochloric acid. The pitch, which is solid at room temperature, was dissolved in quinoline by stirring the mixture at 60 °C for 2 h. Then, the viscous hot solution mixed with 1, 5, 8, or 10 wt.% CNTs was ultrasonicated for 2 min, which resulted in dispersing the nanotubes. Afterwards, the quinoline was fully removed by vacuum treatment. Cooled solid samples of the composites produced were ground and transferred to the fiber spinning apparatus shown schematically in Fig. 13. A heated reservoir pressurized with nitrogen (about 5 atm) was equipped with a singledie hole 0.3 mm in diameter. The fiber pulled through this die was wound up onto a drum rotating with a controlled speed. At a reservoir temperature of 310 °C and drum rotation speed of 400 rpm, the diameter of composite fibers produced was about 18 µm. The experiments performed show that the optimal temperature of the mixture, providing the formation of continuous fibers at a high rotation speed, increases by 10 °C as the nanotube content in the mixture is increased by 2 wt.%. This dependence is caused by an increase in the viscosity of the molten pitch as nanotube content rises. At a content higher than 8%, fibers do no form due to too high a magnitude of the viscosity of the pitch. Fibers obtained at lower nanotube content were oxidatively stabilized by heating at 1°C min<sup>-1</sup> up to 310°C under 11min<sup>-1</sup> air flow. The stabilized fibers were then carbonized under 2 1 min<sup>-1</sup> nitrogen flow in a tubular reactor heated up to 1100 °C at a rate of 20 °C min<sup>-1</sup>.



Figure 14. Dependence of the relative strain of composite filaments on the stress applied [117].

**Table 7.** The measured magnitudes of the breaking strength, Young modulus, and resistivity of composite fibers produced at various CNT contents in the mixture.

CNT content in the composite, wt.%	0	1	5
Tensile strength, MPa	570	620	850
Young modulus, GPa	34	41	78
Resistivity, m $\Omega$ cm	8.4	2.6	2.2

Figure 14 presents the measured mechanical characteristics of the fibers produced. The elastic modulus E of a fiber is represented by the slope of the dependence of the stress on the relative strain, while the tensile strength  $\sigma$  of a fiber is expressed through the maximum strain corresponding to its break. The magnitudes of these parameters evaluated through processing the measured data are given in Table 7. Besides the mechanical characteristics, the electrical resistivities of the fibers vs. CNT content in the composite were also measured. Results of these measurements performed at a direct current of 1 mA are also shown in Table 7. The above measurements indicate that the addition of about 5% CNTs into the pitch promotes an almost twofold increase in the tensile strength, a more than twofold increase in the elastic modulus, and a more than threefold increase in the electrical conductivity of the composite fibers.

Changing the mechanical properties of a polymer material by inserting CNTs depends in particular on the degree of ordering of the nanotubes in the material. Obviously, in the case of nanotubes aligned lengthwise in the material, a spatial anisotropy of the mechanical characteristics of the material should manifest itself, which can become important for some applications. The dependence of mechanical properties of polymer materials on the degree of nanotube alignment has been established experimentally by the authors of Ref. [118], who utilized for this purpose multiwalled nanotubes produced by the standard electric arc method. The nanotube content in the initial sample of soot was estimated as 30% on the basis of TEM observations. As a polymer matrix, a thermoplastic polymer, polyhydroxyaminoether (PHAE), which is distinguished for its good solubility and high mechanical properties, was utilized. A finely dispersed specimen of CNTs was ultrasonicated in chloroform at room temperature for an hour, followed by the insertion of additional PHAE into the homogeneous suspension produced. The content of nanotubes in the composite material

reached 50%. Ultrasonication and drying of this suspension resulted in the formation of a black thin film that was cut into strips  $5 \times 3$  mm in size. The strips were subjected to tension at a constant stress and a temperature of about 100°C. The relative elongation of a strip could reach 500% without fracture. After the desired stretching ratio was obtained, the sample was cooled down and unloaded. Both the initial and stretched samples were studied by the use of an X-ray diffractometer at room temperature. Measurements showed that the tension of the material, stimulating its stretching by 330%, promotes orientation ordering of 58% nanotubes. This ordering has a permanent character and is preserved over a long period of time after unloading.

The ordering effect of CNTs in polymer materials was studied using both the X-ray diffraction method and TEM observations. To this end, membranes 90 nm in thickness were cut from the material by means of a diamond blade. Observations imply a homogeneous filling of the polymer material with nanotubes and an ordered arrangement of CNTs in the samples subjected to tension.

The role of ordering in the mechanical behavior of polymers modified with nanotubes was also noted in the recent work [119], the authors of which utilized in their experiments commercial samples of multiwalled nanotubes with a purity higher than 95%, an outer diameter of 60-100 nm, an inner diameter of 5-10 nm, and a length between 5 and 15  $\mu$ m. Three types of material were used as a polymer matrix: polydimethylsiloxane (PDMS) rubber; three-component thermoplastic elastomer styrene-isoprene-styrene (SIS), and elastomer on the basis of a nematic liquid crystal (LCE) in monodomen and polydomen forms. PDMS samples contained 0, 0.02, 0.3, 0.5, 1, 2, 3, 4, or 7% CNTs and were noted by the symbols PDMS, PDMS0.02, etc.; SIS samples contained 0.01% CNTs and were noted by the symbol SIS0.01; monodomen LCE samples contained 0 or 0.02% CNTs and were noted as monoLCE0 and monoLCE0.02; polydomen LCE samples contained 0 and 0.015% CNTs (polyLCE0 and polyLCE0.015). The polymer samples doped with CNTs in the desired quantity were prepared by the standard methods using protracted thorough stirring, moderate heating, and centrifugation.

The degree of ordering of CNTs in the polymer was studied by the large-angle X-ray diffraction method. At first, the dependence of the orientation ordering factor on the stretching of the sample was measured. It was found that the ordering phenomenon has a reversible character. Measurements showed a monotonic increase in the ordering factor as the stretching degree rises. The dependence is close to the root function, so that 100% stretching corresponds to the degree of ordering equal to 0.25. The action of IR radiation upon the samples was studied at various strains of the material. It was observed that such an action promotes either further stretching (at low strain) or contraction (at large strain), depending on the magnitude of the strain. This behavior is inherent in all of the studied samples. The stress occurring at the irradiation reaches dozens of kPa. Its specific value is determined by the level of the preliminary strain, the content of CNTs, and the types of polymer materials.

Figure 15 presents the measured dependence of the Young modulus of a PDMS nanocomposite on the content of multiwalled CNTs. As can be seen, inserting the nanotubes into a polymer results in a proportional increase in the elastic modulus of the sample. The measurements performed for other polymers resulted in the following magnitudes of the



Figure 15. Dependence of the Young modulus of the nanocomposite PDMS on the content of multiwalled nanotubes [119].

Young modulus: monoLCE0.02: E = 0.2 MPa; poly-LCE0.015: E = 0.2 MPa, and SIS0.01: E = 0.6 MPa.

Along with the measurements of the Young modulus, the authors of Ref. [119] also studied the mechanical behavior of nanocomposite materials containing CNTs under the action of IR irradiation. The polymer material samples under investigation had the form of strips  $1.5 \times 30$  mm in area and 0.2 mm thick. A strip whose length was controlled by means of a micrometer with an accuracy of 1 µm was fixed in a frame facing a source of irradiation. The load applied to the sample was measured by means of a dynamometer. The temperature of the surface was determined by thermocouples T1 and T2 situated on the front and back sides of the sample. The source of IR radiation was placed 2 cm from the sample and provided emission peaking at  $\lambda = 675$  nm with a linewidth of about 200 nm and irradiation intensity of about  $1.5 \text{ mW cm}^{-2}$ . The experimental results indicated the occurrence of a mechanical stress in the polymer material upon irradiation. The characteristic magnitude of the stress at the above-indicated sample parameters and irradiation intensity amounts to several dozens kPa. A nonmonotonic dependence of the stress on the CNT content, having a maximum at a concentration of 2 wt.%, was noted. Thermocouple measurements showed that the increase in the sample temperature due to irradiation does not exceed 15-20 °C, meaning the effect of irradiation does not have a purely thermal origin. The mechanism of the observed effect of the occurrence of stress in a composite material under the action of irradiation is not yet fully understood, however one can assume that the irradiation promotes the formation of chemical bonds between nanotubes and the material of the polymer matrix. A decrease in the magnitude of the effect observed at a nanotube content higher than 2% can be caused by an increase in the influence of intertube interaction on the measured stress.

The degree of volumetric homogeneity of a composite along with the ordering plays an important role in the problem of strengthening polymer materials by means of CNTs. Initial samples of materials containing CNTs synthesized by standard methods form bundles involving about a hundred closely packed individual nanotubes. For this reason it is very hard to ensure in practice the homogeneous filling of a polymer material with such nanotubes. The results of many observations show that samples of composite material, where a lack of attention was paid to the problem of homogeneous mixing, can contain voids and irregularities whose presence negatively affects the mechanical characteristics of the nanotubes. In particular, this was indicated by Ref. [120] where a composite material with added single-walled nanotubes was observed. Samples of an epoxy resin doped with single-walled nanotubes 1.4 nm in diameter synthesized by the laser ablation method were the subject of the investigation. CNTs suspended in ethanol were ultrasonicated for 2 h in order to separate the nanotubes from each other. The composite material was fabricated by mechanically stirring the suspension with a liquid epoxy resin without a hardener; afterwards, the mixture was dried in a vacuum at 50°C for 10 h. Then, a hardener was added, followed by 10-15 min of vacuum treatment in order to remove the remaining absorbed air. Films 200 µm thick fabricated from the material produced were kept in air for 24 h, after which they were heated at 72 °C for 3 h and then cooled slowly. This imparted an initial mechanical stress to the nanotubes. Then, layers 70-100 nm in thickness cut from the film by means of a diamond knife were placed onto a copper grid for TEM observations. The observations indicate the existence in the samples studied of voids in the form of elongated elliptical breaks. In some cases, these brakes are crossed by nanotube bundles that are subjected to a mechanical stress due to thermal effects as a result of the action of the electron beam of the microscope. This stress promotes the destruction of some bundles, which is quite visible in the microimages of the samples. The experimental results imply that the adhesive interaction between individual CNTs and the epoxy material is notably higher than that between the nanotubes composing bundles.

Due to the inhomogeneous filling of the polymer matrix with nanotubes, the composite material possesses an enhanced fragility that manifests itself in the breakdown of individual nanotubes under relatively low loads. Such a phenomenon was observed in Ref. [121] where multiwalled CNTs produced by the standard electric arc method were studied. After the performance of routine procedures of ethanol purification, drying, and dispersing on a glass substrate, the nanotubes were inserted into a polymer, for which was used an oligomer - liquid urethan/diacryl. The substrate surface was covered by means of a knife with a layer of liquid film about 200 µm thick that was then polymerized as a result of 2-min irradiation with a UV lamp 300 W in power. This resulted in a formation of an amorphous rigid polymer film from which rectangular samples were cut. The mechanical characteristics of those samples were studied by means of a commercial device providing a load increased at the rate of 50  $\mu$ m min<sup>-1</sup>. This allowed the determination of the Young modulus (2 GPa), tensile strength (0.6 GPa), and breaking deformation (0.075), which are characteristic of high-quality epoxy resin-based polymers widely used in composite materials. After the mechanical test, the polymer film was cut parallel to the surface into layers 70 µm thick with the use of a diamond knife. TEM observations indicate that the nanotubes incorporated into the polymer contain a lot of breaks stimulated by the mechanical action. The magnitude of the breaking stress is estimated through the expression

$$\sigma_{\rm NT} = \frac{E_{\rm NT}}{E_{\rm m}} \, \sigma_{\rm m} \approx 5.5 \; {\rm GPa} \, ,$$

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where  $E_{\rm NT} = 1.8$  TPa is the Young modulus of the nanotubes,  $E_{\rm m} = 2$  GPa is the Young modulus of the polymer matrix, and  $\sigma_{\rm m} = 0.6$  GPa is the load applied. The reduced length of the fragment,  $l/D_{\rm NT} = 5-20$ , was determined by processing the microimages ( $D_{\rm NT}$  is the outer diameter of the nanotube).

The degree of homogeneity of a composite material containing nanotubes depends considerably on their concentration. A high degree of homogeneity is more achievable at a low concentration of doping, because in this case nanotube bundles manage to separate. As the CNT concentration increases, their bundle structure begins to manifest itself. Due to this, free space forms between various bundles oriented in different manners in the polymer matrix, which is filled with a polymer materials. The occurrence of such regions lowers the mechanical properties of the composite material. The above-described mechanism of lowering the degree of homogeneity of a composite material with increasing CNT concentration has been demonstrated quantitatively by the authors of Ref. [126], who produced composites on the basis of a nonconjugated polymer, poly(methyl methacrylate) (PMMA), doped with single-walled CNTs. The degree of homogeneity and the character of spatial distribution of the CNTs in it were studied with an SEM. Single-walled nanotubes were synthesized through the standard electric arc method and used without ensuing purification. The arc discharge between graphite electrodes was burnt at an He pressure of 0.66 bar. A finely dispersed mixture of Y and Ni at a content of 1 and 4.2 at.%, respectively, was used as a catalyst. The material obtained as a result of the thermal decomposition of graphite contained up to 70% single-walled CNTs bound into bundles between 5 and 20 nm in diameter and about 1  $\mu$ m in length, as well as particles of metal catalyst, amorphous and graphite-like carbon. A suspension of this material in toluene was admixed with PMMA in various quantities (1, 2.5, 5, 7.5, 10, and 20 wt.%) and was ultrasonicated for 24 h. Thin films of the composite were deposited onto a clean surface of crystal KBr (for Raman spectral studies) and onto a glass substrate (for SEM observations).

The experiments showed that the composites holding 20% CNTs contained a large quantity of aggregates including an insignificant quantity of nanotube bundles and a multitude of graphite and amorphous carbon particles. These large aggregates are observed mainly in the central region of the sample. Aggregates constituting the sample with the 7.5% concentration of CNTs contain predominately nanotubes bound into bundles, while the occurrence of carbon particles is not so significant. In the sample containing 1% CNTs, the observed spatial distribution of bundles is more homogeneous, while the number of aggregates in the whole volume of the sample is rather insignificant. Raman spectral analysis implies that the polymer material fills a space between the nanotubes in the bundles and thereby destroys their ordered structure.

The degree of homogeneity in filling a polymer matrix with nanotubes can be enhanced as a result of the modification of the method of production of the composite material. In this connection, a method based on the use of melt mixing [142] should be noted. In accordance with this method, a composite of polymer/CNTs is utilized as an initial material. This composite is inserted into a pure polymer and stirred in the melt obtained. Polycarbonates of various sorts containing 15% CNTs were selected as the initial composite. Three types of nanotubes were used for doping: multiwalled nanotubes

10-15 nm in diameter and  $1-10 \mu m$  in length grown by the CVD method; multiwalled CNTs higher than 95% in purity and 20-50 nm in diameter and up to 100 µm in length grown through thermal catalytic vapor deposition, and single-walled CNTs between 1 and 1.3 nm in diameter. The composite was prepared in a few minutes at a temperature of 260-280 °C with the use of a commercial compounder having a rate of mixing of 50 rpm. Samples of the composite material produced were cut onto either thin plates  $20 \times 3$  mm in size or disks 20 mm in diameter, which were studied by means of a SEM and subjected to mechanical tests. The measurements imply a monotone increase in the Young modulus of the composites as the content of CNTs rises. The maximum magnitude of the Young modulus at a content of 7% amounts to about 900 MPa, which is 50% higher than that for the pure polymer. In addition, the dependences of electrical resistivity of the specimens on CNT content and electric field frequency were measured. The measurements indicate the occurrence of a percolation threshold at a CNT content between 0.5 and 1.5%, depending on the sort of polymer and the type of CNT. Exceeding this threshold promotes an abrupt decrease in the resistivity of the sample from  $10^{11} \Omega$  cm to the level of 10  $\Omega$  cm. The low magnitude of the percolation threshold implies a high degree of homogeneity of filling the polymer with a nanotubes.

Alternative approach to the production of nanocomposites doped with CNTs is based on the usage of electrochemical methods [23]. Due to their good conductivity, nanotubes can be used effectively as an electrode of an electrochemical cell, which opens up the possibility of covering an individual nanotube with a polymer film. Highly oriented multiwalled CNTs were grown on a Ti substrate by the CVD method with the use of an Ni catalyst layer that was deposited by means of a magnetron. Depending on the thickness of the Ni catalyst layer, the diameter of the nanotubes ranged between 30 and 120 nm and the length varied within the range of  $5-13 \ \mu\text{m}$ . A polypyrrol film was applied onto each of the highly oriented nanotubes in a neutral atmosphere of nitrogen using the electrochemical method. A water solution of pyrrol (17.3 M) and LiClO<sub>4</sub> (0.1 M) was utilized. The measurements were performed using the standard three-electrode scheme, increasing the voltage from 0 to 0.8 V at the rate of 5 mV s<sup>-1</sup>. A platinum wire was utilized as a counter-electrode, and a saturated calomel electrode was employed as a reference electrode. The nanotubes were treated in a 15% water solution of HNO3 to ensure their homogeneous coating. The CNTs covered with polypyrrol film were studied by means of a TEM. The observational results given in Table 8 indicate proportionality between the thickness of the coating and the specific charge transferred.

As was noted above, the degree of influence of the addition of CNTs on the mechanical characteristics of composites depends on the efficiency of interaction between

**Table 8.** Properties of CNTs coated with a polypyrrol layer.

No.	Ratio of nanotube diameter to length, $nm \ \mu m^{-1}$	Specific charge $Q$ , mC cm <sup>-2</sup>	Thickness of the film <i>d</i> , nm	Ratio $Q/d$ , mC cm <sup>-2</sup> nm <sup>-1</sup>
1	90-110	86.1	10	8.61
2	80 - 100	207.9	22	9.45
3	100 - 120	681.9	76	8.97
4	30 - 50	1308.6	93	14.07

the nanotube's surface and the polymer matrix molecules. For some types of polymers such an influence can be quite drastic. As an example, Ref. [122] can be mentioned, where poly(methyl methacrylate) (PMMA) with an average molecular weight of 49,000 was used as a polymer matrix. Multiwalled CNTs were synthesized by the standard electric arc method and were utilized as produced, without ensuing purification. Samples were prepared by stirring 0.4 g PMMA with various amounts of CNTs at 200 °C for 20 min at a speed of 120 rpm. Then, the samples produced were compressed under a pressure of about 80-90 bar at 210°C for 5 min, which resulted in the formation of a green transparent film. This film was cut with an ultrathin knife, whereupon the ultrathin films were studied by means of a TEM. Moreover, the samples were subjected both to a thermogravimetric analysis (TGA) in a nitrogen atmosphere within the range between room temperature and 700 °C and to a dynamic mechanical analysis (DMA). TEM images of the composite do not reveal any agglomerates or a breakage of CNTs, which implies a high degree of homogeneity of the samples produced. The TGA results indicate an increase in the polymer degradation temperature as the amount of added CNTs rises. Whereas pure PMMA starts to degrade at 320 °C and fully decomposes at 430 °C, the sample containing 26% CNTs starts to degrade at 350 °C and fully decomposes forming pure CNTs at 450 °C.

The mechanical properties of polymer composites were studied by the DMA method in a pure nitrogen atmosphere within the range from room temperature up to  $150 \,^{\circ}$ C at a heating rate of  $3 \,^{\circ}$ C min<sup>-1</sup> at a frequency of 1 Hz. The method is based on measuring the storage modulus and loss modulus at an oscillating load vs. time, temperature, or frequency. Measurements show that within the specified temperature range the storage modulus of the pure polymer decreases monotonically with temperature from the magnitude of an order of 1 TPa down to a value of about 1 GPa. Inserting CNTs into the polymer results in a 2–3-fold increase in the storage modulus at room temperature, and a 5–27-fold increase in this parameter at a temperature of 120 °C. This reflects the effect of an increase in the rigidity of the polymer upon introduction of CNTs.

Inserting CNTs into a polymer matrix not only promotes an improvement in the mechanical characteristics of such a composite material but also offers new opportunities for using CNTs in electronics. Specifically, such materials possessing an enhanced flexibility and elasticity, in combination with good conductive properties, can be utilized effectively as field emission cathodes [128, 130]. The results of experimental studies [128] reveal that immersing carbon nanotubes into a polymer improves their emission characteristics. In this work, a composite material on the basis of poly(3-octylthiophene) (P3OT) with the addition of singlewalled nanotubes was used as a field emitter. The initial purity of the nanotubes amounted to 60%. CNTs and P3OT dissolved in chloroform were applied onto a silicon-plate substrate. A thin layer of a composite material containing nanotubes was formed on the substrate as a result of the evaporation of chloroform at room temperature.

A cathode 0.25 cm<sup>2</sup> in area fabricated in the abovedescribed manner was studied in terms of its emission characteristics. The measurements were performed in a vacuum of  $10^{-6}$  Torr at an interelectrode gap of 80 µm. Electron emission was observed at an electric field strength exceeding 2.2 V µm<sup>-1</sup>, so that at a strength of 4 V µm<sup>-1</sup> the emission current reached 0.6 mA cm<sup>-2</sup>. If the composite CNT-P3OT was covered with a thin film of nanotubes, the threshold value of the electric field strength decreased to 0.8 V  $\mu$ m<sup>-1</sup>. The measured emission current-voltage characteristics of the samples correspond to the known theoretical Fowler-Nordheim dependence in a rather narrow range of applied voltage. The magnitude of the electric field strength amplification factor obtained with the help of this dependence ranges between 700 and 1580, depending on the type of the sample. The maximum magnitude of this factor (1580) is reached when the CNT layer is placed onto the surface of a composite material. Such a high value of the field amplification factor cannot be explained only by geometrical considerations, viz. on the basis of the known aspect ratio of CNTs. The authors ascribe it to the effect of forming a narrow transition region on the border between the polymer material and the nanotubes.

Multiwalled CNTs were also used for the fabrication of a composite material with good emission characteristics [130]. The material was produced by inserting CNTs about 20 nm in diameter and about 1 µm in length synthesized by the electric arc method into a polymer on the basis of poly(*m*-phenylene/ vinylene-co-2,5-dioctyloxy-p-phenylene/vinylene) (PmPV). The polymer doped with CNTs was dissolved in toluene and ultrasonicated intensively for 1 min, whereupon it was treated with a low-intensity sonic wave for 1 h. The solution was purified of graphite particle contaminations by lengthy sedimentation and filtration. The composite film 80 nm in thickness produced in the above-described manner was applied to a glass substrate with a gold covering. The emission characteristics of such films were studied using an anode with a phosphor covering. The interelectrode gap was kept at a level of 100 µm. The measurements performed for samples containing from 0.44 up to 7 wt.% CNTs demonstrate good agreement between the emission current-voltage characteristics of the cathodes and the classical Fowler-Nordheim dependence. There was observed a lowering in the threshold value of the electric field strength, providing an emission current on the level of 10 nA, from 14.5 V  $\mu$ m<sup>-1</sup> to 8.4 V  $\mu$ m<sup>-1</sup> as the content of CNTs increased from 0.44% to 7%. The estimates performed on the basis of the measured data indicate a slight increase in the electric field amplification factor within the range between 330 and 390 as the nanotube's content increases. The measured magnitudes of the threshold electric field strength and the field amplification factor make it possible to determine the local magnitude of the threshold electric field strength taking into account the field amplification effect. Appropriate data processing provides a weakly decreasing dependence of the local threshold electric field strength on the content of CNTs in the sample. The authors explain such a dependence by percolation effects resulting in a power-like increase in the conductivity of a material containing a disordered network of conductors as their content grows.

Due to a high magnitude of electron affinity, CNTs can be utilized as effective tools for the improvement of polymerbased photovoltaic devices. The operation of such devices is based on the charge transfer from an optically excited polymer to a nanotube. As an example of the effective usage of CNT-doped composite materials in photovoltaic devices we can mention Ref. [129] reporting on the fabrication and investigation of the optical properties of a composite on the basis of poly(*p*-phenylene/vinylene) doped with multiwalled CNTs. A thin homogeneous CNT film was produced by

Composite Parameter	CNTs	CNTs-PA	CNTs-PP- PTS	CNTs-PP- PTS	CNTs-PP- PTS	CNTs-PP- PTS	CNTs-PP- PF <sub>6</sub>	CNTs-PP- PF <sub>6</sub>
$j, mA cm^{-2}$ $\tau, min$ $R, k\Omega$ $\sigma, S cm^{-1}$ T, %	6.6 20 90	20-45 2.5 55 62-90	0.6 6 1.1-7 60-10 75	$ \begin{array}{r} 1.0 \\ 7 \\ 1.5 - 10 \\ 44 - 7 \\ 45 - 75 \end{array} $	$0.24 \\ 10 \\ 1.5 - 10 \\ 43 - 7 \\ 75 - 83$	0.99 30 3.2-15 19-10 85	0.15 10 19-30 3.5 75-80	0.05 12 110 0.60 77-90

**Table 9.** Electrical resistance (*R*), conductivity ( $\sigma$ ), and transparency (*T*) of composite films produced by doping various polymers with CNTs at different magnitudes of deposition current density (*j*) and deposition time ( $\tau$ ) [144].

spinning and stabilized by chemical oxidation. In order to fabricate a composite, a film surface was covered with a polymer precursor, which was followed by the high-temperature conversion procedure. The studies performed showed that the fabricated composite not only possesses enhanced mechanical characteristics but also can be used as the base of a highly effective optoelectronic device. Specifically, the quantum efficiency of the photovoltaic device within the spectral range between 2.9 and 3.2 eV reaches 1.8%, which is about twice as much as that for standard indium – tin oxide (ITO)-based devices.

It should be noted that conducting composite materials doped with CNTs are of special value because they combine the best mechanical properties of polymers with the good electrical conductivity inherent in nanotubes. In this connection, the paper [144] is of interest: its authors undertook a comprehensive study of the electrical and optical properties of thin films (with thickness ranging between 120 and 180 nm) of composites consisting of conducting polymers polypyrrol (PP) or polyaniline (PA) doped with single-walled CNTs. The films possess a transparency between 70 and 95%. A thin network of single-walled CNTs possessing quite high conductivity was applied to a transparent substrate, after which a layer of conducting polymer was deposited on it using the electrochemical method. Some samples of the composite based on polypyrrol (PP) were doped with tetraethylammonium p-toluene sulfonate (PTS) or PF<sub>6</sub>. The content of the conducting polymer in the composite was determined by the deposition time which varied from 7 up to 60 min.

The composite films produced were studied by means of an AFM, an optical and Raman spectrometer, and measuring electrical conductivity and transparency. The results of these measurements are summarized in Table 9. The presented magnitudes of the conductivity relate to the film 150 nm in thickness. As follows from the table, the electrical conductivity of the composites produced is about 10-100 times lower than that for typical conducting films such as ITO, however it can be sufficient for a majority of applications, for example, for the protection of objects from the action of electromagnetic irradiation.

Inserting carbon nanotubes, as well as other carbon nanostructures, can change the mechanical properties of not only polymer materials but also metal-based construction materials. In particular, this follows from the experimental results [192, 193] that point to the formation of a superhard phase as a result of a static action at a pressure of 3-5 GPa upon finely dispersed mixtures of metals with fullerite crystals. Studies revealed that particles of this superhard phase have a nonperiodic nanocomposite structure containing nanodimensional ordered structural elements. Such particles have a hardness of an order of 40 GPa and possess extraordinary elastic properties that manifest themselves in their ability to undergo elastic deformation upon loading and fully regain their original shape when the stress is removed. These works have initiated the development of a new class of metal-based composite materials volumetrically doped with diamond-like particles. Such composite materials combine the characteristic properties of a metal matrix (high mechanical properties, corrosion stability, high thermal and electrical conductivities, etc.) with the extraordinary wear resistance of diamond-like carbon. Results of preliminary experiments indicate that such composite materials in their abrasive wear resistance exceed widely used wear-resistant steels of the type 100Cr6 by 10 times. In the friction coefficient ( $\sim 0.1$ ) they approach materials with a diamond-like coating but not subjected to the drastic wearing that is inevitable for materials with a coating in the case of breakage of their integrity [193].

As one more corroboration of the wide possibilities of using CNTs for hardening construction materials we can mention the discovery made recently at the Technical University of Dresden, Germany [194]. As follows from the observations made by means of a high-resolution TEM, samples of Damascus steel, taken from a museum specimen of an ancient sabre that was fabricated in the sixteenth century, contain multiwalled CNTs. Such an observation became possible after a small sample of the metal was dissolved in hydrochloric acid. The material remaining undissolved contained multiwalled CNTs up to 5 nm in diameter and with a characteristic interlayer distance close to 0.34 nm. The inner cavity of the majority of the nanotubes was filled with cementite (iron carbide, Fe<sub>3</sub>C), which as is known possesses an enhanced hardness and fragility. One can suppose that the origin of the hardening effect for the Damascus steel is similar to that which constitutes the basis of the modification of metals as a result of inserting fullerenes followed by pressure processing. Both these effects are obviously connected with the formation of some modification of iron carbide on the interfacial surface between carbon nanostructures and metal granules as a result of thermal treatment accompanying the fabrication procedure of the relevant samples.

# 4. Applications of carbon nanotubes based on their mechanical properties

# 4.1 CNT-based probes

One of the first areas for using CNTs, which is based on their high mechanical characteristics, relates to the development and design of probes and tips for atomic force microscopes (AFMs) [56, 145-156]. A nanotube combines tiny lateral size with a high elastic modulus, which offers the opportunity to produce on their basis the finest probes and tips for studying surfaces and microobjects with an enhanced resolving power. In particular, the utilization of nanotubes as tips for AFMs has resulted in a considerable enhancement of the resolving power of such devices [25, 26, 145-149]. This parameter is

very sensitive to the size and shape of the probing element, for which purpose pyramidal Si or  $Si_3N_4$  microprobes whose radius of curvature of the edge usually exceeds 10 nm are used routinely. The utilization of such probes imposes a notable restriction on the magnitude of horizontal resolution. Moreover, the pyramidal shape of the probe hinders its utilization for studying narrow and deep objects. The use of a CNT as a tip removes this restriction to a large extent. CNT-based probes with a high aspect ratio offer an obvious advantage in studying deep cracks and structures with a high steepness. Moreover, the nanotubes are subjected to longitudinal deformation at a load exceeding the critical one. This limits the maximum load applied to a sample, which prevents the occurrence of breakage in thin organic and biological objects.

The above-listed advantages of using a CNT as a tip for an AFM have been demonstrated in probing biological objects [25]. Multiwalled and single-walled nanotubes were produced by the electric arc and laser ablation methods, respectively. Under the direct view of an optical microscope nanotubes were attached by means of acrylic adhesive to pyramidal Au-coated Si cantilevers. The multiwalled nanotube tip protruded by 1.8 µm from the edge of the pyramidal silicon cantilever. High-resolution images of biological objects (β-amyloid-1-40, protein-derived fibrils and protofibrils) were obtained by means of an AFM equipped with multiwalled and single-walled CNT probes. Usage of the multiwalled CNT probe permitted improving the resolution by 10-30% and studying fibrils and protofibrils 3-8 nm less in width than with the best silicon probes. This offers new opportunities in understanding the structure and the formation mechanism of an amyloid fibril ensemble. Furthermore, probes of the new type are harder than the silicon ones and less sensitive to contamination. The single-walled nanotube probes permit a notable improvement in the lateral resolution and investigation of fibrils 10-15 nm less in diameter than those using silicon probes. The improvement in resolution is reached mainly due to lowering the effective radius of curvature: 9 nm for a multiwalled nanotube probe compared to 13-20 nm for silicon probes. Even more impressive results were obtained using single-walled nanotubes having an effective radius of about 3 nm. Since the radius of an individual nanotube comprises only 0.5-0.7 nm, the utilization of this type of probes seems to be most promising. Further development of this area will permit images of molecular and biological structures in air and in a liquid.

The possibility of adding various functional groups to nanotubes permits their usage not only as probes for AFMs but also for the chemical analysis of nanometer-sized objects. Thus, the authors of Refs [146, 147] performed for this purpose the functionalization of multiwalled nanotubes with -COOH radicals, which was followed by the addition of amine groups to them. These groups can be involved in a wide class of chemical reactions occurring in both wet and dry conditions. A multiwalled nanotube about 25 nm in diameter synthesized by the standard electric arc method and purified by oxidation in air at 700 °C was attached by means of acrylic adhesive to the pyramidal Au-coated silicon cantilever of an AFM. Application of voltage between the nanotube and an Nb substrate caused a shortening of the nanotube and the opening of its cap. -COOH radicals were added to free bonds on the opened nanotube's end and then used as chemical probes. The action of such a probe is based on the establishment in the works [146, 147] of the interrelation between the adhesive force of the radical found on the nanotube end and

the strength of the pH of the medium where it was immersed. Processing the results of measuring the surface distribution of the pH permits the restoration of the distribution of chemical components over the surface under investigation.

The most impressive results in using nanotubes as the probes of an AFM were reached in the case of single-walled nanotubes. This is due to the small lateral size of such nanotubes and their structural perfection which manifests itself in good mechanical characteristics. Technical difficulties encountered in the fabrication of a single-walled CNT-based tip were overcome since such nanotubes form bundles up to 10 nm in diameter containing up to 100 individual nanotubes. These bundles are not as difficult for preliminary operations as individual ones, and after preparation of a tip an individual nanotube can be selected in a relatively easy way.

The above approach has been demonstrated by the authors of Ref. [26], who used single-walled CNTs obtained by the laser ablation method. Nanotubes bound into bundles were attached by means of acrylic adhesive to pyramidal Aucoated Si cantilevers under the view of an optical microscope. The tip fabricated was sharpened and shortened by applying a voltage between the tip and an Nb surface. The operational characteristics of the AFM tip designed were studied by the example of Au nanocrystals having a spherical shape 5 and 10 nm in diameter. Knowing the radius of a nanocrystal, one can determine the radius of curvature of the tip, which in this case ranged between 12 and 17 nm for silicon tips, and between 6 and 8.6 nm for multiwalled CNT-based tips, and was about 3.4 nm for single-walled CNT-based tips. Therefore, the lateral resolution power of single-walled CNT-based tips exceeds by about 70% that of silicon tips. As a second subject of investigation, a layer of single-walled nanotubes applied onto the surface of highly ordered pyrolytic graphite (HOPG) and Au(111) substrates was chosen. The measurements performed by means of the tip based on a bundle of single-walled CNTs 5.5 nm in radius permitted discriminating between two nanotubes  $1.70 \pm 0.02$  and  $1.72 \pm 0.02$  nm in diameter lying alongside each other, which is unattainable by means of a silicon tip. This observation was confirmed using an SEM. An AFM equipped with a CNT tip was utilized for studying DNA. The image of lambda DNA obtained allows the determination of the height of a spiral that is equal to  $0.36 \pm 0.07$  nm, in agreement with measurements taken by other authors.

The quantitative parameters characterizing the operation of a CNT-based AFM tip were determined by the authors of Ref. [149]. Multiwalled CNTs between 5 and 20 nm in diameter (average diameter was 10 nm) and  $1-5 \,\mu\text{m}$  in length were synthesized by the conventional electric arc method. An isopropyl alcohol suspension containing the nanotubes was applied onto a glass substrate between two knife edges spaced 0.5 mm apart. These knifes were subjected to an alternating electric field 1.8 kV cm<sup>-1</sup> in strength and 5 MHz in frequency, so that the nanotubes under the action of the electrophoresis approached the knife edges. After letting the solvent dry, the nanotubes tuned out to be attached to the edges with an average density of 0.66  $\mu$ m<sup>-1</sup> as a result of the action of van der Waals forces. The SEM images obtained show that the nanotubes oriented, on the average, at an angle of 23.8° in relation to the electric field direction are elevated above the knife edge by about 0.4 µm. The CNT-based tip of the AFM was sharpened by the electric current-induced evaporation of the outer layers of the nanotube [150].





**Figure 17.** (a) Schematic of the method of studying the quality of a surface etching by means of an AFM with a CNT tip: 1 — cantilever, 2 — pyramidal silicon tip, 3 — nanotube, 4 — the surface under investigation; (b) the surface lateral profile obtained by means of the device presented [152].

**Figure 16.** Schematic of the measured stage of an AFM with a multiwalled CNT probe [150]: 1 — silicon tip of the probe; 2 — Si<sub>3</sub>N<sub>4</sub> probe; 3 — nanotube probe, and 4 — contact between the tip and probe.

The nanotube fabricated was attached to a conventional silicon AFM tip by the action of electrostatic forces arising upon application of a voltage to the tip. Usually, when the voltage was switched off, the nanotube remained in contact with the tip. In order to reliably fix it, the tip was deposited with an amorphous carbon layer originating from a hydrocarbon-based vacuum lubricant. The electron beam irradiation of the tip for several dozen minutes notably increased the thickness of the nanotube's base adjacent to the surface of the tip.

The measuring device of the AFM represented schematically in Fig. 16 includes two independent cantilevers. The one that is characterized by an elastic factor of 35 N  $m^{-1}$  and ending with a silicon tip with a nanotube probe was used in the tapping mode. The second one, having an elastic factor of 0.02 N m<sup>-1</sup>, was fabricated from  $Si_3N_4$  and used in the contact mode. When the silicon cantilever moved upward, the nanotube pushed the soft Si<sub>3</sub>N<sub>4</sub> cantilever, so that due to the difference in the elastic factors of silicon and Si<sub>3</sub>N<sub>4</sub> the deformation of the silicon cantilever was low and the deflection of the Si<sub>3</sub>N<sub>4</sub> cantilever was proportional to the load acting upon the nanotube. This deflection was measured by means of an SEM. The measurements imply that the load is proportional to the deflection until the magnitude of the latter is less than 1.8 µm. Upon exceeding this magnitude of deflection, the load lowers rapidly and the nanotube undergoes a deformation. This corresponds to the Euler load of F = 37 nN. Knowing this quantity, one can estimate the Young modulus E of a multiwalled nanotube 2r = 20 nm in diameter and  $L = 1.5 \,\mu\text{m}$  in length in accordance with the expression

$$F = \frac{E\pi r^4}{4L^2} \, .$$

The estimate  $E = 1.1 \pm 0.2$  TPa is obtained, which is in good agreement with the results obtained by other authors (see Table 4). The AFM developed was utilized for imaging the DNA molecule. The image obtained of the double helix is unattainable by using a standard silicon probe.

The new possibility of increasing the resolution power of an AFM through the usage of CNT-based tips in investigating the character of etching semiconductor surfaces is of special practical interest [151]. It promotes the advancement towards the further miniaturization of microelectronic devices and enhancement of information storage of relevant information writing and processing systems. These possibilities have been demonstrated in experiments [151] where highly doped n-GaAs (100) substrates were used. A mask on an Ni film 30 nm in thickness was created by the electronbeam lithography method. Two methods were utilized for ion etching of the samples: (1) a magnetron operating at a pressure of 2 mTorr and a BCl<sub>3</sub> flow of 2 cm<sup>3</sup> s<sup>-1</sup>, and (2) chemical-stimulated ion beam etching at a pressure of  $2 \times 10^{-4}$  Torr, an Ar ion beam energy of 500 eV, and Cl<sub>2</sub> flow of various intensity. The depth of etching and the structure of the surface etched were studied comparatively by means of an SEM with a standard silicon nitride tip operating in the tapping mode and an AFM with a CNT tip attached to a silicon cantilever operating in the tapping mode. Comparison of images of the etched surface with a nonuniformity of a characteristic size of 200 nm indicates that the usage of the AFM with a CNT tip provides a considerably more detailed picture than that reached by means of a silicon nitride-tipped SEM. As another example of the successful use of the AFM with a CNT tip we can mention the image of a structure with a nonuniformity of a characteristic size of 70 nm that was produced by magnetron ion etching. The high level of resolution reached permits one to determine the conditions of etching promoting a considerable erosion of the surface.

The quality of etching of a photoresist is of great importance in present-day microelectronic technology. A deep narrow trench produced as a result of etching should have vertical walls and a horizontal bottom as far as possible. Therefore, the AFM tip used for controlling the quality of such a trench should have a high aspect ratio and good mechanical characteristics. A CNT tip meets these requirements quite well because it is able to penetrate into deep trenches on the surface under processing, as opposed to conventional silicon tips of pyramidal shape. Figure 17a illustrates the operation principle of such a device [152]. Figure 17b shows the profile of a photoresist surface that was processed by a UV laser at  $\lambda = 257$  nm and an irradiation dose of 1.9 mJ cm<sup>-2</sup> [152].

An AFM with a CNT tip can be used not only for investigations of nanostructures but also for nanolithography, i.e., for writing information onto a surface with a density corresponding to a lateral size of the nanotube on a nanometer scale. Such an opportunity has been demonstrated in Ref. [153], the authors of which utilized an AFM with a CNT tip for applying oxide nanostructures onto a silicon surface. The lithography procedure used included the electric field-induced air anodization of a hydrogen-passivated silicon surface Si(100), so that the probe of the microscope was charged negatively in relation to the surface. Multiwalled CNTs synthesized by the standard electric arc method were used as a material for the tip. A bundle consisting of a large number of nanotubes was attached by means of acrylic adhesive to the pyramidal silicon tip of the AFM and was shortened to the proper length. The lithography procedure was performed usually in the tapping mode with the nanotube tip potential biased from -7 to -15 V against the surface. The cantilever deflection amplitude was decreased to less than 1 nm, well below the typical value of free amplitude (15 nm). The lithography procedure had a duration of 100 s and resulted in the formation of 10-nm-wide silicon oxide lines spaced at 100 nm over a 100  $\mu$ m<sup>2</sup> surface area. Therefore, the writing rate turned out to be 0.5 mm  $s^{-1}$ , which is the maximum magnitude for the lithography procedure under consideration. A high wear resistance of the writing device was pointed out.

Another approach to the problem of enhancement of the information writing density by means of an AFM relates to the development of the thermomechanical method of data storage. In this case, the heated tip of a microscope acts locally on a thin polymer film that is usually fabricated from polymethyl methacrylate. Quick cooling of the tip fixes the hollow on the film surface that comprises the information unit. This information is read by scanning the film surface with the tip connected to a cantilever on the basis of records of the deflection of the cantilever at the hollows. The parameters of such a system are determined mainly by the degree of sharpness of the tip. Silicon tips used conventionally for this purpose provide a surface density of information recording on the level of 10<sup>11</sup> bit cm<sup>-2</sup>. However, the drawback of such tips is their quick wear, resulting in an expansion of the hollow, which lowers the information record density. An alternative approach to this problem calls for the usage of CNT tips. Advantages of such a tip relate to the high mechanical properties of CNTs and to the fact that its natural wear is not accompanied by its failure but only causes a shortening of its length. One more advantage of CNTs relates to the high magnitude of the heat conductivity coefficient, which facilitates operations involving heating and cooling of the material under action. This behavior has been demonstrated by the authors of Ref. [154], who used as a tip multiwalled CNTs grown by the standard electric arc method and ranging in radius between 10 and 20 nm. The nanotubes were fixed to the tip of a silicon cantilever with the help of an SEM equipped with a piezo-controlled positioning stage. The length of the free end of the nanotube was established on the level of 150-350 nm. The tip was heated by means of a pulsed resistive heater with a voltage pulse duration of 15 µs, integrated directly into the cantilever. Thus, only a small part of the heat released landed in the region of the contact between the tip and the polymer surface. Information was recorded onto a poly(methyl methacrylate) layer 20 nm in thickness applied to a silicon substrate and covered with a buffer photoresist layer 80 nm thick. The minimum distance between hollows was 50 nm, which corresponds to an information recording density on the level of  $4 \times 10^{10}$  bit cm<sup>-2</sup>. Measurements showed that the

recording of information by means of the CNT tip required heating up to notably lower temperatures (about 600 K) than for silicon tips (about 700 K). This is due to more favorable conditions of heat transport, which are provided by the utilization of CNT tips.

The main obstacle on the way to the proliferation of measuring and technological devices containing CNT probes and tips relates to the time and effort involved in selecting nanotubes of the proper size. These difficulties limit the quality of tips and diminish the prospects of developing the relevant area. It seems to be much more attractive to use for this purpose methods based on the technology of growing nanotubes with the prescribed parameters. In this case, there is a possibility to control the parameters of the process. Such an opportunity has been realized by the authors of Ref. [156], who formed a flat surface on a conventional silicon tip, whereas pores of 50-100 nm in diameter were made on its lateral surfaces along the axis. These pores were filled with an iron catalyst using the electrochemical deposition from an FeSO<sub>4</sub> solution. The nanotubes were grown by the CVD method through the reaction of ethylene and hydrogen at a temperature of 750 °C in the presence of the catalyst. The reproducible growth of nanotubes was observed over 10 min. Nanotubes about 480 nm in length and  $10 \pm 5$  nm in diameter having a well-pronounced multiwalled structure were grown from the peak of a silicon tip. Measurements indicate that these nanotubes attach quite firmly to the silicon tip and are able to repeatedly elastically bend. Preliminary tests of such an AFM have demonstrated the possibility of discriminating objects between 2 and 5 nm in size. This is several times less than the limiting resolution reached earlier by utilizing CNTand silicon-based tips. Other attractive features of the tips fabricated lie in their high strength compared to silicon ones and in the capability of using them repeatedly. In the case of damage to a tip, the remains of carbon material can be removed quite easily by oxidation in air (at a temperature of 500 °C for 10 min), and a new tip is grown at the same site. AFMs with CNT tips grown by the CVD method show good promise for usage in observations of biological objects on the molecular level.

One of the advantages of using CNTs as tips for AFMs and probes is the high adhesive properties of nanotubes, providing quite strong attachment of a tip to the cantilever material. The adhesive characteristics of multiwalled CNTs were studied quantitatively in Ref. [157]. Vertically aligned multiwalled CNTs ranging between 5 and 10 µm in height were grown by the CVD method on a silicon substrate in the presence of an Fe catalyst. Before measuring the adhesive characteristics, the CNT layer was subjected to a mechanical loading of 2 kg in the vertical direction. Then, the normal and tangential stress necessary for detachment of the load from the CNT layer was determined. In the case of adhesion of the CNT layer to an apparent contact area of 4 mm<sup>2</sup> of a glass surface, the maximum stress in the normal direction amounted to 11.7 N cm<sup>-2</sup>. For the tangential stress, the CNT layer with an apparent contact area of 8 mm<sup>2</sup> separated from a glass surface at a stress of 7.8 N cm<sup>-2</sup>. These data are comparable to the magnitude of an adhesive force of about 10 N cm<sup>-2</sup>, measured for a gecko lizard's foot, and exceed by about an order of magnitude those inherent in synthetic filaments. The adhesion of CNTs to gold, parylene, GaAs, and other surfaces is lower than that for a glass surface. Repeating cycles of measurements reveal a lowering in the adhesive force as the number of loadings and separations increases. This is caused by the relatively weak adhesion of CNTs to a silicon substrate surface, due to which a part of the nanotubes detaches from the substrate and attaches to the surface under investigation after several measurement cycles. This obstacle was overcome by using an iron catalyst with the addition of molybdenum. Measurements showed that the specific adhesive force increases as the contact area of the CNTs with the substrate decreases. This can be explained by the statistical spread in the heights of the nanotubes, the magnitude of which grows as the area of the layer increases. Another feature relates to the negative dependence of the adhesive force on the height of a nanotube, which manifests itself in the lowering of the adhesive force of nanotubes 100  $\mu$ m in height to 2 mN cm<sup>-2</sup>. This can also be attributed to a spread in the nanotube's height, due to which the highest nanotubes experience elastic deformation under the action of loading. Upon unloading, an additional force acts upon the surface, which promotes the separation of the nanotubes. The adhesive properties of CNTs can be characterized not only by a specific adhesive force but also by the work of adhesion that is expressed as the product of the adhesive force and the distance that the surface passes before separation. The magnitude of this parameter measured for a CNT layer  $2 \times 20$  mm in area reaches 36 mJ m<sup>-2</sup>. It is of interest to compare the parameters characterizing the adhesion of CNTs to a glass surface with the relevant characteristics of the gecko which is able to move not only on a vertical wall surface but even across the ceiling of a room due to the extraordinary adhesive properties of its limbs. A comparison shows that the nanotubes and lizard's hairs are comparable in adhesive force, however, the separation of a nanotube layer requires considerable effort, while the lizard separates a foot from a surface quite easily.

## 4.2 Nanoelectromechanical systems

The possibility of developing electronics based on nanometersized elements depends mainly on advancements in nanodevices transforming an electrical signal into mechanical motion and vice versa. Such devices, called nanoelectromechanical systems (NEMSs), stir up serious interest in engineers and researchers working in nanotechnology fields. Carbon nanotubes combining nanometer size with high chemical stability and good mechanical and electrical characteristics present an ideal element for building NEMSs. The operation of such systems can be based on both the abovementioned dependence of the electronic properties of CNTs on mechanical action and structural features, in accordance with which the interaction between neighboring layers of a nanotube is much weaker than the interaction between carbon atoms belonging to a common layer.

The simplest version of a nanoelectromechanical system containing CNTs is a generator of mechanical oscillations, the operation of which relies the possibility of a reversible longitudinal transfer of either single-walled nanotubes composing a bundle or specific layers of a multiwalled nanotube [157-173]. Such a possibility was first demonstrated by the authors of Ref. [157], who manipulated the inner layers of a multiwalled nanotube, while the position of the outer layers remained fixed. In such a configuration, the nanotube can be elongated and shortened like a telescopic antenna or a fishing rod. Figure 18a presents the schematic of the experiment [157]. A multiwalled nanotube 35 nm in diameter is attached by one end to a grounded gold electrode, while another one is connected to another nanotube playing a role of the forming electrode to which a voltage can be applied. Applying several volts to this electrode induces a current of several hundred mA, which results in Joule heating and the removal of a few outer layers of the nanotube in the vicinity of its cap. As a result of this operation, the nanotube assumes a conical shape, so that the number of layers in the vicinity of the cap decreases to three and its diameter lowers to 2.5 nm. Such a sharpened nanotube is, in particular, an ideal tip for an AFM. Figure 18a displays the manner in which the manipulation of the nanotube layers is performed. A nanotube with one fixed



**Figure 18.** (a) Schematic of the experiment on lengthening and sharpening multiwalled nanotubes [157]: (1) original nanotube; (2) the nanotube after the procedure of electrothermal removal of outer layers from the tip; (3) the nanotube with the spot-welded manipulator; (4) the manipulator's movements cause reversible displacements of inner layers of the nanotube relative to the outer ones; (5) removing the manipulator results in a spring-like return of inner layers of the nanotube into the initial position; (6) transverse displacements of the manipulator promote a reversible bending of hollow outer layers of the nanotube. (b) Illustration of the operation of the generator of mechanical oscillation, based on a single-walled CNT bundle [159]: (1) the central inner nanotube oscillates; (2) 6 nanotubes belonging to the second shell of the bundle oscillate.

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end (1) is subjected to the procedure of sharpening using an electric current (2). In all the following manipulations, the sharpened nanotube end makes contact with a manipulator (3). Moving the manipulator in the longitudinal direction results in a reversible lengthening or shortening of the nanotube due to the extraction of its inner core out of the outer shell (4). This procedure can be performed repeatedly under the control of a TEM. A quick removal of the manipulator from the extracted inner core gives rise to a spontaneous retraction of the core due to the action of van der Waals attractive forces between nanotube layers (5). A transverse force acting on the partially extracted inner core causes its bending, which becomes irreversible at some excess of a critical load (6). Using the measured retraction time of the extracted inner core, the magnitudes of static  $(2.3 \times 10^{-14} \text{ N atom}^{-1})$  and dynamic  $(1.5 \times 10^{-14} \text{ N atom}^{-1})$ friction force acting between layers were estimated. It was revealed that the action of a transverse force on a multiwalled CNT results in easier bending, if the inner core is partially extracted out of the outer shell. Thus, one particular nanotube 43 nm in diameter consisting of 60 graphite layers was telescoped, so that an inner fragment 29 nm in diameter consisting of 40 layers was pulled out up to a maximum elongation of 150 nm. The transverse bending of such a telescopic tube by 5° gave rise to the formation of a kink in the middle of the section with a larger inner diameter (6). A force causing a 26° bend was followed by destruction of the tube. At bending angles less than 10°, the extracted part of the nanotube could be retracted, accompanied by smoothing of the deformation. A higher angle hindered the retraction of the extracted part of the nanotube into the initial position.

The dynamic behavior of the displacement of multiwalled nanotube layers moving in relation to each other under the action of van der Waals forces has been studied in Ref. [158] through classical mechanics methods. The calculations imply that the van der Waals interaction energy between layers of a multiwalled nanotube 4 nm in diameter at an initial longitudinal displacement of 330 nm is  $\sim 10^{-20}$  J. In this case, the interaction force amounts to 4.4 nN, and the oscillation frequency is estimated as 0.15 GHz. Since the mass of the inner part of the nanotube is proportional to its length, while the restoring force does not depend on the length, the oscillation frequency increases as the nanotube's length decreases. Thus, if the length of the inner part of the nanotube amounts to 100 nm and the initial displacement is equal to a fourth of that, then the oscillation frequency increases to the magnitude of 1.4 GHz. An even higher oscillation frequency is described in the system studied in Ref. [157], which has one end of the nanotube fixed, as distinguished from the system under consideration.

Not only a multiwalled nanotube but also a bundle of single-walled CNTs can be used as an operating element of a generator of mechanical vibrations [159]. In this case, some nanotubes constituting the bundle vibrate lengthwise relating to each other, so that the van der Waals interaction between them plays the role of the elastic force. The concept of such a device is illustrated in Fig. 18b. The upper picture relates to the situation where the oscillating element is the central inner nanotube. In the lower picture, the oscillating element is the first inner shell consisting of six nanotubes. Calculations show that in both cases the dependence of the van der Waals interaction energy of the movable element with its surrounding on the displacement is close to the parabolic one, which is inherent in the harmonic oscillator. The characteristic

magnitude of the restoring force is  $5-10 \text{ eV } \text{nm}^{-1}$ . This corresponds to the magnitude of the characteristic oscillation frequency within the range of dozens of GHz, depending on the length and structure of the oscillating element. Calculated data suggest that the main mechanisms of oscillation damping relate to the friction of the oscillating element, as well as to a transversal vibration of that element in the vicinity of the caps of the fixed CNTs. As the temperature increases, the damping caused by both mechanisms enhances. Due to the considerable level of damping, the oscillator under consideration can work continuously only in the presence of the driving force compensating the energy dissipation during oscillations.

The practical realization of the above-described oscillator concept [159] includes metal electrodes deposited onto an oxide layer. A bundle consisting of some number of singlewalled CNTs is inserted inside an electrode. Outer nanotubes relating to the bundle are firmly bounded with a metal, while one or several of the inner nanotubes are movable and can be extruded from the bundle under the action of a voltage applied to the electrodes. The electrode surface is smoothed by etching flush with the nanotube. Applying a voltage to the electrodes promotes the movement of one or several of the inner nanotubes belonging to the bundle. When the applied voltage is cut off, these nanotubes return under the action of van der Waals attractive forces exerted by the fixed nanotubes. In the case of alternating voltage, the nanotubes can oscillate.

The ability of certain layers of a multiwalled nanotube to execute both longitudinal and rotational movement relative to each other forms the basis of such an important element of a NEMS, as a nanobearing [173–178]. Possible configurations of such a nanobearing first proposed in Ref. [173] are presented in Fig. 19a [174]. According to the concept of the nanobearing, inner layers of a multiwalled nanotube are fixed, whereas a plate playing the role of a rotor is attached to the outer layer. Applying an external electric field promotes the rotation of this plate around the axis of the nanotube. Therefore, the construction under consideration constitutes a motor whose rotation is provided by turning outer layers of a multiwalled nanotube relative to fixed inner layers. The working model of such a motor is shown in Fig. 19b [174]. A multiwalled CNT is suspended between two fixed electrodes A1 and A2 acting as an anchor. A voltage is applied to two lateral electrodes (S1 and S2), as well as to the conducting gate S3 to control the location of the plate and the rotation speed of the rotor. The main obstacle hindering the development of such devices consists in the necessity of modifying the nanotube when manufacturing the bearing and axial assembly on which the rotor plate rotates. In earlier works, turning the rotor by an angle exceeding the elastic rotation limit was performed with the use of a very high electrostatic field which destroyed the walls of the nanotube, providing free turning of the rotor. Experiments executed imply that turning the rotor under the action of the electric field as described is possible only in the case of nanotubes of relatively small diameters (less than 20 nm). For thicker CNTs, the magnitude of the electric field strength necessary for turning the nanotube exceeds the breakdown value. Free turning of the rotor without its sliding along the nanotube's axis was provided by ion etching of the outer layers of the nanotube. The etching procedure was performed on a nanotube with an attached rotor plate in oxygen discharge plasma at a pressure of 100 mTorr and input power of 15 W



**Figure 19.** (a) Illustration of various designs of a bearing based on a multiwalled nanotube [174]: (1) initial state of the nanotube suspended on fixed supports and containing a rotor plate; (2) the plate is able to perform a torsion turn but does not slide along the nanotube axis; (3) the plate is able to rotate freely around the nanotube axis and is displaced along the axis as a result of a partial removal of the outer layers of the nanotube; (4) the plate is able to rotate freely around the axis but cannot slide along the axis as a result of intense (but incomplete) etching of nanotube [174]: A1, A2 are the stationary electrodes (anchor) to which a multiwalled nanotube is attached; S1, S2 are the stator electrodes; R is the rotor, and S3 is the conducting gate.

for 40 min. As a result of the etching, many of the samples showed rotation of the plate upon applying quite a low voltage. However, the ion etching makes many of the nanotubes more fragile, tending to become destroyed after several rotations. Hence, the conclusion can be made that a more thorough approach to the etching procedure is necessary.

An alternative method to the selective removal of the outer layers of a nanotube used as a rotor is based on electric current-induced evaporation [175]. This phenomenon firstly observed in Ref. [179] consists in the simultaneous evaporation of several layers of a multiwalled nanotube during the passage of electric current and is accompanied by an abrupt increase in the resistance. The approach in question has been developed further in Ref. [180], where the alternate evaporation of nanotube walls was observed, which was accompanied by sequential stepwise drops in the current. Investigations performed imply that the reliable resistive evaporation of the outer layers of a nanotube without its total destruction is possible if its resistance does not exceed 10 k  $\Omega$  . In this case, at a fixed magnitude of the applied voltage the current changes in a jump-like manner, which is caused by the evaporation of the outer layers. The characteristic magnitude of the current jump amounts to  $10-20 \,\mu$ A. Homogeneous evaporation of the outer layers of the nanotubes from both sides in relation to the rotor plate was achieved in bringing the contact to the middle part of the nanotube and by applying the voltage

independently to each half of the nanotube, between the anchor and the central part.

Further modification of the above-described design of a nanomotor has resulted in the fabrication of a device about 300 nm in size integrated into a silicon chip [176]. The device operates within a wide range of frequency, temperature, and environmental conditions, from a vacuum to an aggressive chemical medium, demonstrating repeatedly the rotation of the rotor plate by 180° and 360° with no signs of wear or fatigue. The rotating element is a rectangular metal plate attached to a suspended axis. The ends of the axis are inserted inside the anchors A1 and A2 that are fabricated from a conducting material and rest on the oxidized surface of a silicon chip. The rotor plate R 250-300 nm in size is surrounded by three fixed stator electrodes: two (S1 and S2) of them are located in one plane with the rotor axis, and the third 'gate' stator S3 is buried beneath the surface. Four independent voltage signals (d.c. and/or appropriately phased a.c.) can be applied either to the rotor plate or to three stator plates to control the position, speed, and direction of rotation of the rotor plate.

The key element of the device under consideration is a multiwalled nanotube from 10 to 40 nm in outer radius and about 2 µm in length that works simultaneously as the axis of the rotor plate and electric conductor. In addition, the nanotube provides the rotor plate with rotation freedom. Nanotubes synthesized by the standard electric arc method formed the base of a 1,2-dichlorobenzene suspension that was coated onto a doped silicon substrate covered with an SiO<sub>2</sub> layer 1 µm thick. The nanotubes were located with respect to prepatterned alignment marks on the SiO<sub>2</sub> surface using an AFM. Other elements of the device (rotor plate, stator electrodes, anchors, and electric leads) were manufactured by means of electron-beam lithography using a solution of polymethyl methacrylate in dichlorobenzene as a resist. The operation of the device was demonstrated with the aid of an SEM. Observations indicate that applying d.c. voltage up to 50 V between the slightly asymmetric rotor plate and the gate stator electrode promotes a turning of the plate by an angle of up to 20°. When the applied voltage is removed, the rotor plate returns to its initial position. Estimates show that the effective torsion spring constant lies between 10<sup>-15</sup> and  $10^{-12}$  N m and the shear modulus ranges from 100 to 300 GPa. This corresponds to a resonance torsion frequency on the level of dozens or hundreds of MHz.

However, large angles of torsion are unattainable in a low-frequency mode within the framework of the abovedescribed configuration, which is related to the high magnitude of the torsion spring constant. Large angles of torsion are reached using a modified construction of the axis, where one or several layers of the nanotube between the rotor plate and anchors were removed. As a result of this operation, the rest of the layers still attached to the rotor plate serve as one of the elements of the bearing, while the inner nonremoved layers of the nanotube work as a second element. Removal of the outer layers was performed utilizing ion etching, highcurrent passage through the nanotube, and irradiation with the electron beam of an SEM. The most effective approach to this task is based on applying quite high d.c. voltage (about 80 V) to the gate electrode, as a result of which the significant torque is produced that brings out the outer nanotube shells beyond the elastic limit and promotes their partial or complete failure. Therefore, the rotor plate gets practically total rotational freedom and can be turned to any azimuthal position by choosing the appropriate combination of signals applying to the stator electrodes. Operation of the device in the frequency mode is performed at fulfilling proper phase relations between the a.c and d.c. signals applied to various electrodes. In doing so, the rotation and rolling frequencies reach several Hz. Measurements indicate that turning the rotor plate through an angle between 90° and 270° takes less than 33 ms.

Another type of NEMS operates on the basis of the dependence of electronic characteristics of CNTs on an applied load causing a deformation. Such a system is also able to operate in the reverse manner, performing desired movements as a reaction to an electric signal. The practical importance of such systems is extremely high because they operate like a natural muscle and can be used, in particular, as a prosthetic device for a damaged organ [181]. According to the concept of the actuator that has been developed in Ref. [181], its principal element is a cloth-like CNT layer immersed in an electrolyte. Due to the action of applied voltage, electrons are injected into an electrode, the role of which is played by the CNT layer. This polarizes the electrolyte solution and promotes the formation of a double layer on the nanotube-electrolyte boundary. In turn, this generates mechanical stresses in the CNTs due to a change in their electronic structure under the action of the electric field, so that the sign of stress depends on whether electrons are injected, which promotes the compression of the CNTs, or holes are injected, which causes their stretching.

Single-walled CNTs produced by the standard laser ablation method with the use of double laser irradiation pulses have been utilized. The nanotubes ranged from 1.2 to 1.4 nm in diameter were bound into bundles 10 nm in average diameter and several µm in length, and were purified through nitric acid treatment, repeated washing, centrifugation, and filtration. The sheets produced as a result of these procedures were about 10 mg in mass and ranged between 15 and 35 µm in thickness, which corresponds to a density between 0.3 and  $0.4 \text{ g cm}^{-3}$ . The electrical conductivity of the sheets measured by the four-probe method amounted to about 5000 S cm. The specific electric capacitance of the CNT sheets measured in various solutions (1 M NaCl, 38% H<sub>2</sub>SO<sub>4</sub>, 1 M LiClO<sub>4</sub>, acetonitrile, and propylene carbonate) ranged from 12 to 17 F  $g^{-1}$ . A higher magnitude of the specific capacity  $(30 \text{ F g}^{-1})$  was observed in the case of 5 M solution KOH, which moistened the CNTs rather well. The measured specific surface area of the sheets  $(285 \text{ m}^2 \text{ g}^{-1})$  corresponds to that of a cylinder 10 nm in diameter and 1.33 g cm<sup>-3</sup> in density. Hence it follows that the gas  $(N_2)$  does not penetrate the bundles in the specific surface area measurements. The above data correspond to the specific surface capacity of CNT sheets ranging from 4 to 10  $\mu$ F cm<sup>-2</sup>.

To demonstrate the operation of the actuator, strips  $3 \times 20$  mm in area and from 25 to 50 µm thick were cut from CNT sheets. These strips were attached by Scotch Double Stick Tape to opposite sides of a polyvinylchloride film 215 µm thick (Fig. 20). A tiny mirror was attached to the free end of the film, which was necessary for registering deflections of the plate. Thus fabricated three-layer structure equipped with platinum contacts and leads was inserted into a NaCl water solution (1 M) used as an electrolyte. The lower end of this structure was attached to the bottom of a vessel filled with the electrolyte. Applying a d.c. voltage of several tenths volt, the strip was deflected up to 1 cm, which was registered by an optical sensor whose beam was directed onto



Figure 20. Schematic of the experiment demonstrating the operation of a CNT-based actuator [181].

the mirror. Within the range of the applied voltage, between -0.4 and 0.1 V, a linear dependence of the deflection on the voltage was observed. Applying a.c. voltage promoted mechanical oscillations in the sample, the frequency of which reached 25 Hz. Measurements of the length of the strip vs. applied voltage indicated a hysteresis.

The difficulties hindering the proliferation of CNT-based NEMSs are mainly of a technological nature and relate to the necessity of ensuring the high reproducibility of parameters of nanometer-sized devices in large-scale production. In this connection, the technology of fabrication of CNTbased NEMSs is the key issue, the execution of which determines the possibility of resolution of the problem as a whole. As an example of a successful solution to this problem one can mention Ref. [182] describing the procedure of fabricating and operating one- and two-contact switches built around a multiwalled nanotube. Along with the useful properties of such a device, its fabrication procedure is also of a practical interest: its successful realization indicates the existence of the mass production of NEMSs. This procedure involves several stages, at the first of which a trench about 20 nm in depth, 100-300 nm in width, and 10 µm in length is etched on a SiO<sub>2</sub> substrate. This trench is filled with a Ti/Au alloy, so that the surface of the metal used as a lower electrode is found 1-10 nm below the substrate level. At the second stage, shallow massifs 100 nm in width are etched on the substrate surface by utilizing a chemical method. These are used as channels for multiwalled nanotubes fixed by sorption forces. Both twocontact and one-contact configurations of the device are possible due to the use of contact electrodes based on a Ti/Pt alloy. The electrical resistance of the lower electrode was measured as 600  $\Omega$ , while for nanotubes fixed in two points that ranged from 30 to 100 k $\Omega$ .

The one-contact configuration was studied as an electrical switch. A nanotube 22 nm in diameter and 115 nm in length was hung as a cantilever at a height of 4 nm above the electrode buried in the substrate. At a voltage of less than 3 V, no current through the contact was observed. Upon exceeding this magnitude of voltage, the deformation of the nanotube promoted closing the contact, which was followed by an abrupt increase in the current from zero to several hundred nA. One should note that the current does not change when lowering the voltage to about 0.5 V. Such a behavior is caused by the electrode due to applying an external

voltage. The above-described switch may be used in computer devices.

## 4.3 The nanotube as a transport system

The possibility of filling CNTs with gaseous and liquid substances is one of the most interesting features of this new class of objects, attracting the attention of both researchers and practising engineers (see details in Ref. [14]). In addition, the possibility of using CNTs as channels in devices for the selective transport, separation, and purification of gases, which has recently been discovered, is also of considerable interest. This possibility has been studied quantitatively in Ref. [183], the authors of which, using the molecular dynamics computation method, investigated the diffusion transport of CH<sub>4</sub> and H<sub>2</sub> through single-walled nanotubes 1.36 and 0.81 nm in diameter, corresponding to the chirality indices (10, 10) and (6, 6). The data obtained were compared with the relevant results of calculations performed for porous zeolites of various compositions with a diameter of pores of 0.8 nm. The computations leaned upon the previously determined interaction potentials of gaseous molecules with C or O atoms entering into the zeolites and CNTs. The calculations revealed that the diffusion coefficient of the above-mentioned molecular gases through CNTs, determined for the pressure range between 0 and several hundred atmospheres, reaches  $1 \text{ cm}^2 \text{ s}^{-1}$ , which exceeds the relevant value for zeolites by 2-3 orders of magnitude. In this regard, the diffusion coefficient for CNTs with the chirality indices (6, 6) and the smaller diameter exceeds by several times that for CNTs (10, 10).

As follows from the analysis of the data obtained, the main reason for the difference in the diffusion coefficients in zeolite channels and CNTs is a distinction in the activation energy for the desorption of molecules from the channel surface. Whereas for zeolites the magnitude of this parameter calculated using the Lenard-Jones potential ranges between 4 and 4.5 kJ mol<sup>-1</sup> for CH<sub>4</sub>, and 2.5 and 3 kJ mol<sup>-1</sup> for H<sub>2</sub>, in the case of CNTs the activation energy does not exceed 0.066 kJ mol<sup>-1</sup>. While the accuracy of these data is rather limited due to the use of approximate models in calculations, it is beyond question that CNTs possess unique transport properties and are able to pass gaseous flows exceeding by orders of magnitude those for conventional zeolite-based membranes.

The qualitative conclusions on the unique passing capacity of CNTs that were made on the basis of the results obtained in the above-cited Ref. [183] have been confirmed experimentally [184]. A film of closely packed double-walled  $CNTs\sim 2.5\times 10^{11}~cm^{-2}$  in surface density was grown on the surface of a silicon chip by the CVD method in the presence of a catalyst. This film was inserted into a silicon nitride  $(Si_3N_4)$ matrix, permitting the passage of a gas or liquid only through the inner cavity of the nanotubes but not through the intertube space. The excess of silicon nitride was removed by ion etching from both ends of the chip. As a result of this operation, the nanotubes were opened from both ends. Measurements performed utilizing colloidal gold particles of various sizes indicated that the membranes produced are capable of passing particles of a cross section between 1.3 and 2 nm. Electron microscope observations reveal that the average inner diameter of nanotubes is equal to 1.6 nm. The average magnitude of the outer diameter is estimated as 2.3 nm. The passing capacity of the membranes fabricated was determined in relation to water, as well as such gases as

H<sub>2</sub>, He, Ne, N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub>, Xe, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>6</sub>, and C<sub>4</sub>H<sub>8</sub>. Measurements were carried out in the Knudsen regime, when the ratio of the characteristic mean free path of gaseous particles to the nanotube's diameter is much more than unity and ranges between 10 and 70. The measured dependences of the passing capacity on the molecular mass of particles are in agreement with the Knudsen model of diffusion, however, the absolute magnitudes of gaseous fluxes exceed by 1-2 orders of magnitude the relevant value determined by the known relation [185]

$$Q = \frac{2}{3} \sqrt{\frac{8\pi}{MT}} R^3 V_{\rm m} \frac{\Delta p}{L} \sigma A \,,$$

where *M* is the molecular mass of the atomic particle, *T* is the temperature, *R* is the radius of the channel, *L* is its length,  $V_{\rm m}$  is the molar volume,  $\Delta p$  is the pressure drop,  $\sigma$  is the surface density of the channels, and *A* is the total area of the membrane.

The difference in the rates of passage of gases of various masses through a CNT membrane points to the selectivity of the transport process, which can be utilized for separating gases of various sorts or various isotope compositions. The considerable exceeding of the passing capacity of CNT-based membranes over that characteristic of the Knudsen regime is caused by the difference in the character of the interaction of gaseous molecules with the inner walls of a nanotube and a macroscopic surface. The inner surface of a nanotube is smooth down to the atomic scale, whereas macroscopic surfaces of porous materials possess roughness on much larger scales. For this reason, the character of interaction of atomic particles with nanotube walls corresponds to specular rather than diffusive reflection, as occurs in the case of macroscopic surfaces. Moreover, numerous quantum-chemical calculations indicate that the energy of sorption of gaseous molecules on the inner surface of a nanotube does not exceed a few dozen degrees kelvin, which excludes the sorption of such molecules inside a nanotube and facilitates their free movement along the channel. Therefore, a gas passing along the inner cavity of a CNT undergoes much less resistance from the surface than is foreseen by classic expressions for the Knudsen flow regime.

CNT-based membranes are capable of passing not only gaseous but also liquid substances. The experiments [184, 186], as well as the numerical calculations [187, 188], have shown that the passing capacity of the membranes with respect to water exceeds by more than three orders of magnitude that evaluated by the classical Hagen–Poiseuille formula

$$Q = \frac{\pi R^4}{8\mu} \frac{\Delta p}{L} \,,$$

where Q is the liquid flux through a channel, R is its radius, L is its length, and  $\mu$  is the viscosity of the fluid. This effect is also related to the character of the interaction of a fluid with the inner walls of a nanotube, as compared to a macroscopic surface. A liquid is subjected to sliding over the nanotube surface, so that the standard boundary conditions required for zero magnitude of the flux in the vicinity of the surface are not applicable in this case.

#### 4.4 Other mechanical applications of CNTs

The unique mechanical characteristics of CNTs offer the opportunity to use these structures in numerous applica-

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tions. The role of these applications in scientific and technological progress has been rather small; however, the continuous rise in the number of examples implies that nanotubes are becoming an important attribute of modern technologies. Reference [189] can be mentioned as an example, where the authors report on the enhancement of the quality of quartz resonators by applying a thin CNT film to their surface. The problem of enhancing the quality of quartz resonators arises in the development of an extrasensitive balance for the evaluation of the mass of microobjects. The operation of such a device is based on the measurement of the oscillation frequency of a quartz resonator, and its sensitivity is inversely proportional to its quality factor. However, the condition relating to enhancing the quality is in contradiction with the requirement in respect to the miniaturization of the device; therefore, there arises the technically complicated problem of fabricating thin quartz crystals characterized by a high quality factor. An effective way to resolve this problem is based on using CNTs. Quartz resonators 90, 56, and 33 µm thick with a quality factor between 500 and 7500 were cut from a plate 110 µm in thickness through the plasma etching method. The rms roughness of the crystal surface was estimated as 1 nm. The gold electrodes were 0.5 and 1 mm in diameter. The suspension of 1/3 metallic and 2/3 semiconducting nanotubes about 1.4 nm in diameter and about 800 nm in length mixed in N-methyl-2-pyrrolidinyl was applied to a substrate. The content of nanotubes in the suspension amounted to  $10 \text{ mg ml}^{-1}$ . AFM observations indicate that about 80-90%of the nanotubes applied to the substrate were isolated from each other. A similar suspension was applied to the quartz resonator surface by means of a hair brush. After letting the suspension dry the gold electrode surface was covered with a homogeneous layer of disordered single-walled nanotubes. The crystals coated with the CNT layer were subjected to a vacuum treatment for 24 or 48 h in order to remove adsorbed gases that could influence resonator oscillation damping. The quality factor of the resonators was measured in a vacuum of  $10^{-6}$  Torr. Measurements showed a lowering in the resonance frequency of the crystals as the mass of the CNT layer increased. According to observations, applying a CNT layer enhanced the quality factor by more than 100% for all the crystals under investigation. The above-described effect of enhancement in the quality factor of quartz resonators is attributed to the phenomenon of suppression of surface energy losses by the layer of nanotubes possessing extraordinarily high axial rigidity (the elastic modulus is of an order of 1 TPa).

As one more example of the effective use of CNTs can be mentioned Ref. [190], where a nanomanipulator based on CNTs was fabricated. This device, resembling a conveyor, was placed inside a TEM. The instrument was equipped with a piezoelectric positioner and transported tiny metal particles. Metal indium particles a nanometer in size were deposited onto the surface of multiwalled CNTs produced by the electric arc method. An individual nanotube placed inside the TEM chamber was fixed at one end and put in contact with the tungsten tip of a nanomanipulator at the other end. Applying voltage between the nanotube and the tip promoted heat release in the contact, so that the temperature exceeded the melting point for indium. This caused the transport of the metal along the nanotube, which was observable by means of the TEM. Observations performed at a current of about 50 µA through the contact and a voltage of 1.8 V indicate a

displacement of indium particles several dozen nm in size by a distance of several  $\mu$ m along the nanotube outward from the tip. Special measurements showed that the direction of particle transport is determined by the sign of the applied voltage and does not depend on the direction of the temperature gradient. Along with In, similar experiments were performed with the particles of Au, Pt, Sn, and an Sn-In alloy. The device under consideration can be utilized for the delivery of dosed quantities of a metal to a desired point. Specifically, such a system can be considered to be a nano-soldering iron operating with metal particles about a femtogram in mass.

Another type of a CNT-based device designed for manipulations the nanoobjects has received the name 'nanotweezers' [191]. Electrically independent gold electrodes were deposited onto glass pipettes, each having a thin tip 100 nm in diameter. Then, either a multiwalled nanotube or a bundle of single-walled nanotubes ranging between 30 and 50 nm in diameter was attached to each of these electrodes. This resulted in the fabrication of nanotweezers with arms about 4 µm in length and 50 nm in diameter. The electromechanical characteristics of the device were studied by applying to the electrodes a voltage increased from 0 to 8.3 V. This promoted the relevant reversible displacement of the nanotubes, which was registered by means of an optical microscope. As a result of the displacement, the gap between the nanotubes decreased, so that at a voltage of 8.3 V the relative decrease in the distance was 50%. At a voltage of 8.5 V, the distance decreased to zero, so that the tweezers were closed. The nanotweezer arms remained closed after removal of the voltage, which is caused by the action of van der Waals forces. The nanotweezers can be opened by applying a voltage of the same polarity to both tweezer arms relative to a nearby ground electrode. The nanotweezers described are able to grab and pick up objects a nanometer in size. As one such object were used polystyrene balls 0.31 µm in diameter colored with a fluorescent dye. The coloration allowed the observation of ball displacement by means of an optical microscope. Moreover, nanotweezers having conductive arms permit measurements of the electrical characteristics of β-SiC nanoclusters and GaAs nanowires. The results of the measurements are in agreement with the relevant data obtained through other means.

# 5. Conclusions

The discovery of carbon nanotubes and other types of surface carbon nanostructures is one of the most considerable achievements of modern science. This carbon modification is intermediate in structure between graphite and fullerenes. However, with respect to many properties carbon nanotubes have nothing in common with either graphite or fullerenes. This permits one to consider and study nanotubes as a proper material possessing unique physical and chemical characteristics.

One of the most interesting properties of carbon nanostructures, which is of importance from the viewpoint of both basic research and applied development, relates to their extraordinarily high mechanical characteristics. Thus, results of a large body of experimental research imply that the Young modulus of a single-walled nanotube exceeds the record magnitude of 1 TPa. Such a high rigidity of nanotubes in combination with their flexibility, relatively low mass density and chemical stability leads one to consider this object to be a foundation for future materials possessing unique mechanical properties. One of the possible structures of such a material is a polymer-based composite doped with some quantity of CNTs. The main problem emerging in the development of such materials relates to the necessity of ensuring the transfer of the mechanical load from a nanotube to the polymer matrix. This transfer can be provided for through the proper choice of polymer material whose molecules form a strong chemical bond with the nanotube surface. At present, the efforts of many laboratories are directed toward the resolution of this problem.

The high aspect ratio, tiny size, and flexibility of nanotubes determine their possible effective usage as probes and tips for AFMs. Utilization of nanotubes has already brought notable progress in this branch of microscopy. Substitution of silicon tips having pyramidal shape with cylindrical nanotubes has resulted in a drastic increase in the resolving power of such systems. Nanotube tips are used not only for studying the structural characteristics of surfaces of semiconducting systems but also for determining the quality of etching of deep trenches in photoresist fabrication and even for writing information onto a polymer surface.

Another important property of nanotubes determining the possibility of their utilization in modern nanoelectromechanical systems concerns the interrelation between their mechanical and electronic characteristics. Applying a mechanical load to a nanotube promotes its deformation, which in turn reflects on such electronic characteristics as the energy gap width, conductivity, carrier concentration, and other parameters determining the behavior of the nanotube. Conversely, applying an electric potential to a nanotube changes its electronic structure, which in turn generates inner mechanical stresses that can provoke its deformation. Therefore, a nanotube can be considered to be a miniature transformer of an electric signal into mechanical displacement and vice versa. Such a feature of CNTs suggests the possibility of using them as actuators of NEMSs that form the basis for future superminiature devices intended for processing and storing information. The first samples of such systems have already been developed and described, and their further distribution depends on progress in the methods of production of CNTs with the prescribed characteristics.

The ongoing efforts of researchers focused on the study and use of the mechanical characteristics of CNTs have required the design and development of unique experimental equipment, including nanomanipulators, electron microscopes, and Raman spectrometers. Furthermore, numerical approaches based on molecular dynamics methods that permit establishing the dependence of the mechanical characteristics of CNTs on their geometry (diameter, chirality) and external conditions (temperature, load) have been developed. Obtaining these data through experiments is rather difficult, so that the usage of numerical methods is often the only way to obtain reliable and necessary information. Therefore, the development of research in the field of the mechanical properties of CNTs has a beneficial effect on both the physical experimental technique and the elaboration of methods for numerical modeling of quantum objects. This effect has manifested itself in the progress of related branches of nanotechnology and nanomaterials, such as quantum dots and other nano-sized objects.

In the 16 years that have passed since the discovery of carbon nanotubes researchers working in this area have come a long way. In analyzing the stages of this progress by the

example of the exploration and usage of the unique mechanical properties of carbon nanostructures one can conclude that we are witnesses to a quick transition from the description of elongated objects formed as a result of thermal sputtering of graphite, through the synthesis of nanotubes with specified structural and electronic characteristics, to the design of reliably working CNT-based devices. This example is one more demonstration of the important fruitful role of basic research, which can under the appropriate circumstances result in the quick development of and progress in applied technologies.

The solution to the problem of the application of CNTs depends primarily on the production costs of nanotubes in a macroscopic amount. As of now, it considerably exceeds that of gold, which apparently excludes the possibility of largescale applications of this material. Nevertheless, such nanotube properties as their extra tiny size, high mechanical and chemical stability, and good electrical conduction allow one to hope even now for their effective application in the fields of chemical technology, hydrogen power engineering, nanoelectronics, and so on, where their miniature size in combination with electrical conduction and extraordinary mechanical characteristics are of great importance. The successful solution to these problems will become one more example of the effective influence of basic research on scientific and technological progress.

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