Russian Chemical Reviews **80** (8) 787 – 806 (2011) © 2011 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2011v080n08ABEH004196

Epoxide composite materials with carbon nanotubes

V I Irzhak

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Abstract. Methods of formation and physical properties of epoxide composite materials reinforced with carbon nanotubes are considered. An analogy is made between the relaxation properties of carbon nanotubes and macromolecules. The concentration dependences of the electrical conductivity of the epoxy polymers filled with single-walled and multi-walled carbon nanotubes are discussed. Modern views on the mechanism of reinforcement of polymers with nanotubes are outlined. The bibliography includes 143 references.

I. Introduction

At present, a number of reviews on polymeric composites reinforced with carbon nanotubes (CNTs) are available.[1–11] As a rule, they also concern epoxy polymers. Yet another review[12] is solely devoted to epoxide nanocomposites. However, taking into account new data not included in these reviews and high importance of the problem, we decided to dwell on it again.

Wide use of epoxy polymers in technology is due to good workability of epoxy resins and unique combination of their operating characteristics.[13–15] High reactivity of the epoxy group and thermodynamic compatibility of epoxide oligomers with many substances allow one to use various curing agents and to conduct curing under various process conditions.[16,17] Also, the lack of volatile products during the synthesis and low shrinkage on curing are of importance.

The distinctive features of epoxy polymers include high static and impact strength, high hardness and high wear resistance. These systems are characterized by rather high heat resistance. Hard surfaces of many substances form strong adhesive bonds with epoxy polymers.[18] All these features predetermine their use as compounds, glues, paint materials and coatings. A particular place is occupied by composite materials[19] including fibrous materials.[20] In most cases, these are highly filled reinforced plastics with high-modulus and high-strength fibres as load-bearing elements.[21] The matrix is mainly needed for realization of their properties in structural materials. The properties of epoxy polymers are listed in Table 1.

We begin with a brief outline of the properties of fibrous composite materials, CNTs and polymeric composites based on them. We believe this is necessary for better representa-

Table 1. Physicochemical properties of epoxy matrices.[21]

Parameter	Notation, dimensionality	Numerical value
Density	ρ /kg m^{-3}	1110 – 1390
Tensile strength	σ /MPa	28 – 90
Young's modulus	E/GPa	0.69 – 3.45
Limiting deformation	ε (%)	3 – 50
Impact strength (Izod impact)	σ_I /J cm^{-1}	1.09 – 5.44
Thermal conductivity	λ /cal (cm s deg)$^{-1}$	0.10 – 0.25
Linear thermal expansion coefficient	α /10^{-6} × deg^{-1}	10 – 20
Softening temperature (1.8 MPa)	T/°C	40 – 260
Adsorption of water after 24 h	%	0.08 – 0.15

V I Irzhak Institute of Problems of Chemical Physics, Russian Academy of Sciences, prosp. Akad. Semenova 1, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-496) 515 32 44, tel. (7-496) 522 36 90, e-mail: irzhak@icp.ac.ru

Received 16 November 2010
Uspekhi Khimii **80** (8) 821 – 840 (2011); translated by A M Raevskiy

tion of the prospects for use of CNTs as fillers for composite materials based, in particular, on epoxy resins. Then, we will analyze the published data on the electrical and thermal conductivities and the mechanical properties of carbon nanotube filled epoxide composites. Summing up, we will discuss the mechanism of polymer reinforcement with carbon nanotubes.

II. Fibrous polymer composites

The advantage of unidirectionally aligned composites is the ability to realize high mechanical properties of fibres along the direction of alignment (these properties are low along the transversal direction). This is of little importance when such composites are used as structural materials (*e.g.*, spinning items), but has a negative effect for some applications. To avoid this drawback, filling with randomly oriented cut fibres is used. Such materials exhibit isotropic properties, but their numerical values are lower compared to those of unidirectionally aligned composites along the direction of alignment, although being much higher along the transversal direction.

The mechanical properties of composite materials filled with cut fibres depends not only on the degree of filling, but also on the aspect (length-to-diameter) ratio (χ) of the fibre. For instance, if the volume fraction of unidirectionally aligned fibres is low, the Young modulus of the composite along the alignment direction (E_{11}) is given by [22]

$$\frac{E_{11}}{E_m} = \varphi_f A, \tag{1}$$

where E_m is the modulus of the matrix, φ_f is the volume fraction of the fibre and A is a function of the fibre modulus (E_f) and χ (Fig. 1).

At high fibre moduli (plateau region in the curves), it is the aspect ratio that mainly determines the A value.

In the case of randomly oriented fibres, the Young modulus of a composite (E_c) is given by:[23]

$$E_c = \frac{3}{8}E_{11} + \frac{5}{8}E_{22}. \tag{2}$$

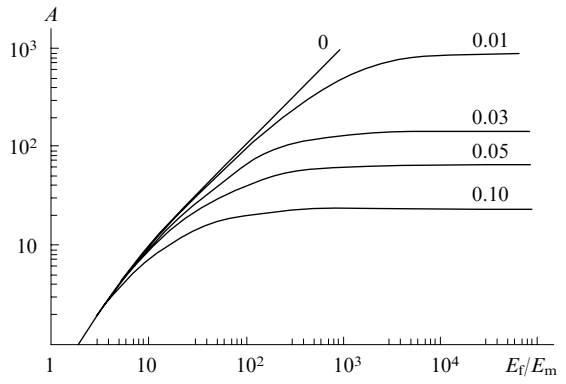


Figure 1. Young modulus of unidirectionally aligned composite plotted *vs.* parameter A of the fibre.[22]
Numbers near the curves denote the χ^{-1} values.

At low degrees of filling, the transversal modulus (E_{22}) can be calculated using the simple Rule of Mixtures relation [24]

$$E_{22} = E_t\varphi_f + E_m(1-\varphi_f), \tag{3}$$

where E_t is transversal modulus of the fibre. Usually, for organic and carbon fibres one has $E_t \ll E_f$.

From Eqns (1)–(3) one gets

$$\frac{E_c}{E_m} = \frac{1}{8}\left[5 + \varphi_f\left(3A + 5\frac{E_t}{E_m} - 5\right)\right] \approx \frac{5}{8} + \frac{3}{8}\varphi_f A, \tag{4}$$

i.e., the major contribution to the Young modulus comes from the parameter A. From expression (4) and the data shown in Fig. 1 it follows that at low degree of filling ($\varphi_f < 0.01$), the use of fibres can be efficient only at $\chi \gg 100$.

In an ideal case (the Kelly model), the strength of a composite (σ_c) obeys the Rule of Mixtures [22, 25]

$$\sigma_c = \eta\xi\sigma_f'\varphi_f + \sigma_m(1-\varphi_f), \tag{5}$$

$$\sigma_f' = \left(l - \frac{l_{cr}}{2l}\right)\sigma_f,$$

$$l_{cr} = \frac{\sigma_f d}{2\tau}.$$

Here, η is the orientational factor equal to 0.2 for random distribution of fibres along different directions;[25] ξ is the coefficient that includes the degree of realization of the property of the fibre; σ_m and σ_f are the strengths of the matrix and the fibre; l and l_{cr} are the total and critical length of the fibre, respectively; d is the fibre diameter and τ is the shear strength of the interfacial layer.

From expressions (5) it follows that the strength of unidirectionally aligned composites along the direction of alignment ($\eta = 1$) is close to the strength of the fibre

$$\sigma_c = \xi\sigma_f'\varphi_f,$$

if $l_{cr} \ll l$ (long fibres), while this property along the transversal direction ($\eta = 0$) is lower than the strength of the matrix

$$\sigma_c = \sigma_m(1-\varphi_f).$$

When using cut fibres, the strength of the material decreases by several times along one direction and increases by more than an order of magnitude along other directions (to tens of MPa for the matrix, and from a few GPa to 10 GPa for fibres).[21] Of course, this holds at $l_{cr} \ll l$.

Among fibrous composites, a special place is occupied by carbon fibre reinforced plastics.[26] They are thermally stable, fire resistant and chemically stable materials, but what is most important, they exhibit high electrical and thermal conductivities. Carbon fibres are much more efficient fillers than traditional carbon black additives. Fibres form a conducting three-dimensional network at a very low content, *viz.*, the percolation threshold can be reduced to a few per cent or even fractions of a per cent depending on the aspect ratio and fibre orientation [27] and on the conditions for composite formation. Even higher efficiency can be attained using CNTs.

III. Carbon nanotubes

The synthesis of CNTs† was for the first time reported in 1982;[28] however, the Iijima communication[29] is commonly recognized as a pioneering study.

Carbon nanotubes are obtained by various methods[30] including arc discharge (the chronologically first and the most widely used technique),[29] laser synthesis and other methods of graphite vaporization, as well as pyrolysis of hydrocarbons, catalytic growth by decomposition of metal carbides, *etc*.

Despite the relatively high cost of CNTs, their use as fillers for polymer composite materials[1–5] is due to unique physical and mechanical properties.[31–38] Carbon nanotubes represent regular honeycomb structures rolled into hollow cylinders; the ends of cylinders are 'capped' by fullerene hemispheres. Hexagons are formed by C(sp^2) atoms.

There are two types of CNTs, namely, single-walled and multi-walled ones. The former type includes CNTs 0.7–3 nm in diameter. The diameters of the CNTs from the other group depend on the number of interleaved cylinders held together by weak van der Waals bonds (interlayer distance is 0.34 nm) and usually lie in the interval from 2 to 25 nm and even to 100 nm.[33,35] Carbon nanotubes are a few micrometres long, so the aspect ratio can reach a value of a hundreds and even thousands.

A rough estimate[33] of the CNT density is about 0.6 g cm^{-3} for single-walled CNTs and 1–2 g cm^{-3} for multi-walled CNTs depending on their composition (*cf*. 1.3 g cm^{-3} reported in Ref. 3). Compared to carbon fibres, CNTs have a looser structure and a higher Young modulus and strength (Table 2).

Table 2. A comparison of the mechanical properties of CNTs and carbon fibres.

Fibre	E/GPa	σ/GPa	ε (%)
Nanotubes[6]			
270–3600	11–200	2–25	
Carbon fibres[21,27]			
Low-modulus	<100	–	to 2
High-modulus	>400	–	<1
Medium-strength	–	3	~1
High-strength	–	>4.5	<1

Thus, the mechanical properties of CNTs are much better than those of carbon fibres. The scatter of numerical values is due to the dependence of the properties of CNTs on their structure. According to calculations based on the equations of molecular structural mechanics,[6] the Young modulus of single-walled CNTs is inversely proportional to their diameter. Under low loads, CNTs behave as hard elastic materials, but under high loads, they exhibit plastic properties.[6,31–37,39] The ability to withstand high deformations is due to structural rearrangements. First, transformation of four hexagons to two pentagons and two heptagons leads to defect formation on the tube surface. This is accompanied by accumulation of such defects and subsequent rearrangements. As a result, CNTs become deformed. An increase in the load leads to necking and drawing of CNTs into strings similarly to deformation of polymers through necking. In the case of multi-walled CNTs, a 'telescopic' mechanism is possible which involves drawing of inner nanotubes. This provides an explanation for large limiting deformation and, correspondingly, strength of CNTs.

The electronic and, therefore, the conductivity properties of CNTs depend on their chirality. The chirality emerges during the synthesis and characterizes the method of rolling the graphene sheet into a cylinder. It is related to the nanotube diameter and helicity. The limiting cases of CNTs have the zigzag and armchair configurations. The former structure is completely symmetrical (zero helicity), while the latter is a helical structure with an angle of 30°. The chirality is defined by two indices, n and m. The chiral angle (θ) is given by

$$\theta = \arctan\left(\frac{m\sqrt{3}}{2n+m}\right).$$

At $m = 0$, one has $\theta = 0$ or a zigzag-type CNT. If $n = m$ and, therefore, $\theta = \pi/6$, one has a 'chair'-type CNT. The nanotube diameter is defined by

$$d = \frac{b\sqrt{3}}{2\pi}\sqrt{n^2+mn+m^2},$$

where b is the C–C bond length.

Zigzag- and armchair-type single-walled CNTs exhibit the properties of semiconductors and conductors, respectively; multi-walled CNTs always exhibit the properties of conductors. The conductivity of macroscopic samples of single-walled CNTs (nanotube whiskers with random orientation of individual CNTs) is as high as 10^3 S cm^{-1} (Ref. 40). However, the specific resistance of the system is determined by contacts between CNTs rather than the properties of the CNTs, *i.e*., the limiting stage of conductivity occurs by jumping.[37]

Similarly to metals, CNTs are characterized by high heat capacity (more than 0.8 J g^{-1} K^{-1} at room temperature for single-walled CNTs) and thermal conductivity (more than 200 W m^{-1} K^{-1}).[41]

The chemical properties of CNTs are due to the fact that dehybridization of carbon atoms, *i.e*., the transition $sp^2 \rightarrow sp^3$ (Ref. 42) occurs with relative ease. Covalent modification of the surface of CNTs to some extent affects their electronic properties. Noncovalent interaction with low-molecular and polymer sorbates through, in particular, the formation of π–π bonds[43,44] has almost no effect on these properties. The ability of CNTs to enter into chemical reactions offers great prospects for their modification.[7,45] A ariety of reactions thus becomes possible, including oxidation with the formation of carboxyl and hydroxyl groups, halogenation, addition of free radicals and radical ions, the Diels–Alder reaction, *etc*.

Carbon nanotubes are always formed as agglomerates. Therefore, to obtain polymer composites, one should first of all break them down.[46] This is achieved using ultrasonic generators[47] or high-speed mixers.[48] However, dispersions

† The first observation of carbon whiskers by electron microscopy was reported by L V Radushkevich and V M Lukyanovich in 1952 [see L V Radushkevich, V M Lukyanovich *Zh. Fiz. Khim*. **26** 55 (1952); *J. Phys. Chem. USSR (Engl. Transl.)*].

of CNTs are stable only if dispersion is carried out in low-molecular surfactants[49,50] or polymers.[51] Also, single-walled CNTs can be efficiently dispersed by sonication in aqueous-alcohol NaOH solution.[52]

Mechanical action can lead to destruction of CNTs. It was shown that dispersion dominates in the first stage of sonication of an aqueous suspension of single-walled CNTs stabilized by a methyl methacrylate/ethylene oxide block copolymer.[53] This manifests itself in a decrease in the relative viscosity of the system. In the subsequent stages, the decrease in viscosity is accompanied by shortening of CNTs. For instance, mixing (80 rpm) of a dilute suspension of multi-walled CNTs in polystyrene causes dispersion of agglomerates and destruction of CNTs to occur simultaneously,[54] but the initial rate of the former process is higher than that of the latter.

IV. Spatial distribution of carbon nanotubes and the percolation threshold

Long length and small diameters of CNTs relate them to linear macromolecules. Indeed, the rheological properties of semi-dilute solutions of both types of systems are close.

The concentration dependences of the viscosity of polymers and CNTs are analogous.[55] As in the case of polymers, at high dilutions, the viscosity of the system is proportional to the concentration of CNTs; which allows one to characterize the CNT size by the intrinsic viscosity $[\eta]$, namely, the values $[\eta] = 100$ and 48 ml g^{-1} were obtained for the CNTs 10 ± 2 nm in diameter having the aspect ratios of 110 and 37, respectively. At higher concentrations, the viscosity abruptly increases. This is associated with the formation of a network of entanglements in the polymer systems. The critical concentration of long CNTs is about 0.5 vol.%, short CNTs do not go in the regime of abrupt increase in the viscosity in the concentration range studied (up to 2 vol.%).

It is assumed[57,58] that macromolecules and CNTs are equally involved in the network formation. The critical CNT concentrations (φ_{cr}) necessary to form the network of entanglements in some polymeric systems are listed in Table 3.

Table 3. Critical concentration of CNTs from rheological data.

Matrix	CNT parameters			Ref.
	d/nm	l/μm	φ_{cr} (mass %)	
Multi-walled CNTs				
Polyethylene terephthalate	10–20	5–15	0.6	56
Polycarbonate				
170 °C	12	–	5	58
220 °C	12	–	1.25	58
280 °C	12	–	0.5	58
Polycarbonate 260 °C	10–15	1–10	<2	59
Polyether ether ketone	9.5	1.5	1	60
Poly-ε-caprolactone	10–20	10–30	<3	61
Single-walled CNTs				
Styrene/isoprene copolymer, 90–130 °C	–	–	0.033–0.14	62
Poly(methyl methacrylate)	–	–	0.12	57

This concept is supported by the results of a study[63] whose authors showed that grafting of poly(methyl methacrylate) macromolecules onto multi-walled CNTs causes φ_{cr} to decrease from 2.5 mass % to 1.5 mass %.

The temperature dependence of φ_{cr} (rows 2–4) probably suggests a partial aggregation of CNTs, which decreases with temperature. A similar behaviour was also reported in another study.[61]

An analysis of the published data[59] showed[64] that the mechanical loss tangent ($\tan\delta$) is independent of the deformation frequency (ω) in the concentration range 0.5 vol.%–2 vol.%. In the case of polymeric systems, this usually indicates a reversible or irreversible gelation.[65,66] Thus, the critical concentration can with good reason be related to the instant of formation of the fluctuation network.

Dynamic tests of aqueous solutions of multi-walled CNTs ($d = 11 \pm 3$ nm, $l = 910 \pm 650$ nm) in the concentration range 0.4 vol.%–11 vol.% showed[67] that the dynamic moduli G' and G'' are independent of the deformation frequency at small amplitudes; as a rule, this is treated as an indication of a network structure. The dynamic moduli increase by a power law depending on the CNT concentration (φ)

$$G' = 621\,\varphi^{2.6},$$

$$G'' = 122\,\varphi^{2.4}.$$

The relation between the shear rate and strain can be reasonably described following Bingham.

These regularities are typical of concentrated suspensions.[68] From this point of view, polymer composites containing CNTs can be considered as disperse solid-like systems having anisodiametric particles. At low concentrations of CNTs in a shear flow, they are aligned, which favours a decrease in the viscosity, as was shown for a polypropylene melt filled with multi-walled CNTs.[69] An increase in the nanotube concentration causes the viscosity to increase owing to formation of an elastic network[70] which is characterized by the shear modulus (G) and yield stress (σ) that depend on the CNT concentration

$$G \propto \varphi^{7.1},$$

$$\sigma \propto \varphi^{3.5}.$$

Unfortunately, the relaxation data on the formation of CNT-containing networks are scarce. However, many results on the determination of the percolation threshold were obtained by conductivity measurements (see, *e.g.*, Table 2 in review[7]). Taking into account intertube contacts (electrical conductivity), it is clear that the percolation threshold in a system containing sufficiently long-chain macromolecules can exceed φ_{cr}. Indeed, the conductivity percolation threshold is 0.9 for poly(ethylene terephthalate),[56] 0.39 for poly(methyl methacrylate)[57] and 0.2 mass % for a styrene/isoprene copolymer[62] (*cf.* the data of Table 3). Therefore, this method gives the upper bound of the critical concentration.

Application of shear strain leading to alignment of CNTs[69] causes the φ_{cr} value[61,71,72] and the percolation threshold (p)[73] to increase. The percolation threshold increases on annealing of the oriented system.[74] This effect is probably due to aggregation of the aligned nanotubes. The dependences of the percolation threshold on the degree

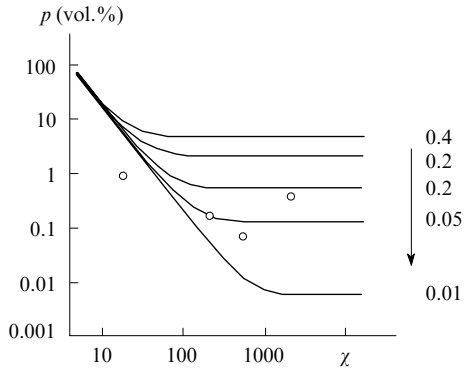


Figure 2. Percolation threshold plotted *vs.* aspect ratio and degree of aggregation of CNTs.[73]
Numbers on the right of the arrow denote the volume fraction of agglomerates, solid lines denote the results of calculations and open circles denote the experimental data.

of clustering of CNTs were studied theoretically and experimentally.[75] The results obtained are shown in Fig. 2. At $\chi \geqslant 1000$, the curves reach a plateau and it is the CNT aggregation that now plays the decisive role.

A fundamental distinction between macromolecules and CNTs is rigidity of the latter. Despite the fact that nanotubes are bent due to surface defects, their shape remains unchanged with time. The persistent length of single-walled CNTs was estimates as 27 μm,[76] being much greater than that of conventionally used nanotubes. It seems natural that finite-size CNTs can exist in a liquid-crystalline state.[61,76–78] Considering an analogy with polymers, one should follow the studies by Flory,[79,80] who predicted the possibility of formation of structures with orientational ordering (in fact, nematic liquid crystals) in systems of rigid-chain and rod-like macromolecules. In the former case, the critical concentration corresponding to transition from the isotropic to locally ordered state (φ^*) is determined by the rigidity parameter (f) equal to the percentage of flexible units in the chain (in other words, f characterizes the extension of straight chain segments). In the latter case, φ^* depends on the aspect ratio only

$$\varphi^* = \frac{8}{\chi}\left(1 - \frac{2}{\chi}\right). \qquad (6)$$

Indeed, an isotropic aqueous solution of multi-walled CNTs undergoes separation with the formation of a nematic phase if the nanotube concentration exceeds 4.3 vol.%.[81] Nuclei of the liquid-crystalline phase appear at lower concentrations determined by relation (6) because one has $\chi \gg 1$.

The aforesaid to one extent or another determines the of epoxide composite materials filled with CNTs.

V. Electrical conductivity of epoxide nanocomposites

As mentioned above, the electrical conductivity of polymer composite materials depends on the aspect ratio, on the character of alignment and on the degree of dispersion of fillers. This governs the percolation threshold.

A detailed study of the conducting properties of an epoxide nanocomposite was reported.[82] The matrix was prepared by curing bisphenol A diglycidyl ether (BADE) with a cyclic aliphatic amine. Single-walled CNTs containing an impurity of two-walled nanotubes about 3 nm in diameter were used as filler. No modification of the nanotubes was done. The diameters of nanotube bundles were reduced to 40–70 nm by dispersion.

The frequency dependences of the real part of the complex conductivity (σ') at different concentrations of multi-walled CNTs are shown in Fig. 3 *a*. As the frequency decreases, the curves reach a plateau starting with 0.3 mass %. As the curve reaches the first point in the plateau region, a dc conductivity (σ_{dc}) appears. The concentration corresponding to this instant can be treated as the percolation threshold.

Figure 3 *b* shows the dependence of $\sigma'\ \omega = 10^{-1}\ s^{-1}$ on the concentration of CNT at $\omega = 10^{-1}\ s^{-1}$. At $\varphi \geqslant p$, the equality $\sigma'(0.1) = \sigma_{dc}$ holds. The inset demonstrates the $\sigma_{dc}(\varphi)$ dependence in the scaling coordinates [83]

$$\sigma_{dc} \propto (\varphi - p)^{\gamma},$$
$$\gamma = 1.44 \pm 0.30.$$

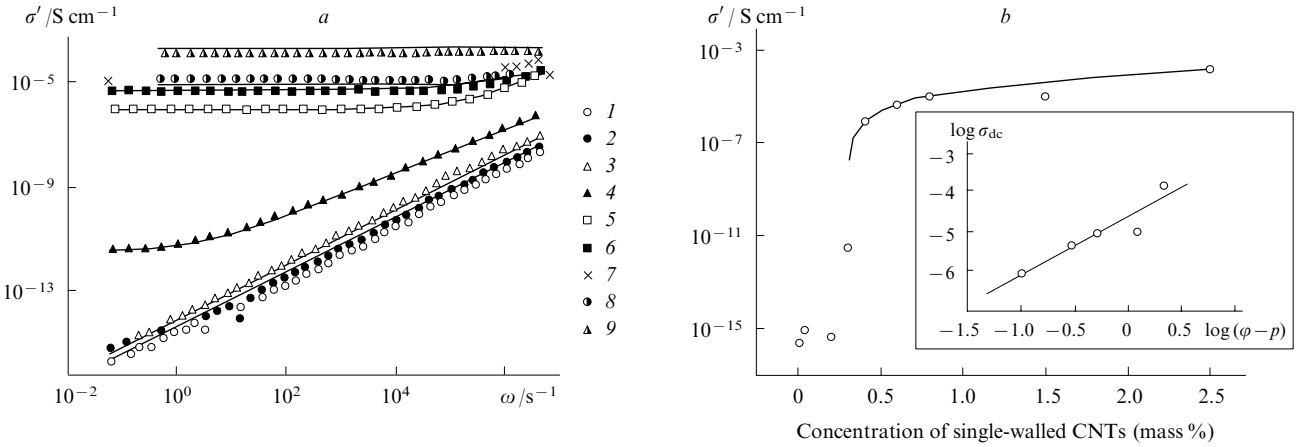


Figure 3. Frequency dependences of σ' at 20 °C and different CNT concentrations (*a*) and the plot of σ' *vs.* φ at $\omega = 10^{-1}\ s^{-1}$ (*b*).[82]
(*a*) φ (mass %): 0 (*1*), 0.04 (*2*), 0.2 (*3*), 0.3 (*4*), 0.4 (*5*), 0.6 (*6*), 0.8 (*7*), 1.5 (*8*) and 2.5 (*9*); (*b*) the inset presents the function $\sigma_{dc}(\varphi)$ in the scaling form.

In the temperature interval 20 – 70 °C (the region of glassy state), σ_{dc} increases slightly as temperature increases and reaches a plateau above the glass transition temperature (T_g). Probably, this is due to the effect of the nature of the matrix on the jumpwise mechanism of electron transfer between CNTs.

The conductivity of an epoxy polymer filled with multi-walled CNTs a few hundreds of micrometres long with diameters varied from 15 to 400 nm (100 nm on the average) was studied.[84] The nanotubes were used 'as is' and the diameter of their agglomerates was reduced to 100 nm by vigorous stirring in ethanol. The elastic matrix was obtained by curing a mixture of bisphenol A with epichlorohydrin and triethylenetetramine. The conductivity of the composite was measured in the frequency range $10^{-1} - 10^{6}$ Hz. It was shown that the conductivity of the composite containing 0.5 mass % of CNTs increases with frequency, whereas at concentrations of 1 mass % and 4 mass % of CNTs, it is frequency independent and equals 6×10^{-2} S cm^{-1}. Thus, the percolation threshold lies in the interval from 0.5 mass % to 1 mass %. Probably, the main reason for the increase in the percolation threshold is the lower degree of dispersion of CNTs (see Fig. 2).

The nature of the matrix (more exactly, of the interfacial layer) is of great importance.[85] The properties of materials containing different types of CNTs, *viz*., untreated and modified (bearing grafted amine groups) were compared. A composite filled with carbon black was studied for comparison. Figure 4 presents the specific conductivities (σ) of the epoxide nanocomposites plotted *vs*. volume fraction of the fillers whose properties are listed in Table 4.

The percolation threshold of the untreated tubes was not determined; one can only say it is lower than 0.1%. Functionalization significantly increases the percolation threshold. Amination led to shortening of CNTs and, consequently, to a decrease in the aspect ratio, but its effect is too small to be responsible for such a large shift. Chemical modification of CNTs with NH_2 groups (content of about 1%) leads to transition of carbon atoms from the

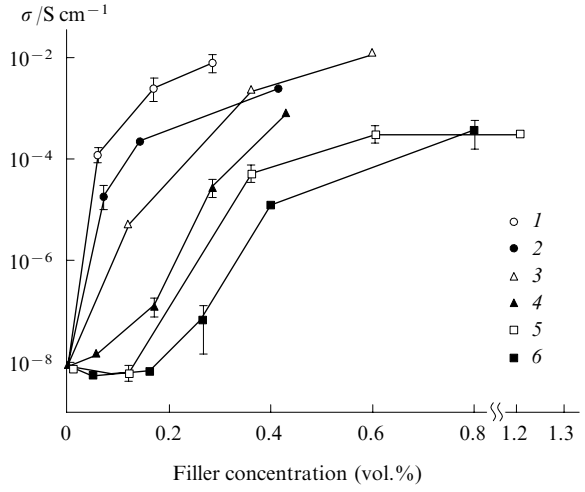


Figure 4. Specific conductivity plotted *vs*. volume fraction of filler.[85] Multi-walled CNTs (*1*), single-walled CNTs (*2*), double-walled CNTs (*3*), multi-walled CNTs with grafted amino groups (*4*), double-walled CNTs with grafted amino groups (*5*) and carbon black (*6*).

Table 4. Characteristics of fillers used in Ref. 85.

Filler	d/nm	l/μm
Carbon black	~30	–
Single-walled CNTs	< 2	to 10
Double-walled CNTs	2.8	to 10
Amino-functionalized double-walled CNTs	2.8	0.5 – 5
Multi-walled CNTs	15	to 50
Amino-functionalized multi-walled CNTs	15	0.5 – 10

sp^2 to sp^3 hybridization and to changes in their electronic characteristics. But the main reason for the decrease in the conductivity is the change in the near-surface layer and, therefore, intertube contact conditions.

Probably, a higher degree of dispersion governs the attainment of very low percolation thresholds in the epoxide nanocomposites filled with single-walled and multi-walled CNTs, namely, 0.015% and 0.04%, respectively.[86] When using a mixture of single-, double- and multi-walled nanotubes as filler, the percolation threshold was 0.0225 mass %, thus having an intermediate value. However, the electrical conductivities are in the reverse order at the concentrations that exceed the percolation threshold concentration (Fig. 5).

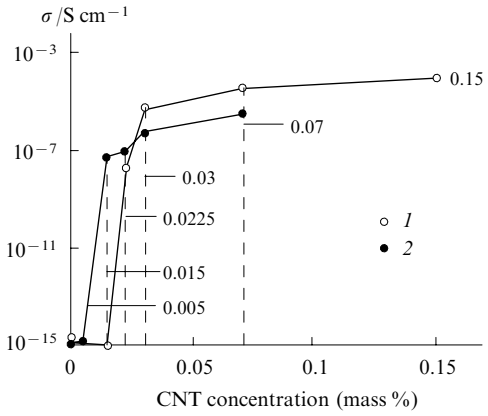


Figure 5. Plots of conductivity *vs*. concentration of a mixture of single-walled and multi-walled CNTs (*1*) and single-walled CNTs (*2*).[86] Numbers near the curves denote the concentration of CNTs.

These dependences were explained using a model[87] which assumes that the percolation threshold is reached if the intertube distance becomes short enough, although remains nonzero. The critical intertube distance suitable for the jumpwise mechanism of conductivity to occur is independent of the nanotube diameter. In this case, the larger the nanotube diameter the higher the percolation threshold concentration. Qualitatively, this conclusion can be illustrated as follows. To fill the surface area S, N circles of radius r with adjacent layer of thickness h are needed:

$$N\pi(h + r)^2 = S.$$

The corresponding proportion (φ_r) will increase with an increase in r

$$\varphi_r = \frac{N\pi r^2}{S} = \left(\frac{h}{r} + 1\right)^{-2}.$$

At high concentrations of CNTs, the conductivity of the composite material will be determined by the electronic properties of CNTs. Multi-walled nanotubes exhibit the properties of conductors, while a fraction of single-walled CNTs are semiconductors. As a consequence, single-walled CNTs will have a lower electrical conductivity than multi-walled CNTs at equal concentrations.

Probably, the results[88] shown in Table 5 demonstrate ambiguous role of modifiers.

Table 5. Dependence of electrical conductivity (S cm^{-1}) of composites on the concentration of multi-walled CNTs and hexadecanoic acid.[88]

Nanotube concentration (mass %)	Multi-walled CNTs/$C_{16}H_{32}O_2$ mass ratio		
	2 : 1	1 : 1	1 : 2
0.1	3.6×10^{-16}	1.7×10^{-8}	3.0×10^{-16}
0.2	2.8×10^{-9}	7.1×10^{-7}	9.7×10^{-8}
0.3	1.4×10^{-6}	1.1×10^{-5}	8.2×10^{-6}

The efficiency of dispersion of CNTs by sonication depends on surfactants employed. To this end, hexadecanoic acid ($C_{16}H_{32}O_2$) was used.[88] If it was in deficiency (see second column in Table. 5), the degree of dispersion was insufficient. Therefore, the conductivity is low and the threshold concentration exceeds 0.1 mass %. Excess hexadecanoic acid (fourth column) probably increases the thickness of the adsorption layer, precludes intertube contacts and thus causes the threshold concentration of CNTs to increase. At optimum ratio of the dispersing agent and filler (third column), the threshold concentration was less than 0.1%. At the same time, the composite prepared with no hexadecanoic acid was characterized by a percolation threshold concentration of about 0.2 mass %.

The method of synthesis of CNTs determines their type and properties. Correspondingly, the properties of the composite material will depend on the nature of filler. In particular, a comparison was made[89] of composites filled with single-walled CNTs synthesized by high-pressure CO conversion on iron catalyst (HiPco) and laser ablation of graphite using an iron–nickel catalyst (L). The nanotubes were untreated and no surfactants were added. The nanotube parameters and the percolation threshold values are listed in Table 6.

The introduction of fillers into binders was accompanied by sonication of the systems under study. In some cases, the samples were exposed to sonication in the course of curing; in other cases, sonication was switched off. Experiments showed that the smaller the aspect ratio the larger the percolation threshold value. Additional sonication causes the percolation threshold to be almost doubled. This effect was explained by the possibility of reaggregation of CNTs when sonication is off during curing. Probably, aggregation mainly leads to extension of agglomerates and it is this factor that is responsible for the efficiency of formation of the percolation network.[90]

An epoxy-amine binder was mixed with multi-walled CNTs synthesized by CVD at a moderate temperature.[91] Straight nanotubes had narrow diameter (50 nm) and length distributions (17 ± 3 μm). The percolation threshold

Table 6. Parameters of single-walled CNTs and the percolation threshold values.[89]

Parameter	Single-walled CNTs synthesized by	
	HiPco	L
d/nm	1.1 ± 0.3	1.35 ± 0.15
l/nm	167 ± 90	516 ± 286
Percolation threshold (vol.%)		
no sonication	0.0085	0.0052
under sonication	0.023	0.010

of pristine nanotubes was found to be 0.0025% mass %, being much lower than that of CNTs in the initial state (highly entangled nanotubes).

A study[92] of the same system using nanotubes 10 and 43 μm long gave the percolation thresholds of 0.0021 mass % and 0.0039 mass %, respectively. The results obtained in Refs 91 and 92 contradict the theoretical predictions, namely, the percolation threshold increases with an increase in the aspect ratio. This effect was related to the rate of formation of the percolation network. An attempt to substantiate this hypothesis was made, involving experiments on curing of the matrix at different temperatures and shear rates under spinning. The composite with a CNT content of 0.01% obtained at room temperature with no shear deformation exhibited the properties of an insulator, namely, its conductivity increases as the frequency increases. Raising the curing temperature to 80 °C leads to the appearance of a plateau region in the frequency dependence of conductivity, which indicates the onset of dc conductivity. As the temperature increases, the conductivity also increases. The shear rate (50 and 200 rpm, respectively) has same effect on the system. The longer the nanotubes the lower their mobility; therefore, the rate of network formation decreases with an increase in the nanotube length. As a consequence, one gets an 'incorrect' dependence of the threshold concentration on the aspect ratio.

A comparison of the conducting properties of the epoxy polymers filled with multi-walled and single-walled CNTs revealed the advantage of the former.[93] The composite materials were prepared as reported earlier[91,92] and the single-walled CNTs were dispersed using a known technique[52] and a ball mill (in this case, shorter nanotubes were obtained). The multi-walled and single-walled CNTs that were only chemically dispersed and mechanically treated were characterized by the percolation thresholds of 0.0025 mass %, 0.05 mass % and 0.23 mass %, respectively. Probably, the last value is due to destruction of the nanotubes. The first two values differ by a factor of 20, although the single-walled CNTs at least compete with the multi-walled ones in aspect ratio, being dispersed much better. Seemingly, an important role in the network formation is played by the length of nanotube bundles (80 μm *vs*. a few micrometres) and the need to achieve the optimum degree of dispersion.

A marked illustration of the role of the boundary layer in the determination of conductivity is provided by the data reported in Refs 94 and 95. To increase the degree of dispersion of multi-walled CNTs, they were covalently functionalized with 3-glycidyloxypropyltrimethoxysilane[94] and noncovalently functionalized with polyoxyethylene gly-

col octylphenyl ether.[95] In the first case, the conductivity increased only slightly up to a CNT concentration of 0.5 mass %, although the percolation threshold of the pristine nanotubes was equal to 0.05 mass %. In the second case, the addition of surfactant had no effect on the percolation threshold value (Fig. 6).

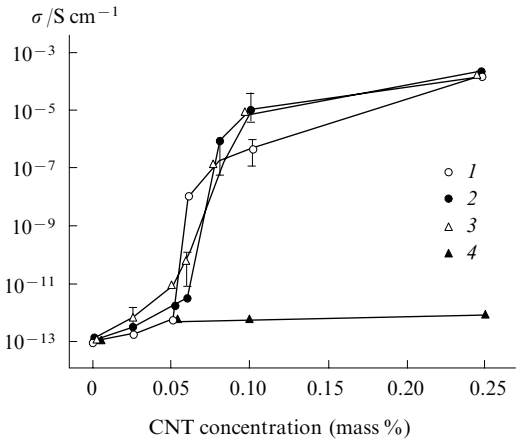


Figure 6. Conductivity of composites plotted *vs.* concentration of multi-walled CNTs.[94, 95]
Pristine CNTs (*1*); CNTs treated with 1% (*2*) and 10% (*3*) of polyoxyethylene glycol octylphenyl ether and silane (*4*).

This was confirmed in a study[96] whose authors compared the chemically equivalent agents and concluded that covalent functionalization which improves the mechanical properties of the composite material influences its conducting properties only slightly.

VI. Thermal conductivity of epoxy nanocomposites

According to the Wiedemann–Franz law, the thermal conductivity (λ) of a metal is proportional to its electrical conductivity

$$\frac{\lambda}{\sigma} = \frac{\pi^2}{3}\left(\frac{k}{e}\right)^2 T,$$

where k is the Boltzmann constant and e is the charge of an electron.

However, this regularity does not hold for epoxy composites whose conductivity is determined by CNTs. A study of systems with different-type CNTs showed[85] that in the concentration range from 0 mass % to 0.5 mass % (see Table 4), the electrical conductivity changes by seven orders of magnitude, whereas the thermal conductivity increases by at most 3% and even decreases in the system containing single-walled CNTs. A decrease in the thermal conductivity was also discovered in a comparative study[93] of multi-walled and single-walled CNTs dispersed in different manner (Fig. 7). For comparison, the calculated straight line *1* corresponding to the additive Rule of Mixtures is also presented.[97] Functionalization of CNTs leading to an increase in the degree of dispersion favours an increase in thermal conductivity, as was shown taking multi-walled CNTs modified with triethylenetetramine as an example.[98]

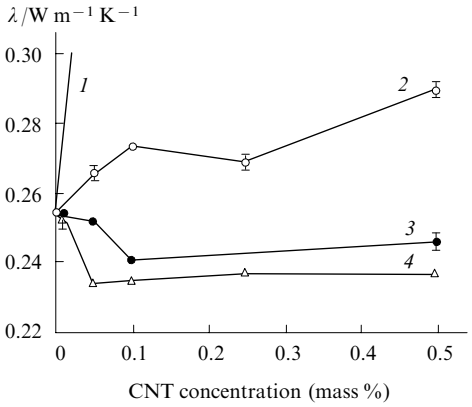


Figure 7. Thermal conductivity plotted *vs.* concentration of CNTs.[93]
The rule of Mixtures (*1*); multi-walled CNTs (*2*); single-walled CNTs dispersed using NaOH (*3*) and mechanically dispersed single-walled CNTs (*4*).

A fundamental difference of experimental data from the results of calculations is first of all due to the fact that the simple theory ignores the effect of the interface region.[99] The so-called Kapitsa thermal resistance estimated for CNTs as $\sim 8 \times 10^{-8}$ m^2 K W^{-1} is almost independent of the nature of the environment. A nonzero Kapitsa thermal resistance causes the theoretical thermal conductivity to decrease by orders of magnitude and the larger the specific surface area of the filler the greater this decrease. Unlike multi-walled CNTs, single-walled CNTs appear to be inefficient as agents for increasing the thermal conductivity of polymers.

VII. Mechanical properties of nanocomposites

The use of CNTs as reinforcing agents for epoxy polymers is assumed to be useful for solving some problems common to polymer composite materials, *viz.*, the dispersion of agglomerates and transfer of mechanical strain from the matrix to the filler through interface interactions. The first problem is usually solved by mechanical treatment of suspensions of CNTs in the presence of surfactants (see above). In the second case, one should take into account specific features of curing of the epoxy binder in the presence of CNTs used as filler as well as the chemical and physical structures of the matrix.

1. Unmodified carbon nanotubes

The surface energy of CNTs is rather high; therefore, their characteristic feature is adsorption of various molecules.[100] In this respect, components of epoxy binders present no exception. A molecular dynamics simulation[101] showed that the binding energy of diphenylolmethane diglycidyl ether (DMDGE) and 3,5-diethyltoluene-2,6-diamine (DTA) to single-walled CNTs is nearly 6 kJ mol^{-1}. The major contribution to adsorption comes from the $\pi-\pi$ interaction between aromatic nuclei of the sorbates on the one side and nanotubes on the other side.

One could expect that the adsorption interaction will influence the matrix structure and should first of all manifest itself in the kinetics of the matrix structure formation.

A differential scanning calorimetry (DSC) study on the kinetics of polycondensation of BADE and diethylenetri-

amine (DETA) in the presence of single-walled CNTs sonicated in an epoxy oligomer for 2 h was reported.[102] In the nonisothermal regime, the time of maximum heat generation decreases as the nanotube concentration increases. In the non-isothermal regime, the process had an autocatalytic character and the time needed to achieve the maximum speed also decreased with the nanotube concentration. The kinetic effects observed were explained by an increase in the thermal conductivity in the reacting system in the presence of CNTs rather than specific chemical interaction. Probably, such an interpretation is incorrect (see above about the effect of single-walled CNTs on the thermal conductivity).

Yet another point of view was reported in a study [103] on high-temperature isothermal curing of tetraglycidyl-4,4′-diaminodiphenylmethane with 4,4′-diaminodiphenyl sulfone in the presence of multi-walled CNTs. The kinetics was analyzed using the empirical Kamal equation [104]

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n, \qquad (7)$$

where α is the conversion of epoxy groups, t is time and the sum of the indices $m+n$ gives the total reaction order which usually equals two.

It was found that the constant k_1, which determines the initial reaction rate, increases while the corresponding activation energy decreases with an increase in the nanotube concentration. The autocatalytic constant k_2 is almost not influenced by nanotubes. The authors believe that these effects are due to the catalytic effect of the surface hydroxyl groups formed as a result of the oxidation during purification of CNTs.

Initial acceleration of the reaction under the action of different-type single-walled CNTs [105] and multi-walled CNTs [106] was reported (the effect was more pronounced when carboxyl-functionalized multi-walled nanotubes were used). In the former case, the binder was the system DMDGE + DTA, in the latter case, this was BADE + 2-ethyl-4-methylimidazole. The effect appeared to be weak. A similar result was obtained using a liquid-crystalline system [107] on curing of 4,4′-dihydroxy-α-methylstilbene diglycidyl ether with sulfanilamide.

The authors of all kinetic studies reported that the degree of completion of reactions somewhat reduced in the presence of CNTs.

A specific interaction of CNTs with products of the reaction in the epoxy-amine system containing hydroxyl groups cannot be ruled out either. Probably, this is the reason for retardation of the process in the final stage.

In a study [108] of the polycondensation of BADE with triethylenetetramine (TETA) the matrix structure was varied by changing the ratio of functional groups and the reaction duration, *i.e.*, the conversion. The modulus of the matrix changed correspondingly. The character of the interaction between the matrix and filler influenced the mechanical properties of the composite (Fig. 8).

Clearly, loosening of the network structure of the polymer and a decrease in its modulus should also cause the mechanical properties of the composite to deteriorate. The fracture character changes from brittle to plastic. At a specified shear strength of the interface layer, the nanotube will act as reinforcing agent for the low-modulus matrix at strains not exceeding the limiting values governed by the mechanical properties of the interface, whereas high strain in the high-modulus matrix will cause its fracture and pulling of nanotubes. But the authors believe that, probably, high mobility of chain fragments in an imperfect network provides close contacts between the filler and the matrix, thus forming a rather stable boundary layer, whereas the rigid matrix precludes it, especially with inclusion of shrinkage.

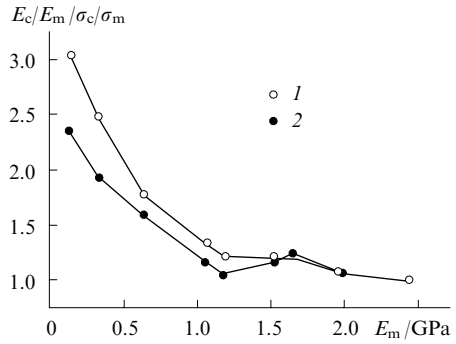


Figure 8. Efficiency of multi-walled CNTs as reinforcement materials plotted *vs.* structure of the epoxy matrix.[108]
Young modulus (*1*) and tensile strength (*2*). Concentration of CNTs is 0.5 mass %.

The results presented below are consistent with those considered above. Using a twofold advantage in functionality of amine (TETA) with respect to epoxide (BADE), a soft matrix with a Young modulus of 118 MPa was prepared.[84] The strain–stress curves of the pristine matrix and of the composites filled with multi-walled CNTs (concentrations 1 mass % and 4 mass %) are shown in Fig. 9 which clearly demonstrates the reinforcing effect of the unmodified multi-walled CNTs. The modulus becomes almost doubled (236 MPa) in the former case and nearly quad-

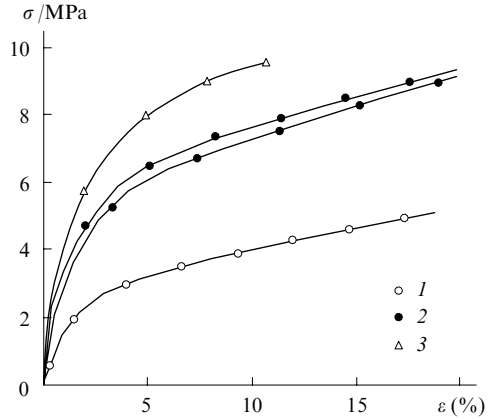


Figure 9. Stress–strain curves for epoxy matrix (*1*) and composite filled with multi-walled CNTs (*2* and *3*).
Nanotube concentration: 1 mass % (*2*) and 4 mass % (*3*).[84]

rupled (465 MPa) in the latter. Note that in the first case, the limiting deformation also increases.

A noticeable effect was also reported [109] for a sufficiently rigid matrix obtained on curing of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexylcarboxylate with 4-methyltetrahydrophthalic anhydride in the presence of multi-walled CNTs cleaned from impurities by successive washing with hydrochloric and nitric acids and then with water to a neutral reaction. A Raman spectroscopy study of the composites (Fig. 10) revealed no nanotube aggregation up to a concentration of 0.5 mass %. At a nanotube content of 1%, the D- and G-bands disappear, which suggests agglomeration of nanotubes. At the same time, the shift of the G- and D-bands increases as the nanotube concentration increases, thus indicating their interaction with the epoxy matrix.[110]

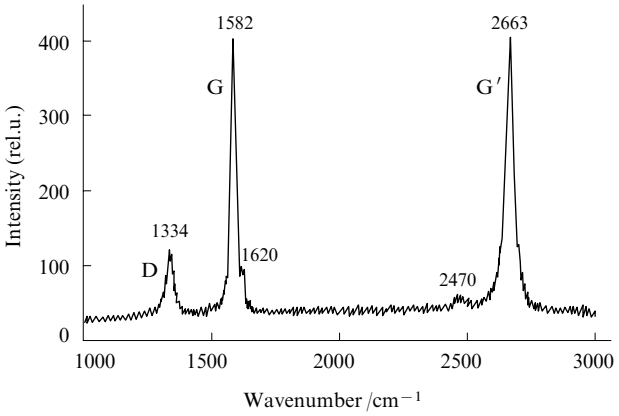


Figure 10. Raman spectrum of multi-walled CNTs.
The G-band corresponds to ordered network of C(sp^2) atoms, the D-band is due to local defects and corresponds to disordered network of C(sp^3) atoms and the G′ band corresponds to graphene in-plane vibrational mode.

Numerical data on the mechanical properties of composites are listed in Table 7. The most pronounced effect was obtained at a nanotube concentration of 0.05 mass %, then the properties are improved insignificantly, although the composite with a nanotube concentration of 0.5 mass % is characterized by the highest fracture energy. An increase in the strength is due to a rather strong interface interaction probably originating from the presence of COOH and OH groups on the CNT surface; these groups can react with epoxy groups under the curing conditions. Deterioration of the properties at a degree of filling of 1% is associated with agglomeration of nanotubes. At lower concentrations, one deals with a more or less uniform distribution of CNTs within the composite.

Table 7. Dependence of the strength properties of a composite on the concentration of multi-walled CNTs.[109]

Concentration of multi-walled CNTs (mass %)	σ /MPa	ε (%)	Cracking energy /N cm
0	31.9	2.38	196.0
0.05	55.9	3.07	245.0
0.1	55.0	3.57	273.6
0.5	62.0	3.60	490.0
1.0	58.4	3.00	372.4

Raman spectroscopy allows one not only to reveal the interface interaction, but also to estimate its intensity. For instance, a study was reported [111] of composite materials whose matrices were prepared by low-temperature curing of epoxy-novolac resin; two types of single-walled CNTs synthesized by different methods and multi-walled CNTs served as fillers. Calibration tests showed that stretching of the nanotubes causes the G′-band (wave numbers for various CNTs are somewhat different) to undergo a hypsochromic shift and that the larger the deformation the larger the shift. The stretching force applied to the sample of the composite led to deformation of the filler, the deformation was determined from the shift of the spectral band. Using this method, the apparent Young modulus of the nanotubes was estimated. Depending on the assumption of the character of their orientational distribution, the numerical values of the moduli were in the intervals 80 – 230 GPa for one type of single-walled CNTs, 780 – 2340 GPa for the other type of single-walled CNTs and 200 – 640 GPa for multi-walled CNTs. Taking into account the fact that the modulus of single-walled CNTs is a few TPa and that of multi-walled CNTs is 500 GPa, the last two composites provide almost ideal conditions for strain transfer from the matrix to the filler. In the first case, the interface layer seems to be insufficiently strong and stretching of the composite is accompanied by slip of nanotubes.

Yet another study [86] was carried out with two types, SW and XD, of single-walled CNTs about 1 and $\sim$10 nm in diameter, respectively, synthesized by different methods and used without additional purification. The matrix was obtained by curing of DMDGE with amine. The relaxation characteristics of the composites at 30 °C and a frequency of 1 s^{-1} are listed in Table 8.

As can be seen, no noticeable reinforcement is observed, *viz*., the E' values are close to those typical of the epoxy matrix. An increase in the loss modulus E'' is probably due to friction at the CNT/matrix and CNT/CNT interfaces. The authors believe that an increase in the glass transition temperature characterizes the role of the filler as an obstacle to the motion of polymer fragments.

Compared to tension, the flexural strength of fibrous composite materials is to a greater extent determined by the nature of the interface layer.[22] It was shown [112] that the flexural strength of a composite material cannot be increased by introducing multi-walled CNTs (2 mass %). Fracture of the composite is accompanied by pulling fibres out of matrix, which indicates a rather weak interface interaction. A similar result was obtained in another study.[113]

However, an investigation [114] of the effect of the concentration of unmodified multi-walled CNTs in a matrix synthesized by curing of epoxy-novolac resin with 4-methylhexahydrophthalic anhydride showed that a weak strengthening effect (nearly 10%) manifests itself only up to a nanotube concentration of 0.1 mass % (Fig. 11). An analogous result was obtained in a study [115] at a single-walled CNT concentration of 0.05 mass %.

Table 8. Relaxation properties of composites at 30 °C and a frequency of 1 s^{-1} (see Ref. 86).

CNT concentration (mass %)	SW single-walled CNTs			XD single-walled CNTs		
	E'/GPa	E''/MPa	T_g/°C	E'/GPa	E''/MPa	T_g/°C
0	2.8 ± 0.3	91.6 ± 12.3	129 ± 0.1	–	–	–
0.015	2.5 ± 0.1	101.6 ± 22.1	141 ± 1.2	3.0 ± 0.1	173.4 ± 9.3	140 ± 7.0
0.0225	2.7 ± 0.1	110.0 ± 23.2	148 ± 2.0	2.8 ± 0.2	117.9 ± 7.0	149 ± 1.0
0.03	2.9 ± 0.1	131.5 ± 21.5	149 ± 1.6	3.3 ± 0.2	175.1 ± 65.4	133 ± 1.4

Note. Notations are as follows: E' is the relaxation modulus and E'' is the mechanical loss modulus.

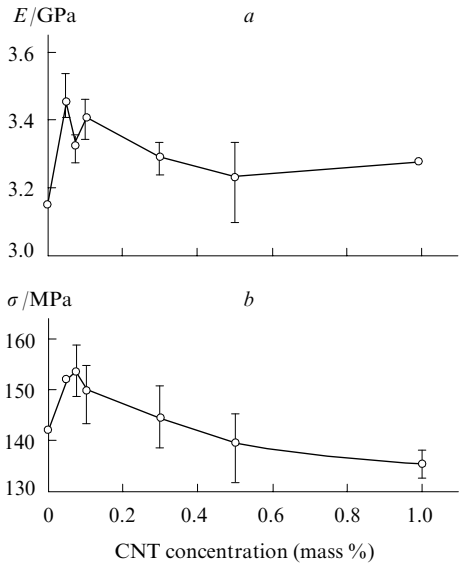


Figure 11. Bending test results: Young's modulus (*a*) and flexural strength (*b*) of a composite plotted *vs*. concentration of multi-walled CNTs.[114]

Table 9. Properties of composites based on the EPON and LY epoxy resins.[116]

Matrix	CNT concentration (mass %)	E_c/E_m	σ_c/σ_m	T_g/°C
Single-walled CNTs				
EPON	0.01	0.98	1.15	92
	0.05	1.08	1.18	93
Multi-walled CNTs				
EPON	0.05	1.02	1.18	93
	0.50	1.04	1.10	91
Single-walled CNTs				
LY	0.01	1.02	1.20	104
	0.05	1.03	1.35	103
Multi-walled CNTs				
LY	0.05	1.07	1.50	98
	0.50	1.07	1.70	90

It is believed [114] that aggregation is developed at CNT concentrations higher than 0.1 mass %. Greater reinforcement was achieved [116] at low concentrations of single-walled and multi-walled CNTs (Table 9) in the composites based on the epoxy resins EPON (EPON815/T403) and especially LY (LY564/HY560). The matrices exhibit similar properties (glass transition temperature is 90 and 105 °C, respectively, and the modulus at 20 °C is 2.8 and 2.9 GPa, respectively); however, the character of their interaction with CNTs is different.

The EPON-based polymer and the corresponding composite matrices exhibit almost identical relaxation properties (Fig. 12 *b*,*d*), *viz*., the peaks have equal width and the glass transition temperatures increase only slightly (see Table 9). At the same time, a low-temperature component appears and T_g decreases in the LY-based composites (Fig. 12 *a* and *c*).

A possible reason for this effect is selective adsorption of polymeric curing agent (polyetheramine) used in the LY binder. As a consequence, homogeneous distribution of reactants over the volume and uniformity of the matrix structure are violated. Also, it is believed [117] that adsorption of macromolecules on the nanotube makes its bond with the matrix stronger; this seemingly manifests itself in relatively high strength values.

An attempt to experimentally determine the shear strength of the interface layer at the multi-walled CNT/epoxy matrix interface led to a large scatter of data from 35 to 376 MPa.[118] Molecular simulation taking into account only the electrostatic and van der Waals interactions gave a value of 138 MPa.[119] The authors of another molecular simulation study [120] found that the energy of the interaction of single-walled CNTs with the epoxy matrix is nearly 500 kcal mol^{-1} and the shear strength of the boundary layer is about 75 MPa.

The adhesive strength of carbon, glass, organic fibres at the interface with some epoxy polymers varies from 35 to 55 MPa.[21] Therefore, CNTs are expected to be more efficient reinforcement materials for polymers than conventionally used cut fibres, especially taking into account the aspect ratio.

However, stripping of rather long nanotube fragments on bending failure of materials [112, 113] is more probably an indication of weak interface.

Thus, the results of experiments with unmodified CNTs give no grounds for unambiguous conclusions about the possibility of using this type of CNTs as fillers to reinforce epoxy polymers.

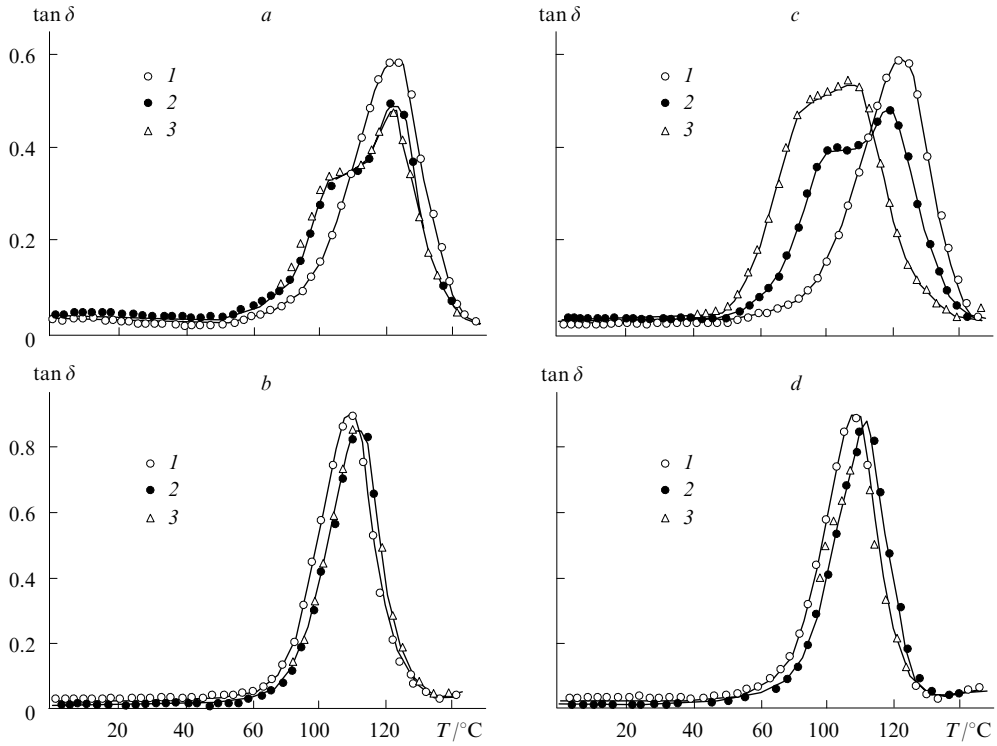


Figure 12. Temperature dependence of tan δ of composites based on the LY (*a*, *c*) and EPON (*b*, *d*) epoxy resins containing single-walled CNTs (*a*, *b*), and multi-walled CNTs (*c*, *d*).
Single-walled CNT concentration (mass %): 0 (*1*), 0.01 (*2*) and 0.05 (*3*). Multi-walled CNT concentration (mass %): 0 (*1*), 0.05 (*2*) and 0.5 (*3*).

2. Modified carbon nanotubes

To decrease the degree of aggregation of nanotubes and to improve their compatibility with binders, noncovalent and covalent modification (functionalization) is used.[45, 96] In the former case, low-molecular-mass and polymeric surfactants are efficient,[46, 49, 51, 96, 121] whereas the latter case involves a wide range of chemical reactions of mainly radical type.[45, 122] These approaches differ in efficiency of dispersion and, which is most important, in effect on the properties of composites. It was shown [96] that polyethyleneimine either used as surfactant or grafted on the surface of multi-walled CNTs influences the conductivity and mechanical properties of composites in different manner. The electrical conductivity in both systems decreases compared to the composite based on untreated CNTs, the decrease being larger in the case of grafting. At the same time, the Young modulus increases in the last-mentioned case, whereas noncovalent modification appeared to be inefficient. The last composite shows a higher thermal expansion coefficient in the rubbery state; this probably suggests a weaker interface interaction.

Covalent modification creates prerequisites for the formation of covalent bonds between CNTs and the matrix. A molecular dynamics simulation [123] showed that even at low bond concentration (one bond per 100 carbon atoms), the shear strength increases by more than an order of magnitude and causes the critical length of the nanotube to decrease.

At the same time, one should keep in mind that, unlike noncovalent modification, covalent modification introduces defects into the nanotube structure and thus deteriorates the mechanical properties. For instance, the introduction of $-$COOH groups by CNT oxidation leads to bending of nanotubes (Fig. 13).[124]

Grafting of molecules bearing functional groups capable of reacting with components of the binder onto CNTs should first of all affect the kinetics of curing. Indeed, analyses [125, 126] of the polycondensation of BADE with 4,4′-diaminodiphenylmethane using the Kamal equation (7) showed that functionalization of multi-walled CNTs with 4-aminobenzoic acid causes the k_1 value to increase more than 1.5-fold while the activation energy remained almost unchanged. A DSC study revealed that the temperatures corresponding to the maximum rate of curing for the binder, CNTs and NH_2-CNTs are respectively equal to 171, 171 and 158 °C at a nanotube concentration of 3%

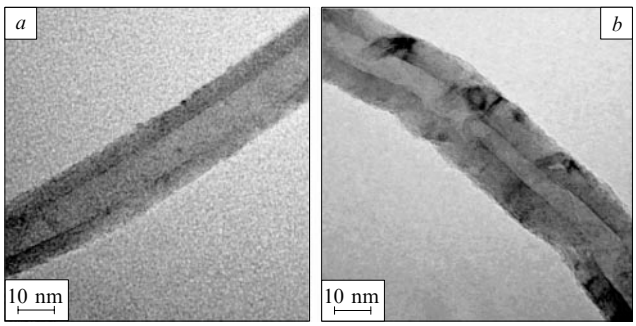


Figure 13. TEM micrographs of a pristine (*a*) and oxidized (*b*) multi-walled CNT.[124]

(Ref. 125) and to 170, 162 and 156 °C at a nanotube concentration of 1 mass %.[126]

Thus, the reaction is accelerated under the action of both aminated and untreated nanotubes (nanotube content is 1 mass %).

In most studies on the development of methods of reinforcement of epoxy polymers using CNTs, covalent modification of CNTs is aimed at introducing amino groups as components that react with epoxy groups of the binder.

Single-walled CNTs were treated with a dicarboxylic acid peroxide and then with bis(n-hexamethyleneamino)-methane.[127] The matrix was prepared by curing of BADE with aromatic diamine EPON W. The tensile strength data of the composites synthesized are listed in Table 10.

Table 10. Properties of composites based on untreated and modified single-walled CNTs.[127]

CNTs	CNT concentration (mass %)	E/GPa	σ/MPa	ε(%)
Matrix		2.026	83.0	6.5
Single-walled CNTs				
Untreated	1	2.123	79.8	5.8
Aminated	1	2.650	104	8.5
	4	3.400	102	5.5

As can be seen, the introduction of untreated nanotubes (1 mass %) somewhat increases the Young modulus of the composite compared to the unfilled matrix, but the tensile strength and relative elongation decrease. The introduction of the same concentration of aminated CNTs increases all three parameters. However, further increase in the nanotube concentration to 4 mass % leads to embrittlement of the material. In this case, a possible reason for the decrease in the limiting deformation is the accumulation of defects (micropores) owing to increased viscosity of the initial system.

Dynamic mechanical analysis (frequency 1 s^{-1}) provides a convincing proof of the reinforcing effect of CNTs.

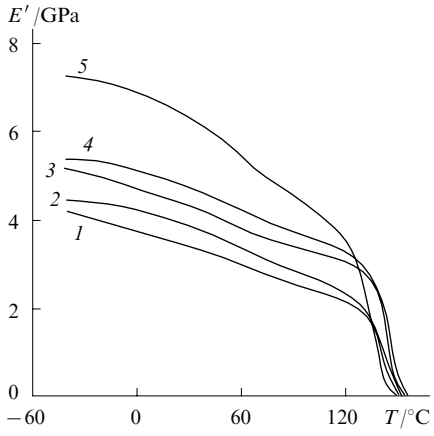
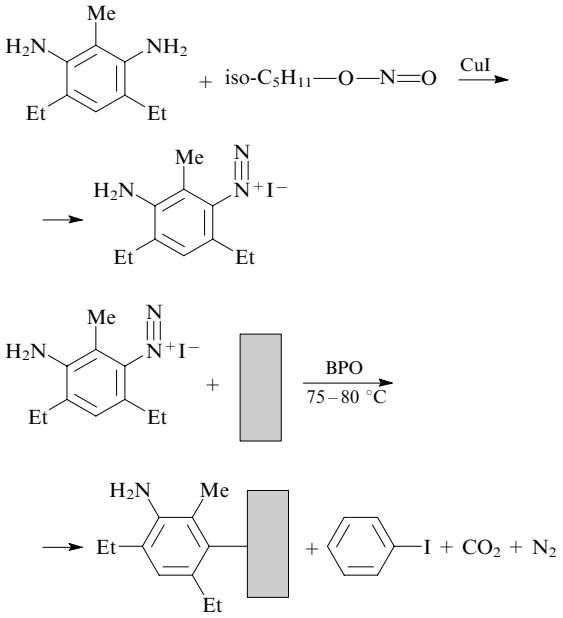


Figure 14. Temperature dependences of the relaxation moduli of epoxy polymers.[127]
Matrix (*1*); pristine single-walled CNTs (mass %): 1 (*2*) and 4 (*3*); and aminated single-walled CNTs (mass %): 1 (*4*) and 4 (*5*).

Figure 14 presents the temperature dependences of the real part of the dynamic modulus. It significantly increases in the whole temperature interval of existence of the glassy state, especially in the case of covalent modification. A change in the glass transition temperature at the maximum concentration of functionalized nanotubes (curve *5*) was related to violation of the equifunctionality due to amino groups of the filler.

Fragments containing amino group (*e.g.*, 3,5-diethyltoluylene-2,6-diamine) were grafted [128] using the diazotization reaction.



BPO is benzoyl peroxide.

The chemical properties of the matrix prepared by polycondensation of DMDGE and TDA and of the composites containing untreated and functionalized single-walled CNTs (0.5 mass %) are listed in Table 11.

Table 11. Mechanical properties of composites containing single-walled CNTs (0.5 mass %).[128]

System	E/GPa	σ/MPa
Matrix	2.0 ± 0.1	72.6 ± 2.3
Pristine CNTs	2.3 ± 0.21	71.5 ± 2.1
Modified CNTs	2.5 ± 0.18	88.5 ± 3.5

As in the preceding case, the Young modulus increases at low concentrations of pristine CNTs, but the tensile strength decreases due to a decrease in the limiting deformation. Functionalization causes improvement of all properties.

A shear strength at the interface equal to 306 MPa was obtained [128] assuming that nanotubes do not form clusters and that grafting leads to formation of one bond per 25 carbon atoms on the average.

Thus, there will not be a large error if we assume that covalent bonds make the single-walled CNT – epoxy matrix interface layer from 2 to 5 times stronger.

A study [129] was reported on the role of the specific surface area (s) of CNTs, which is inversely proportional to the nanotube diameter (d),

$$s = \frac{4}{\rho d},$$

where ρ is the nanotube density. The larger the s value the stronger the nanotube/matrix interaction and therefore one should expect a higher efficiency of nanotubes as reinforcement material. Indeed, the Young modulus of the composite is directly related to the surface area of nanotubes which was calculated from their diameters and concentration (Fig. 15).[130]

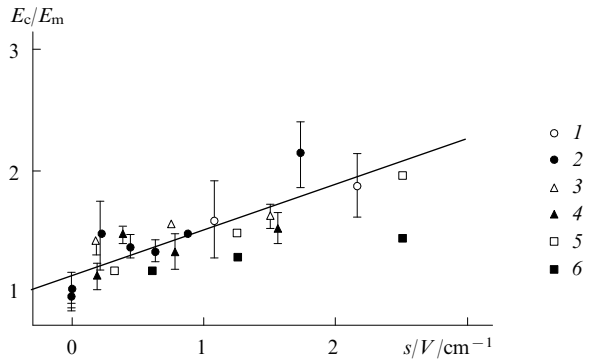


Figure 15. Young modulus of a composite material based on polyvinyl alcohol plotted *vs.* surface area of CNTs;[130]
d/nm: 2.8 (*1*), 14 (*2*), 16 (*3*), 15 (*4*), 24 (*5*) and 9 (*6*).

As can be seen, a linear law holds quite correctly in all cases. The exception is the results for data set *6*. At the calculated nanotube diameter of about 1 nm, measurements gave an average value of 9 nm (*i.e.*, nanotubes are agglomerated). But even in this case, the moduli appeared to be underestimated.

At the same time it should be noted that the Young modulus of an individual CNT is inversely proportional to its diameter.[6] Therefore, this regularity can be due to just this feature. The Young modulus of a bundle of single-walled CNTs is underestimated because the covalently nonbonded nanotubes can slip relative to one another when loaded, *viz.*, the shear modulus decreases from a few GPa to some fractions of a GPa as the aggregate size increases.[131]

Clearly, single-walled nanotubes form even larger bundles with larger diameters. Therefore, a large initial surface area can make dispersion difficult. In addition, curing of the matrix is accompanied by additional aggregation of CNTs, a kind of local phase decomposition induced by the reaction.[132]

It is this phenomenon that was investigated in a comparative study [129] of single-, double- and multi-walled CNTs with the specific surface areas of 1300, 700 and 200 m^2 g^{-1}, respectively. The most homogeneous system was formed in the second case. Double-walled CNTs appeared to be the best reinforcing agents for the epoxy polymer. The mechanical properties of the composites improved when using nanotubes functionalized by ball milling in ammonia atmosphere (Fig. 16). The nanotubes had little effect on the

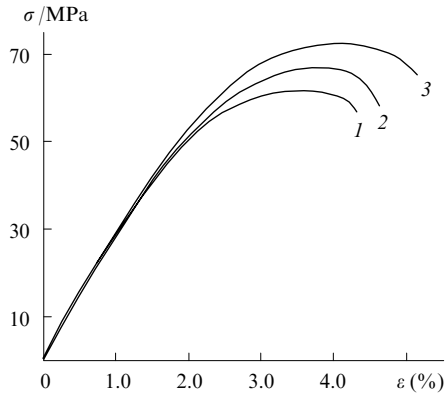


Figure 16. Stress–strain curves of epoxy matrix (*1*) and composites containing pristine (*2*) and functionalized (*3*) double-walled CNTs (0.3 mass % in both cases).[129]

Young modulus, but the tensile strength and the relative elongation were appreciably improved, with clearly seen forced elasticity.

Purified multi-walled CNTs were treated [133] with a mixture of nitric and sulfuric acids and then propionic acid was grafted by radical addition. Subsequent reaction of these nanotubes with hexamethylenediamine gave amino-functionalized nanotubes. As can be seen from the concentration dependences of the tensile strength and impact viscosity shown in Fig. 17, the composites containing amino-functionalized CNTs exhibit better properties than the composites filled with unmodified nanotubes at all concentrations. Clearly, grafted amino groups react with

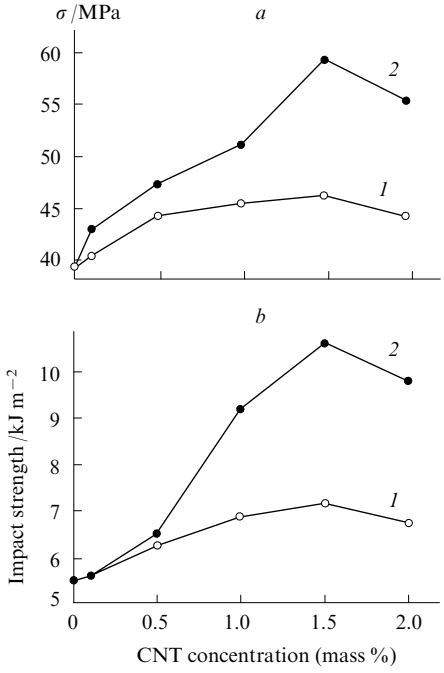


Figure 17. Tensile strength (*a*) and impact strength (*b*) of epoxy composites plotted *vs.* concentration of purified (*1*) and amino-functionalized CNTs (*2*).[133]

the epoxy groups of the binder and thus covalently bind the CNTs to the matrix.

Purified multi-walled CNTs were also treated with a mixture of nitric and sulfuric acids and then boiled in a mixture of $SOCl_2$ and dimethylformamide.[134] The nanotubes were cleaned from excess reactants and treated with triethanolamine. Thus, in principle, the nanotubes were the same as those used in the preceding case, but the matrix was fundamentally different. In Ref. 133, curing was achieved through polycondensation, while in Ref. 134, BADE was polymerized using triethanolamine as catalyst. The composites containing purified CNTs (0.05 mass %) treated with a mixture of acids and triethanolamine showed an impact strength of 15.3, 15.7 and 23.1 kJ m^{-2}, respectively (*cf.* 11.7 kJ m^{-2} for the initial polymer). However, the efficiency of the COOH-modified nanotubes is slightly different from that of the untreated ones. At the same time, amination of CNTs allows one to significantly improve the tensile strength of the composite material.

Multi-walled CNTs were treated with a mixture of aminobenzoic and polyphosphoric acids.[125] The epoxy matrices (BADE + 4,4′-methylenedianiline) and the composites containing untreated and functionalized CNTs (3 mass %) had the following characteristics: the moduli of the composites increased by 32% and 53% and the flexural strength increased by 17% and 28%, T_g of the matrices and composites is 189, 190 and 199 °C, respectively.

Single- and multi-walled CNTs were treated with a mixture of nitric and sulfuric acids, which resulted in the appearance of surface carboxyl groups.[132] These groups were esterified with phenyl glycidyl ether. The matrix was obtained by curing BADE with polyether triamine. At a frequency of 10^{-1} rad s^{-1}, the relaxation moduli of the composites containing pristine single-walled CNTs and the single-walled CNTs bearing carboxyl and ester groups (1 mass %) were in a 1 : 3.3 : 6.3 ratio; the terms of this proportion somewhat increased with frequency. Different treatment procedures affect the structure of the boundary layer in different manner, which also manifests itself in the relaxation spectra (Fig. 18).

The composites based on both single-walled and multi-walled CNTs exhibit a high-temperature transition typical of the matrix. But in the case of the pristine and COOH-modified CNTs, an additional transition at a lower temperature is observed. This points to a structure whose defectiveness is higher than that of the matrix and which is seemingly localized within the interface layer. It was assumed that the observed effect is due to selective adsorption of the epoxy oligomer on nanotubes, which is impossible in the presence of ester fragments on the surface. Note that in the case of single-walled CNTs, the effect is more pronounced than in the case of multi-walled nanotubes. This is probably due to the fact that the single-walled nanotubes were modified to a greater extent (8.6% *vs.* 4.9% with respect to carboxyl groups and 21.1% *vs.* 13.7% with respect to the ester fragments).

The amino group is the best reactant for the formation of covalent bonds between CNTs and the epoxy matrix. However, other methods can also be used. As shown above, CNTs are often treated in such a manner that grafted carboxyl groups appear. In particular, nanotubes are purified with a mixture of sulfuric and nitric acids which is a strong oxidant leading to the formation of COOH groups.

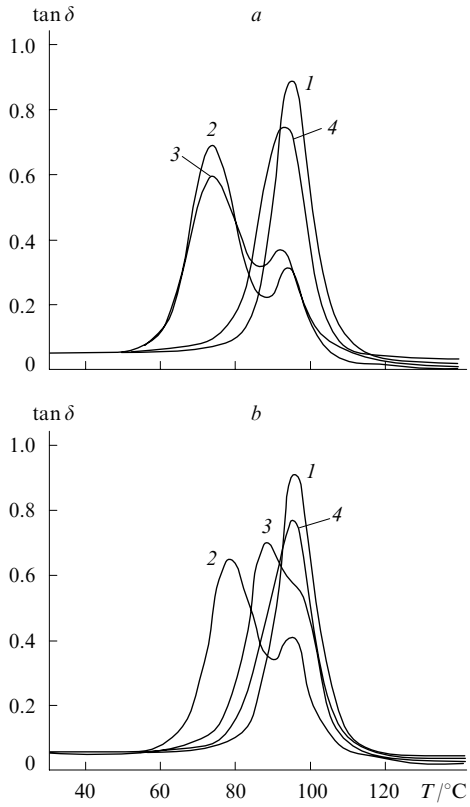
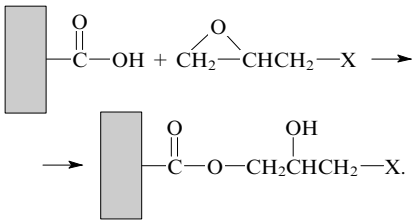
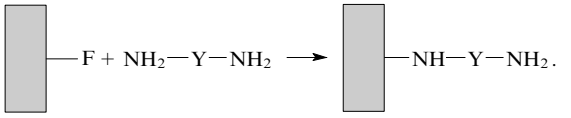


Figure 18. Temperature dependences of tan δ for epoxy matrices and composites filled with single-walled (*a*) and multi-walled (*b*) CNTs (nanotube content is 1 mass %).[132]
Epoxy matrix (*1*), untreated CNTs (*2*), COOH-modified CNTs (*3*) and esterified CNTs (*4*).

It is believed[115, 135] that they react with epoxy groups as follows:



High-temperature treatment of CNTs with gaseous fluorine leads to formation of C—F bonds. It is believed[135] that the fluorine atom reacts with the amino group of the curing agent



It was shown[135] that the modulus and tensile strength of the composite (matrix BADE + 3,5-diethyltoluylene-2,5-diamine) filled with F-modified single-walled CNTs increased to a greater extent than that of the pristine nanotubes.

VIII. On the mechanism of polymer reinforcement with carbon nanotubes

The mechanical properties of low-filled composite materials are described assuming that the Rule of Mixtures (3) holds.[22,24] In this case, the modulus, E_c, of the composite is given by

$$E_c = \eta E_t \varphi_t = E_m(1-\varphi_t), \quad (8)$$

where the coefficient η takes into account the character of the spatial distribution of nanotubes, E_t and E_m are the Young moduli of CNTs and matrix, respectively, and φ_t is the volume fraction of the filler. For randomly distributed orientations, one has $\eta = 0.2$.[25]

It follows that the relative increase in the modulus is proportional to the volume fraction of CNTs

$$\frac{E_c - E_m}{E_m} = \frac{\eta E_t - E_m}{E_m}\varphi_t . \quad (8a)$$

Relation (8a) shows that the larger the difference $\eta E_t - E_m$ the higher the efficiency of reinforcement. In other words, the more rigid the matrix the lower the efficiency; this is consistent with the published data [108,136] (see Fig. 8). However, this is essentially qualitative agreement. Indeed, assuming that $E_m = 2.5$ GPa,[108] $E_t \sim 1$ TPa and $\eta \approx 0.2$, the difference is far from approaching zero, although there is no reinforcement effect (see Fig. 8). Moreover, the Young modulus, E_t, of single-walled CNTs (1 mass %) calculated for a low-modulus matrix using expression (8) and the published data [136] is at least three orders of magnitude lower than the expected value (Table 12). At the same time, calculations for a high-modulus composite give a realistic result (456 GPa).

At the same time, both systems show a qualitative correspondence, *viz*., the modulus of nonfunctionalized nanotubes is much lower than that of functionalized nanotubes; this indicates a poorer strain transfer from the matrix to CNTs.

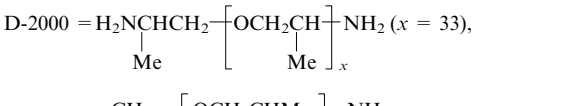
A study [136] was carried out using multi-walled CNTs 30 to 50 nm in diameter and 1 to 5 μm long. Thus, the critical concentration determined from expression (6) should be much higher than 1% (this value was reported in that publication). Therefore, one would expect that nanotubes in these systems are not aggregated. The results obtained in Ref. 137 showed that criterion (6) is not sufficient. Indeed, agglomeration of multi-walled CNTs having a length of 1.2 μm and a diameter of 16.6 nm should occur if their volume fraction exceeds 0.11. However, a linear increase in the modulus is observed until a CNT concentration of about 0.001 mass %. At higher concentrations, this regularity violates. It is commonly accepted that the linear region corresponds to the 'functioning' of individual nanotubes, whereas the nonlinear region is governed by nanotube aggregates. Probably, the boundedness of criterion (6) is due to the fact that the Flory theory [80] takes into account the excluded volume but ignores mutual attraction between rods (nanotubes).

Thus, the correctness of the Rule of Mixtures can be verified only at the lowest CNT concentrations ($< 0.1\%$). Unfortunately, there are almost no published data for epoxy composites. Therefore, we will consider the results obtained in Ref. 129 (Table 13).

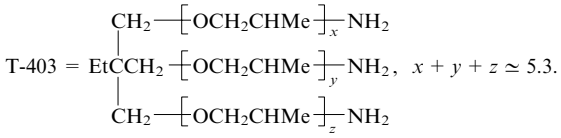
Table 12. Calculated values of the moduli of CNTs according to Ref. 136.

System	E_m /MPa	E_t /GPa
BADE/D-2000 matrix		
Matrix	1.89	–
Untreated CNTs	1.97	0.042
Functionalized CNTs	2.41	0.262
BADE/T-403 matrix		
Matrix	2161	–
Untreated CNTs	2166	5
Functionalized CNTs	2250	456

Note. Notations are as follows:



D-2000 = $H_2NCHCH_2(OCH_2CH)_xNH_2$ ($x = 33$), with Me groups.



T-403 = $EtC(CH_2(OCH_2CHMe)_xNH_2)(CH_2(OCH_2CHMe)_yNH_2)(CH_2(OCH_2CHMe)_zNH_2)$, $x + y + z \simeq 5.3$.

Table 13. Calculated values of the modulus E_t (according to Ref. 129).

CNTs	Concentration (mass %)	E_c /GPA	E_t /GPA
Single-walled CNTs [a]	0.5	2.3	300
Single-walled functionalized CNTs [a]	0.5	2.5	500
Single-walled CNTs	0.05	2.68	833
	0.1	2.69	473
	0.3	2.81	368
Double-walled CNTs	0.1	2.785	945
	0.3	2.885	490
	0.5	2.79	204
Double-walled amino-functionalized CNTs	0.1	2.61	68
	0.3	2.94	588
	0.5	2.98	392
Multi-walled CNTs	0.1	2.78	918
	0.3	2.765	290
	0.5	2.61	23
Multi-walled amino-functionalized CNTs	0.1	2.88	1439
	0.3	2.82	380
	0.5	2.82	221

[a] According to Ref. 128.

The calculated values of the modulus E_t decrease with an increase in the CNT concentration. Expression (8a) used to calculate the E_t value does not include the possibility of agglomeration of nanotubes. Otherwise, assuming that the modulus of a composite is proportional to the surface area rather than to the volume fraction of the filler, the decrease in E_t with an increase in concentration can be explained by an increase in the effective diameter of aggregates and, consequently, a decrease in the surface area. In the case of single-walled CNTs, agglomeration is most pronounced, namely, the smaller the nanotube diameter the higher the

CNT – CNT binding energy.[138] Functionalization plays a dual role. On the one hand, it favours dispersion. On the other hand, it provides efficient strain transfer from the matrix to the filler. Therefore, the corresponding E_t values increase.

The formation of matrix is unavoidably accompanied by phase decomposition induced by chemical reactions.[139, 140] Indeed, analysis of the Raman spectra of single-walled CNTs showed that the degree of their dispersion in a composite decreases as follows: COOH-modified > pristine > ester-modified CNTs.[132] In the initial binder, the highest degree of dispersion is found for the ester-modified CNTs. Therefore, curing is accompanied by an increase in the degree of nanotube aggregation (in essence, local phase decomposition).

At the same time, noteworthy are high E_t values obtained for double-walled and multi-walled nanotubes (concentration 0.1 mass %); in the free state, such nanotubes are characterized by the Young moduli ranging from 20 to 600 GPa. Probably, this fact was first reported by Bai.[141] According to his calculations, the E_t values were 2.21 and 1.21 TPa at a volume fraction of multi-walled CNTs of 0.0025 and 0.005, respectively, in the matrix prepared by curing of BADE with triethylenetetramine.

Similar results were also reported for some other polymer composites. For example, calculations using expression (8a) and the data presented in Fig. 19 give $E_t \approx 3$ TPa, which is too high for multi-walled CNTs. It follows that the simple Rule of Mixtures is inapplicable even in the concentration range corresponding to unaggregated CNTs.

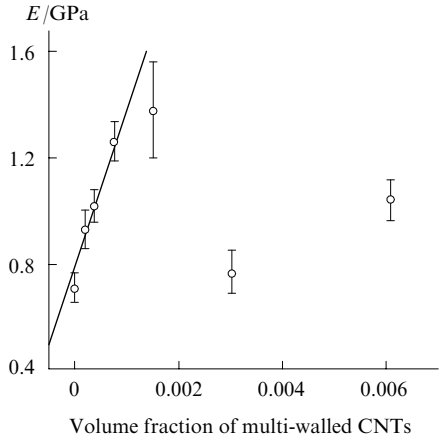


Figure 19. Young's modulus of a composite with polyethylene matrix plotted *vs.* concentration of multi-walled CNTs.[137]

Difficulties in the interpretation of polymer reinforcement with CNTs within the framework of classical concepts[6, 22] caused the introduction of the term 'pseudoreinforcement'.[25] This means that, physically, nanotubes modify rather than reinforce the matrix. The problem of the influence of CNTs on curing of the matrix was discussed above. A sure evidence of the effect of filler on the structure of the epoxy network is provided by the results obtained in Ref. 134 (see Fig. 20), namely, an increase in the concentration of multi-walled amino-functionalized CNTs from 0 mass % to ~0.75 mass % causes the glass transition temperature of the composite to increase by more than 20°.

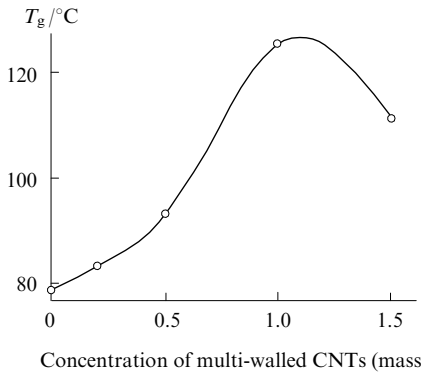


Figure 20. Glass transition temperature of epoxy composite plotted *vs.* concentration of multi-walled CNTs.[134]

In the composites based on semi-crystalline polymers, nanotubes act as centres of crystallization and change the rate of the process and the limiting degree of crystallization.[5] Coleman *et al.*[142] showed that the degree of crystallinity (n) of polyvinyl alcohol increases with an increase in the concentration of multi-walled CNTs as follows:

$$n = \varphi_t\left(\frac{b^2}{r^2} + 2\frac{b}{r}\right) + n_0\,,$$

where φ_t and r are volume fraction and radius of CNTs, b is the thickness of the matrix crystalline layer adjacent to the nanotube and n_0 is the initial degree of crystallinity of the polymer. A comparison with experimental data gave $b/r \approx 2.77$, *i.e.*, if multi-walled CNTs are 15 nm in diameter, the parameter b is 21 nm. Such a large value suggests a long-range action of nanotubes as centres of crystallization.

Calculations using the dependence of the Young modulus of the composite on the concentration of multi-walled CNTs and the Rule of Mixtures, gave $\eta E_t \simeq 2$ TPa.[142] Note that a lower-modulus matrix (*e.g.*, chlorinated polypropylene) is characterized by $\eta E_t \simeq 0.19$ TPa. In this case, the 16-nm thick layer surrounding the nanotube was formed by grafting of chlorinated polypropylene on lithium-functionalized CNTs.

Taking into account these facts, it was concluded[142] that the classical theories developed to describe fibrous composite materials are inapplicable to the systems containing CNTs as reinforcing fillers. At the same time, an attempt was made to use a conventional approach to describe the results of tensile strength experiments.

The equation ‡

$$\sigma_c = \left(\frac{l\tau}{d} - \sigma_t\right)\varphi_t + \sigma_m\,,$$

where σ_c, σ_t and σ_m are the strengths of the composite, nanotubes and matrix, respectively; τ is the shear strength of the interface layer between the nanotube and matrix, and

‡ This equation refers to composites filled with unidirectionally aligned long fibres. Vagner's correction for nanotubes[143] has the form:

$$\sigma_t = \frac{2\,l_{cr}\tau}{D}\left(1 - \frac{d^2}{D^2}\right)^{-1},$$

where d and D are the inner and outer nanotube diameter, respectively.

$$\sigma_t = \frac{2\, l_{cr}\tau}{d},$$

gives a too large τ value, *viz*., 350 MPa. Direct experiments showed that fracture develops through pulling of CNTs surrounded by a layer whose thickness is approximately equal to b out of the composite rather than across the nanotube–matrix interface. Taking into account this fact, the calculated τ value decreases to $\sim$180 MPa but still remains somewhat higher than the values typical of covalently nonbonded systems. Clearly, a physically correct model for polymer reinforcement with carbon nanotubes should take into account the structure, properties and eventually the role of the near-surface layer in the matrix.

* * *

Similarly to other polymer composite materials, obtaining a maximum reinforcement effect for epoxy polymers filled with carbon nanotubes requires the following:

— attainment of a maximum possible degree of dispersion of CNTs by combining chemical and mechanical treatment procedures;

— the use of CNTs with maximum aspect ratios provided by the nanotube diameter rather than length, because the longer the nanotubes the more difficult their dispersion; the CNT diameter and length should be chosen taking account of the critical fibre length at fracture of the composite in such a manner that $l_t \gg l_{t\,cr}$;

— the use of CNTs with a minimum degree of bending;

— functionalization of CNTs to provide a maximum possible reinforcement of the interface layer; one should also take into account specific features of the matrix curing procedure.

The concentration of CNTs should be chosen from the standpoint of optimization of the Young modulus, strength and relative elongation. As shown above, the best results are obtained for low-filled systems. It should be noted that data for epoxy composites containing less than 0.1 mass % of CNT are scarce, so there is no question of optimum.

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[a] — *Mendeleev Chem. J. (Engl. Transl.)*
[b] — *Russ. Metallurgy (Metally) (Engl. Transl.)*
[c] — *Physics-Uspekhi (Engl. Transl.)*