Physics of the Solid State, 2024, Vol. 66, No. 4

13,08

Changing the Thermal Conductivity of the Percolation Network of Carbon Nanotubes Through Functionalization

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Received December 23, 2023
Revised February 16, 2024
Accepted February 29, 2024

A study on the dependence of the thermal conductivity of percolation systems of carbon nanotubes (CNTs) on the type and degree of functionalization, number of defects has been carried out. The influence of the most commonly used $-$COOH, $-$OH and $-$CONH$_2$ groups has been studied. A nonlinear dependence of conductivity on the number of functional groups has been detected. A small number of functional groups can improve conductivity, while a large number reduces it. We assume the existence of competing processes that increase thermal conductivity (changes in the geometry of CNTs, improved contact between them) and increase phonon scattering (the appearance of defects and scattering centers). The data can be used for manipulating the thermophysical properties of CNTs, as well as selecting the optimal degree of functionalization while developing composites and nanodevices.

Keywords: carbon nanotubes, thermal conductivity, functionalization, percolation network.

DOI: 10.61011/PSS.2024.04.58208.277

1. Introduction

The thermal conductivity of carbon nanotubes (hereinafter CNT) can vary and is determined by its geometry and the number of defects. CNTs are often functionalized before use, i.e. radicals $-$OH, $-$COOH, $-$CO are covalently chemically attached. Most often, radical addition occurs during a reaction involving oxidants (HNO_3, H_2O_2, $KMnO_4$) [1]. This procedure simultaneously changes the electrical conductivity, thermal conductivity and sorption capacity of CNTs, adhesion to the polymer, which must be taken into account when creating composites. At the moment, there are no detailed comprehensive studies of the impact of the number of functional groups and their type on the properties of CNTs, and in studies of composites with the addition of CNT [2–7], it is often customary to simply state the fact that properties changed for the better as a result of functionalization. This is explained in [3,6] by more efficient dispersion, it is explained by the improved agglomeration kinetics in [5], it is explained in [2,4,7] by the fact that the functional group covalently bound CNT to the polymer matrix.

It was found in [8,9] in the result of modeling of the properties of single-walled CNT that the thermal conductivity of CNTs in the presence of functional groups always decreases with an increase of their number. The experiment in [10] also showed that the functionalization of single-walled CNTs worsened the thermal conductivity of the composite, while the functionalization of multi-walled CNTs slightly worsened the thermal conductivity of the composite. It is also stated in [11] that the thermal conductivity of single-walled CNTs deteriorates as a result of functionalization.

The dependence of the thermal conductivity of percolation systems of carbon nanotubes (hereinafter CNT) on the type and degree of functionalization was studied in this paper. The impact of the most frequently used functional groups of $-$COOH, $-$OH and $-$CONH$_2$ type was studied. These data can be used to control the thermophysical properties of CNTs, as well as to select the optimal degree of functionalization in the development of composites and nanodevices.

2. Materials and methods

CNTs of the grades „Taunit“, „Taunit-M“, „Taunit-MD“ and „Tuball“ were studied in this paper, their characteristics are given in the table. The reactions well-known in the literature were used for their functionalization: attachment of groups$-$COOH [12] (CNT heating in solution of $KMnO_4$ at $T = 64^\circ$C, the degree of functionalization was determined by the CNT/$KMnO_4$ mass ratio, the ratio varied from 0.2 to 12), — OH groups [13] (heating in 30% hydrogen peroxide at $T = 100^\circ$C, the degree of functionalization was determined by the reaction time, from 20 to 180 min), heating of CNT-COOH in ammonia vapor at $T = 250^\circ$C for 12 h to get $-$CNT-CONH$_2$ [1]. The presence of functional groups was determined by conductometric titration.

The thermophysical properties of the obtained CNTs were measured using the IT-Lambda-400 thermal conductivity meter with an accuracy of 5%. The measurements were carried out at a sample temperature of 50$-$60°C. The sample was prepared for measuring thermal conductivity

Characteristics of carbon nanoparticles according to manufacturer's data

Characteristic of	„Taunit“	„Taunit-M“	„Taunit-MD“	„Tuball“
Outer diameter, nm	20−50	10−30	8−30	1.6
Inner diameter, nm	10−20	5−15	5−15	1.2
Length, μm	2	≥ 2	≥ 20	> 5
Admixtures, %	≤ 10	≤ 5	≤ 5	< 15
Specific surface, m^2/g	≥ 160	≥ 270	≥ 270	> 400
Bulk density, g/cm^3	0.3−0.6	0.025−0.06	0.025−0.06	> 0.02
Price for 1 g, rub.	~ 50	175	175	800

as follows: the weighed quantities of CNT were pressed on hydraulic press PVG-20 at a pressure of up to 12 MPa, after which they were kept under pressure for 15 min. The resulting tablets had a diameter of 15 mm. The weight of the sample was selected in such a way that the density of the sample in the measured series was practically the same. The principle of the method is to measure the temperature differences on the sample and the working layer of the heat meter in the monotonous heating mode. The sample is placed between the copper rod and the contact plate of the IT-lambda-400 thermal conductivity meter. Next, the IT-lambda-400 thermal conductivity meter is turned on and the test sample is heated to a predetermined temperature in it, the thermal conductivity was calculated from the temperature difference on the upper and lower surfaces of the sample according to the documentation attached to the device.

3. Results and discussion

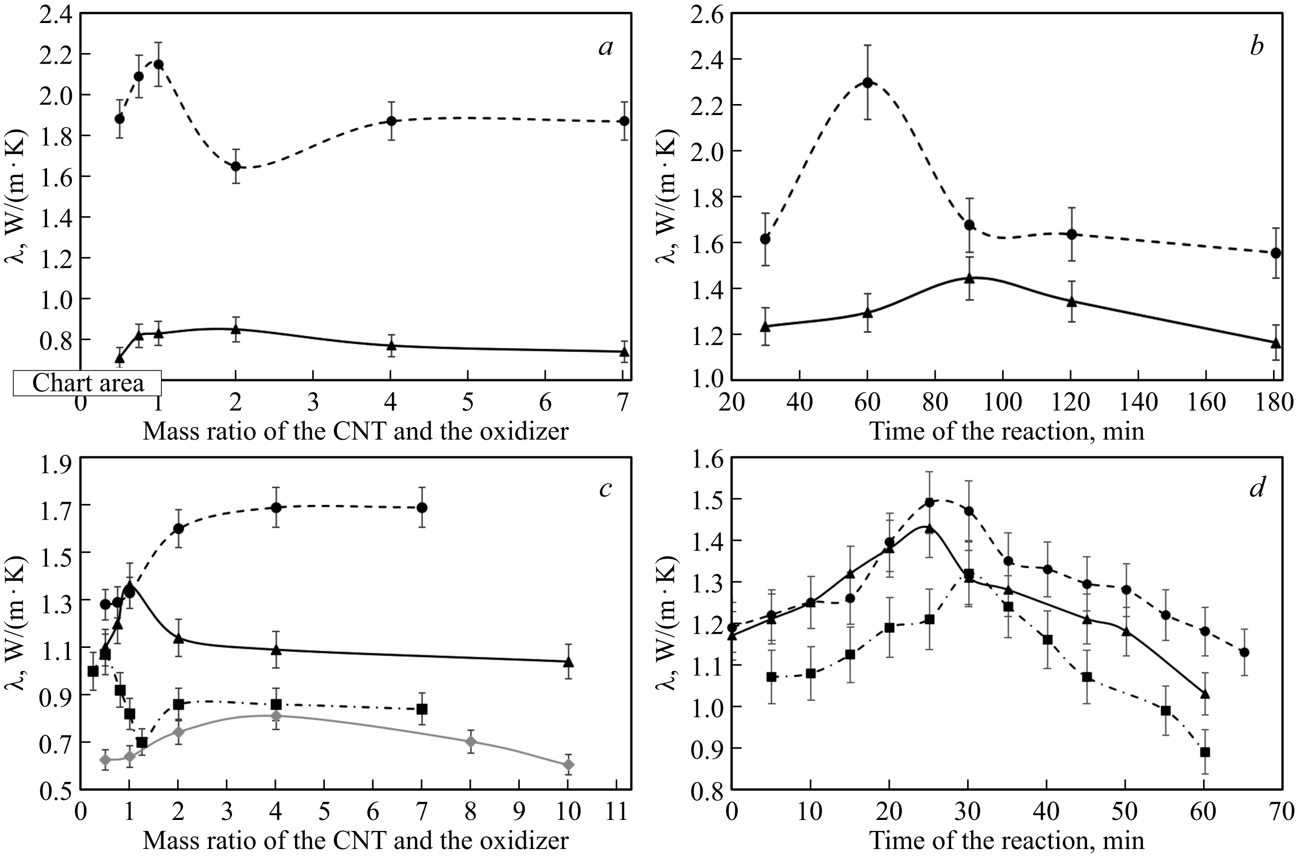
The obtained data (Figure) suggest that the qualitative type of dependence of thermal conductivity on the degree of functionalization is similar for different types of functional groups and multilayer CNTs. The dependence can be divided into two sections.

Section A — the thermal conductivity increases with an increase of the number of functional groups. CNT is cleaned of impurities (amorphous carbon, metal catalyst nanoparticles) during oxidative functionalization. The removal of the amorphous phase should increase the thermal conductivity, since the amorphous carbon among CNT worsens the contact between them. The geometry of CNTs changes [14], and this always results in the changes in interatomic distances, structure and vibrational modes. CNT agglomerates increase their density, as they are now connected not only by weak Van Der Waals forces, but also by a stronger interaction between polar functional groups. In these composites, CNTs are dispersed more evenly, forming a more homogeneous percolation network at a lower concentration.

Section B — a decrease of thermal conductivity with an increase of the number of functional groups. Functionalization was carried out using oxidative reactions, so the number of defects increases. The insertion of functional group opens the covalent bond in the carbon skeleton, which leads to the creation of an additional defect. The defects scatter phonons. An ideal defect-free CNT has ballistic conductivity [15], phonons in it move without scattering, their free path length exceeds the length of the CNT, and the resistance of the CNT does not depend on its length. As the number of defects increases, the conductivity mechanism becomes quasi-ballistic — the conductivity decreases, but the dependence on the tube length does not appear. A further increase of the number of defects initiates a transition to the usual conductance mechanism. Also, an excessive number of functional groups can interfere with the close contact of CNTs with each other, playing the role of an insulation layer.

Data on the thermal conductivity of single-walled CNTs „Tuball“ contradict the data of [8–11], where it is stated that functionalization always worsens thermal conductivity. Probably, the authors of these papers took an excessively high degree of functionalization for study, which resulted in the excessive agglomeration of CNTs or shortening of nanoobjects as a result of their destruction.

The dependences of thermal conductivity on the number of defects shown in the figure, (*d*) deserve special attention. These dependencies are of the same type. First, CNT is purified from amorphous carbon (it is oxidized faster than CNT), which results in the improved contact between CNTs and increases thermal conductivity, then accumulated defects begin to worsen heat transfer. It is possible to assume that there is no positive impact of functional groups at all since the rise in thermal conductivity in figure, (*d*) corresponds in order of magnitude to similar rises in other figures. However, this would be a hasty conclusion. Firstly, pressed CNT samples, although they are a percolation network in terms of heat transfer, are very different from CNTs in a polymer matrix. There, the ability of functional groups to facilitate the deagglomeration of CNTs will be affected, thereby ensuring a more uniform distribution of



The dependence of the thermal conductivity of the CNT sample on the degree of functionalization of $-\mathrm{CONH_2}$ by groups (*a*), $-\mathrm{OH}$ by groups (*b*), – by groups (*c*) and defects (*d*). Thermal conductivity is along the vertical axis, a physical quantity that determines the number of functional groups grafted to CNT is along the horizontal axis. This is the reaction time in the case of hydroxyl groups and defects, it is the ratio of the mass of CNTs and oxidizer in the case of all others. Solid line — CNT „Taunit-MD", dotted line — CNT „Taunit-M", dotted line — CNT „Taunit", solid gray — „Tuball".

the additive throughout the entire volume of the composite. Secondly, functional groups can be covalently crosslinked with the polymer, which can facilitate the penetration of phonons into CNTs.

4. Conclusion

The dependence of the thermal conductivity of percolation systems of carbon nanotubes (CNTs) on the type and degree of functionalization and the number of defects was studied. The highest thermal conductivity was achieved using the functionalization type $-\mathrm{OH}$ for both CNT brand „Taunit-MD" and CNT brand „Taunit-M". The thermal conductivity of „Taunit-MD" is greater than thermal conductivity of „Taunit-M" as a result of a larger aspect ratio. The thermal conductivity is also affected by the diameter of the nanotube — the smaller the diameter, the higher the thermal conductivity [16].

We assume the existence of competing processes that increase the conductivity (a more uniform distribution of CNT agglomerates, improved contact between CNTs, easier penetration of phonon into CNTs through a functional group, change of the geometry of CNTs) and increase the resistance (the occurrence of defects and scattering centers). The data obtained can be used to control the conductive properties of CNTs, as well as to select the optimal degree of functionalization when developing composites and nanodevices. In particular, the authors of the article apply the obtained data to improve the protective superhydrophobic coating [17].

The technology of covalent functionalization of CNTs allows the production of CNTs with a given concentration of functional groups, so that the thermal conductivity of CNTs can be varied. The authors hope that this article will arouse interest in the proposed problem and possibly provide researchers with material for constructing theoretical models describing charge and heat transfer in percolation systems CNT.

The mechanism of impact of the covalent functionalization is not completely clear. All CNTs have anisotropic thermal conductivity: it is good along the axis of the tube, while manifesting a property known as the ballistic conductivity of phonons. The thermal conductivity is significantly less across the CNT axis. The mechanisms determining changes in the CNT conductivity upon covalent functionalization require further study. It is necessary to measure the thermophysical properties of single functionalized CNTs.

Attention should also be paid to the possibility of using the functionalization of carbon nanotubes to reduce the thermal conductivity of the percolation network. Climate change requires the development of ways to protect constructures, communication lines, structures and equipment from corrosion, pollution and icing. The use of hydrophobic and superhydrophobic coatings is one of the passive methods of protection that do not require energy. On the one hand, they have pronounced water-repellent properties and self-cleaning ability, on the other hand they can act as de-icing agents. The heat exchange with a cold surface is greatly slowed down for such coatings due to the small contact area of the droplet with the surface — the droplet manages to slip off the coating without having time to freeze [18]. It was proposed in [17,19,20] to use xerogel from CNT for obtaining superhydrophobic de-icing coatings. A properly selected type and degree of functionalization can enhance their anti-icing properties by slowing down the heat exchange between a cold surface and a drop of liquid that has fallen on it. This will increase the probability of a drop rolling off. Studies will continue in this direction.

Funding

The research was supported financially by the Russian Science Foundation (grant No. 22-22-20115.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by A.Akhtyamov