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MODEL FOR THERMAL CONDUCTIVITY OF COMPOSITES WITH CARBON NANOTUBES

A. Andreescu[1*], *Adriana Savin*[1], *Rozina Steigmann*[1], *Nicoleta Iftimie*[1], *E. Mamut*[2] *and R. Grimberg*[1]

[1]National Institute of R&D for Technical Physics, 47 D. Mangeron 700050, Iasi, Romania
[2]University Ovidius Constanta, 124 Mamaia Blvd 900527, Constanta, Romania

This paper presents a model for evaluation of effective thermal conductivity for the composites with carbon nanotubes (CNT) having log-normal function of distribution of CNT, with direct effect over depolarization factor. The CNT are considered having cylindrical shape with L/d ratio very high. The model parameters are calculated in function of the data from literature. The influence of volume fraction of reinforced materials, of the aspect ratio of the particles included and of the ratio of the two thermal conductivities is presented.

Keywords: *carbon nanotubes, polarization factor, thermal conductivity*

Introduction

The discovery of carbon nanotubes by Sumia Iijima [1] released many researches about these novel materials. The carbon nanotubes (CNTs) belong to class 'carbon allotropes' which include graphite, diamond, amorphous carbon, buckyballs and others. These states are builded up by carbon molecules in hollow sphere or tube forms.

The CNTs dimensions are comprised between 4–100 nm for diameters and lengths up to 200 μm. The aspect ratio (L/d) can vary between 100–100.000. The CNTs can exist as single tubes (called single-walled nanotubes (SWCNT)) or in form of concentric tubes (called multi-walled nanotubes (MWCNT)). A SWCNT is a hollow cylinder of graphite sheet whereas a MWCNT is a group of coaxial SWCNTs.

Bonding in the nanotubes is essentially through sp^2 hybridization. The sp^2 hybrid orbital allow carbon atoms to form pentagon and hexagon units by in-plane, σ-bonding, and out-of-plane, π-bonding. The π-bonding is more delocalized outside the tube, that is the *p*-character in the hybridization is increased to some extent than that of the graphite. This makes nanotubes mechanically stronger, electrically and thermally more conductive and chemically and biologically more active than graphite [2–4].

The carbon nanostructures can be obtained by several synthesized methods such as: arc-discharge in vacuum, arc-discharge in solution (ADS), laser ablation, chemical vapor deposition (CVD) or electrochemical deposition. The applications are diverse from chemical sensors for gas and bio-molecules detection to the utilization them to obtain new composites materials applied in hydrogen storage or energy industry.

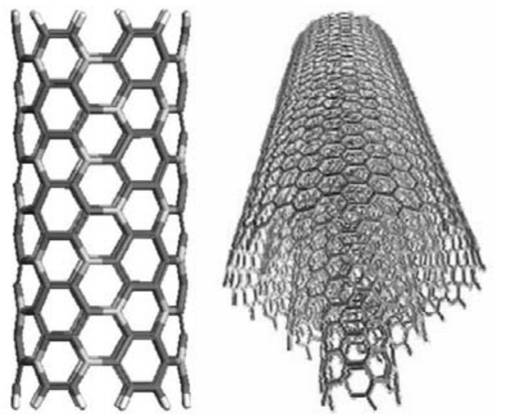

Fig. 1 Structural models of SWCNTs and MWCNTs

By a point of view of thermal properties of carbon nanotubes-based composites, these materials may be utilized to build a thin film of conductive polymers or the electronics and mechanical device where the amount of the heat energy must be removed. The nanotubes composites can also be used in bio-chemical area as membranes for molecular separation or for osteointegration-growth of bone cells.

The thermal conductivity of CNTs was studied by a lot of researchers but the values of this property are different reported, the range is about up to 6000 W mK^{-1} for SWCNT [5] and up to 3000 W mK^{-1} for MWCNT [6]. The late experimen-

* Author for correspondence: andreescuaurel@yahoo.com

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

tally measurements have proved the enhancement of thermal conductivity of MWCNT in oil suspension by more than 2.5 times at approximately 1% volume fraction [7] and the increase of thermal conductivity of SWCNT in industrial epoxy by 1.25 times [8, 9].

The classical models for the calculus of effective thermal conductivity of bi-phase composites predict the values larger than experimental measurements. The new models for the effective thermal conductivity of CNTs-based composites were built based on Maxwell theory of field factor and the introducing a distribution function of CNTs in composites [10, 11].

Modelling of thermal conductivity in composites

Considering a mixture of N components, each having the volume fraction f_i and a thermal conductivity k_i, the heat flux $\vec{q}_i$ and thermal gradient grad$\vec{T}_i$ are correlated by Fourier law

$$\vec{q}_i = -k_i \overline{\text{grad}\vec{T}_i} = k_i \vec{T}_i \tag{1}$$

where $-\text{grad}\vec{T} = \vec{T}$ for an easier presentation.

The macroscopic mean value of heat flux $\vec{q}$ is correlated by

$$\vec{q} = k_e \vec{T} \tag{2}$$

k_e – the effective thermal conductivity of the composite.

By introduction of superposition principle, the axial heat flux takes the form

$$\vec{q} = \sum_{i=1}^{N} f_i \vec{q}_i \tag{3}$$

where

$$\sum_{i=1}^{N} f_i = 1$$

which can be written in terms of conductivities and temperature gradient as

$$k_e T = \sum_{i=1}^{N} f_i k_i \vec{T}_i \tag{4}$$

The field factor Ψ_i, for each constituent, is determined by relation

$$\Psi_i = \frac{\vec{T}_i}{\vec{T}} \tag{5}$$

as the ratio of thermal gradient of *i* phase and thermal gradient on the whole composite.

The field factor represents in fact the screening of temperature field in nanocomposites because of embedded CNTs. The field factor depends of the depolarization coefficients.

The relation (4) after the calculation and according Eq. (5) turn to

$$\sum_{i=1}^{n} f_i \Psi_i \left(1 - \frac{k_i}{k_e}\right) = 0 \tag{6}$$

The field factor must be calculated or experimental measured.

Stratton [10] gave the following relation for Ψ_i for inclusions of ellipsoidal forms embedded in composites,

$$\Psi_i = \sum_{j=1}^{3} \frac{\cos^2\alpha_j}{1 + B_i\left(\frac{k_i}{k_m} - 1\right)} \tag{7}$$

where B_{ij} – the depolarization coefficients which are depending of the principal axes of ellipsoids phase *i* on the three *j* directions, α_j – the angles between the ellipsoids principal axes and the applied temperature gradient

$$\sum_{j=1}^{N} \cos^2\alpha_j = 1 \tag{8}$$

If the equivalent inclusion has one of their main axes parallel to the temperature gradient, then

$$\Psi_i = \frac{1}{1 + B_{ij}\left(\frac{k_i}{k_m} - 1\right)} \tag{9}$$

The values of B_i are functions of particles shapes and their aspect ratio. They can vary between [0, 1] [11] and [0, 1/2] [12].

In order to describe the distribution of the embedded particles in composites, it is introduced a distribution function $P(B_i)$ of the depolarization factor. So, the equivalent field factor will be expressed as

$$\Psi_i = \int_0^{1/2} \frac{P(B_i)\,\mathrm{d}B_i}{1 + B_i\left(\frac{k_i}{k_m} - 1\right)} \tag{10}$$

The probability density function of depolarization coefficients may be of different forms after geometric shape of the inclusions (CNTs) in matrix of composites. The following distributions were frequently found in nanomaterials with carbon nanotubes: β-distribution, log-normal distribution, normal distribution.

Result and discussion

Consider a CNTs-based composites compound of the polymeric matrix with MWCNT. As accelerator substance was used N-tetra-butyl-2-benzothiazolesulfenamide ($C_{11}H_{14}N_2S_2$).

The matrix is the type Rubber (1,4-polyisopren). The CNT are type ENF 100 AA-GFE and HTF 110 FF-HHT. The composition of CNT: graphite>80%, amorphous carbon<20%, impurity<0.5%. For HTF 100FF-HHT the impurities are less than 2%.

Properties of CNTs are [13]:

- average diameter 20–150 nm
- length ≥20 μm
- bulk density 600 kg m^{-3}
- thermal conductivity: $600<K<3000$ W mK^{-1}
- The morphology of utilized CNTs was effectuated on the TEM image using 100 samples. The diameter distribution is log-normal type. In Figs 2 and 3 are presented the TEM image and the CNT diameter distribution for ENF 100 AA-GFE (NT 1) respectively HTF 110 FF-HHT (NT 2).

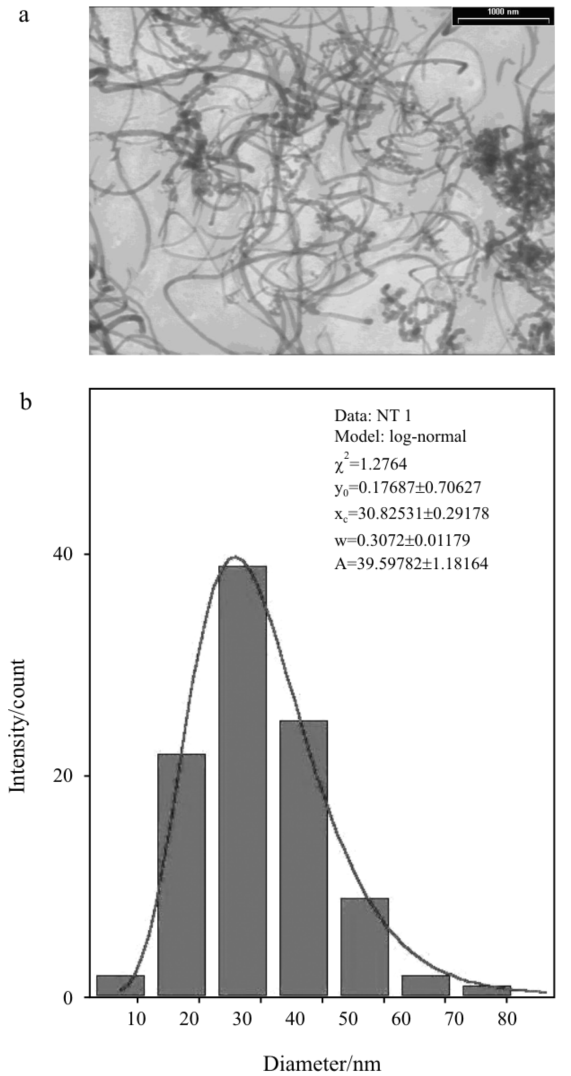

Fig. 2 a – TEM image and b – the CNT diameter distribution for ENF 100 AA-GFE

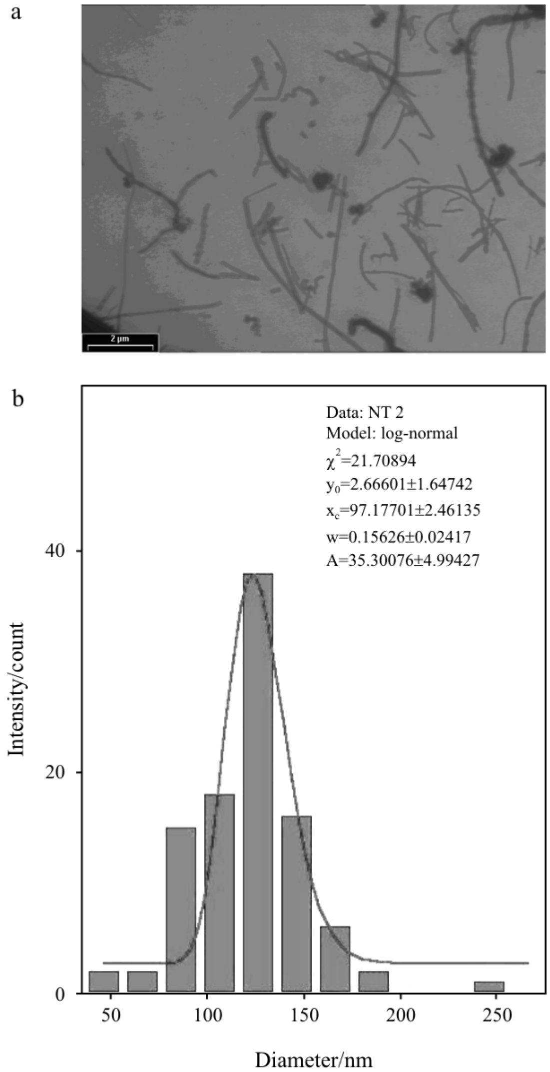

Fig. 3 a – TEM image and b – the CNT diameter distribution for HTF 110 FF-HHT

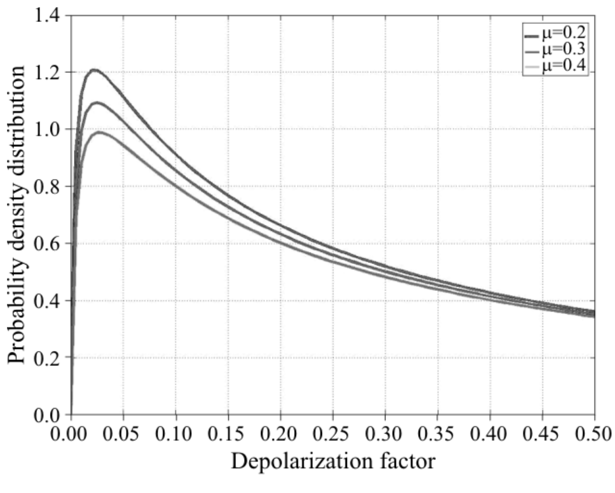

Fig. 4 The probability density distribution of the depolarization factors for CNT type: ENF 100 AA-GFE

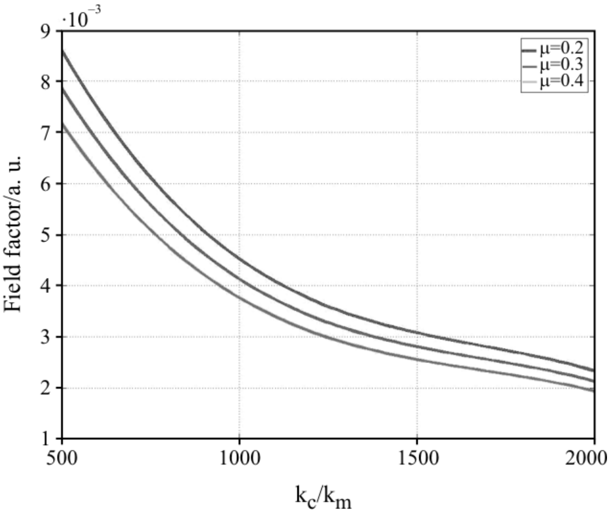

Fig. 5 Field factor dependence for the ratio k_c/k_m and the probability density distribution – log-normal (σ=2 and μ=0.2, 0.3, 0.4)

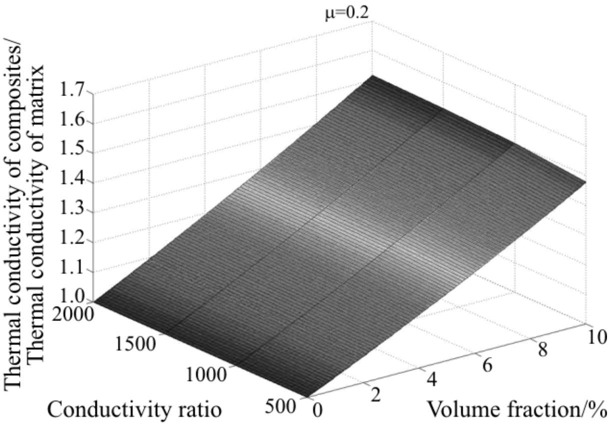

Fig. 6 The ratio k_e/k_m dependence in function of ratio conductivity k_c/k_m for volume fraction up to 10% and μ=0.2

The effective thermal conductivity, k_e for CNTs-based composites with temperature gradient along fiber of CNT are obtained from Eqs (4) and (5), in particular for 2 phases with the concentration *f* for CNTs and (1–*f*) for the rubber

$$k_e = \frac{\vec{q}}{\vec{T}} = \frac{f k_c T_c + (1-f) k_m T_m}{f T_c + (1-f) T_m} \tag{11}$$

where k_c – the thermal conductivity of CNT and k_m – the thermal conductivity of matrix.

By introduction the field factor, relation (11) become

$$k_e = \frac{f k_c \Psi_j + (1-f) k_m}{f \Psi_j + (1-f)} \tag{12}$$

with

$$\Psi_j = \frac{\vec{T}_c}{\vec{T}_m}$$

or

$$\frac{k_e}{k_m} = \frac{f \Psi_i \frac{k_c}{k_m} + (1-f)}{f \Psi_i + (1-f)} \tag{13}$$

In particular, Ψ_i depends of $P(B_i)$ and B_i are given in Eq. (10). The depolarization coefficients have an assumed distribution type log-normal. The probability density function of log-normal distribution is

$$P(B_i) = \frac{1}{\sqrt{2\pi\sigma B_i}} e^{-\frac{1}{2}\frac{(\ln B_i - \mu)^2}{\sigma^2}} \tag{14}$$

where μ and σ are the mean and standard deviation of the variable's logarithm.

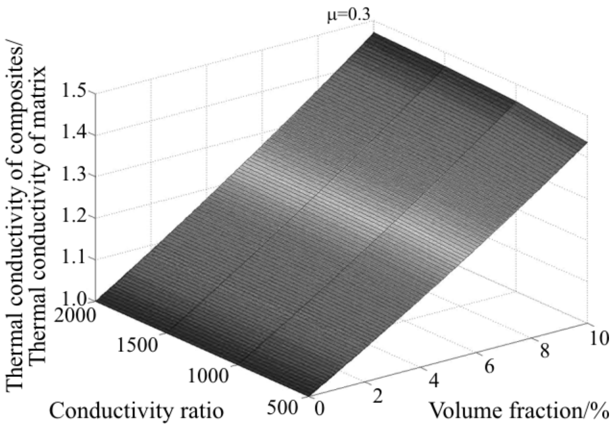

Fig. 7 The ratio k_e/k_m dependence in function of ratio conductivity k_c/k_m for volume fraction up to 10% and μ=0.3

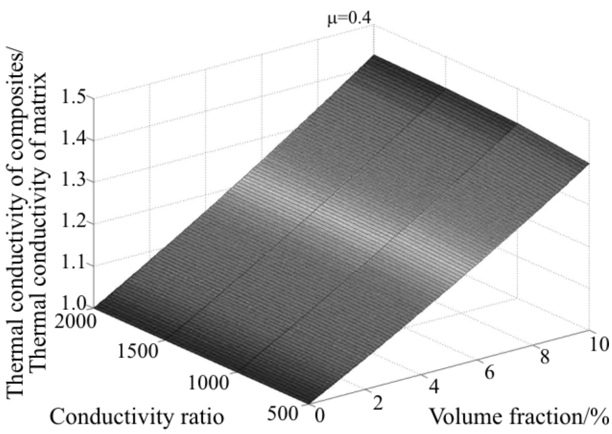

Fig. 8 The ratio k_e/k_m dependence in function of ratio conductivity k_c/k_m for volume fraction up to 10% and μ=0.4

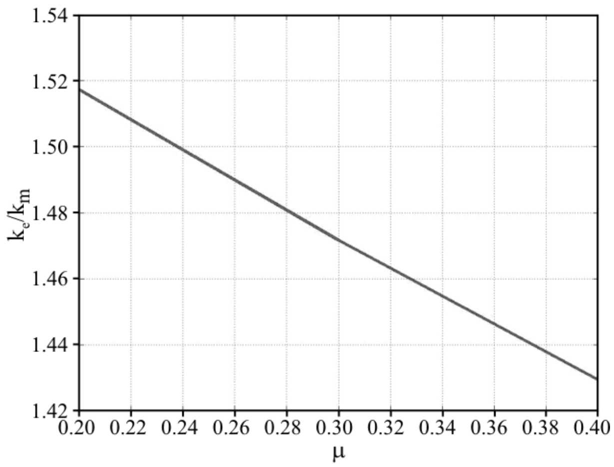

Fig. 9 The maximum values of the ration k_e/k_m function of μ

To investigate the effects of kinds of factors on the affective k_e of CNT-based composites, it was simulation the variation of the factors using Eq. (13). The results are presented in Fig 5–9.

Conclusions

The model shows that dispersion of a quite small amount of nanotubes can result in a remarkable enhancement in the effective thermal conductivity of the composites. The dependence of the effective thermal conductivity on volume fraction, ratio k_c/k_m, probability density function, shape factors has been taken in our treatment. Statistical analysis was combined with the 'conventional model' to estimate the influence of up factor on the effective conductivity.

The model predicts that ratio k_e/k_m increases with the ratio of k_c/k_m. It is to say that k_e/k_m increase with the increase of k_c or decreasing of k_m, when the other parameters are constant. The influence of probability density function is account for by σ=2 and mean values μ=0.2, 0.3, 0.4. The increase of the mean values of the depolarization factors leads to the decrease of k_e/k_m, for the k_c/k_m and a given volume fraction f.

The influence of the concentration CNTs (the volume fraction) is very strong when f>1%.

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