

Theoretical Analysis of Thermal Conductivity of Polymer Systems Filled with Carbon Nanotubes

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(Received 21 April 2019; revised manuscript received 02 August 2019; published online 22 August 2019)

The theoretical models of thermal conductivity of polymer nanocomposites, such as Russell's, Lewis-Nielsen, Nan's, Lichtenecker's, percolation models, and their accordance to experimental results for the polymer-carbon nanotubes (CNT) systems are analyzed. The experimental results of the concentration dependence of the thermal conductivity for polyethyleneoxide-CNT (crystalline matrix) and crosslinked polyurethane-CNT (amorphous matrix) systems were used to establish the correspondence between the theoretical models and the experiment. It is set that Russell's model partially describes the experimental data, when the filler's content is low. However, this model cannot describe the change in thermal conductivity with an increase in the filler content for systems filled with CNT. The Lewis-Nielsen model assumes a linear relationship between the thermal conductivity and the filler content. However, such behavior of the theoretical curve does not correspond to the jump-like dependence of the thermal conductivity obtained from the experiment. It is established that using the Nan's model, it is impossible to accurately describe the experimental results of the thermal conductivity of the selected systems. Using the modified Lichtenecker's model, it is possible to obtain a partial agreement of the theoretical curve with the experimental results. This model allowed to determine the value of thermal resistance of the investigated polymer-CNT systems, which is equal to $2 \cdot 10^7$ W/(m²·K). It is discovered that the percolation model demonstrates good correspondence with the experimental data of the thermal conductivity for the polymer-CNT systems. This model accounts the presence of the percolation threshold. The advantage of this model is the accounting of the structural features of the percolation cluster formation, which are expressed through the universal critical indexes k and q . However, the critical indexes for the investigated polymer-CNT defined using the percolation model systems were found to be lower than the theoretical ones that is associated with a high degree of aggregation of CNT.

Keywords: Thermal conductivity, Polymer nanocomposites, Models of thermal conductivity, Carbon nanotubes, Percolation.

DOI: [10.21272/jnep.11\(4\).04004](https://doi.org/10.21272/jnep.11(4).04004)

PACS numbers: 73.63.Fg, 74.50.+r

1. INTRODUCTION

Polymer nanocomposites that contain carbon nanotubes (CNT) have attracted much attention during the last decade. The increased interest in them is caused by the unique complex of their functional characteristics, which allows them to be used as coatings, structural and polyfunctional materials, etc. [1]. Besides, CNT attracted considerable interest as fillers in matrix for thermal conductivity enhancement. According to experimental measurements of Pettes and Shi [2], the intrinsic thermal conductivity of single-walled carbon nanotube achieved 2400 W/(m·K). It was shown that the thermal conductivity of CNT depended strongly on the number of walls and aspect ratios.

The effective thermal conductivity of filled polymer composites depends not only on the component properties and the filler content, but also on the filler shape, filler distribution, and interaction between the filler particles. A number of theoretical and empirical models have been proposed to predict the effective thermal conductivity of composites [3]. It is noted that mostly theoretical models for predicting the effective thermal conductivity of filled polymer composites are based on assumptions for simplicity. Such models estimated the effective thermal conductivities of composites with uniformly and periodically distributed regular particles. The 2D and 3D finite element models of filled polymer

composites are also based on the assumptions of randomly distributed cylindrical fibers [4]. These models cannot reflect the actual microscopic irregularities of the filler shape and distribution, especially for the case of high filler content when a continuous network of filler is formed. Some models are inadequate for estimating the effective thermal conductivity of filled polymer composites [3].

Most models do not take into account the existence of interfacial thermal resistance. However, the presence of the thermal resistance between the nanotubes and the polymer matrix is the main factor limiting the heat flow in nanocomposites filled with CNT. The interfacial resistance between the two phases serves as a barrier for the heat flow and therefore reduces the total thermal conductivity of the material.

In recent years, a significant number of papers, which reported a jump-like increase in thermal conductivity when reaching the critical concentrations of the filler, have appeared [5, 6]. The authors explained this effect by forming a percolation cluster of filler particles inside the polymer matrix, that is, by the existence of a percolation transition. In the papers [7, 8], the authors have studied the effect of percolation at high volume fractions of filler materials. In literature, there are many models to predict the thermal conductivity on polymer composites. Most of these models are empirical and lack the physical understanding of the heat transfer mechanism.

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Consequently, there is no single model of thermal conductivity, so for each individual nanofilled system, it is necessary to select the most accurate model. Therefore, the purpose of this work was to analyze the basic theoretical models of thermal conductivity of polymer nanocomposites and their application for describing experimental data on an example of systems based on polymers of different phase state and CNT.

2. THEORETICAL MODELS OF THERMAL CONDUCTIVITY

2.1 The Russell's Model

In a study on the thermal conductivity of porous insulating bricks, Russell identified the size, shape and distribution of the pores as having potential to influence the effective thermal conductivity of the brick. Using his effective thermal conductivity model (eq. (1)), he calculated the effective thermal conductivities for idealized material structures over a range of volume fractions and component thermal conductivities. According to the similarity between the principle of electric conduction and heat conduction, Russell's model [9] is given as

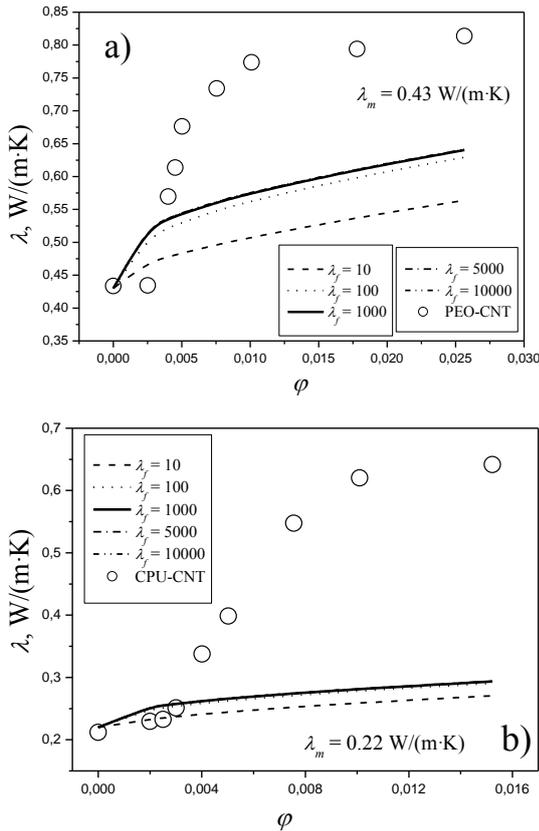


Fig. 1 – The experimental data simulated using equation (5) for nanofilled systems based on PEO (a) and CPU (b). Solid lines are the Russell's model

$$\lambda = \lambda_m \frac{\varphi^{\frac{2}{3}} + \frac{\lambda_m}{\lambda_f} \left(1 - \varphi^{\frac{2}{3}}\right)}{\varphi^{\frac{2}{3}} - \varphi + \frac{\lambda_m}{\lambda_f} \left(1 - \varphi - \varphi^{\frac{2}{3}}\right)}, \quad (1)$$

where λ , λ_m , and λ_f stand for the thermal conductivity of the composites, matrix, and filler, respectively; φ is the volume fraction of the filler. This model indicates that the thermal conductivity of filled composites is related to the volume fraction of the filler and the thermal conductivity of the composites and filler.

2.2 The Lewis-Nielsen Model

This empirical model is quite popular in the literature and gives relatively good results even though its equations do not include the interfacial thermal resistance. It was created for moderate filler volume fractions (up to 40 %). For higher values, it becomes unstable [8].

By revising the Halpin-Tsai formulation, Nielsen et al. obtained the empirical model to predict the thermal conductivity of polymer composites [10]:

$$\lambda = \frac{1 + AB\varphi}{1 - B\psi\varphi}, \quad (2)$$

where $A = 1 - K_E$, $B = \frac{\lambda_f/\lambda_m - 1}{\lambda_f/\lambda_m + A}$, $\psi = 1 + \frac{1 - \varphi_m}{\varphi_m^2} \varphi$.

Here A and φ_m are the factors related to particle size and shape, φ_m is the maximum compacted volume fraction of fillers; K_E is an Einstein constant, which is related to the shape and orientation of particles; B is a constant, which is related to the thermal conductivity of each part and particle parameter; ψ is a function related to the volume fraction of fillers. Some φ_m values can be considered, such as $\varphi_m = 0.64$ for the particles without fixed shape dispersed randomly in polymer composites [11]. At the limits of $A \rightarrow 0$ (for particles with low aspect ratio) and $A \rightarrow \infty$ (for particles with high aspect ratio), the Lewis-Nielsen model reduces to the series or parallel thermal conductivity models.

2.3 The Nan's Model

Since CNT have a very large aspect ratio and anomalous thermal conductivity, the prediction of the thermal conductivity of CNT incorporated polymer composites from the existing theoretical model is not possible. Nan et al. have derived a theoretical model for predicting the thermal conductivity of 1D CNT incorporated composites [12]:

$$\frac{\lambda}{\lambda_m} = 1 + \frac{f \lambda_f}{3 \lambda_m}, \quad (3)$$

where λ denotes the effective thermal conductivity of a composite, λ_m and λ_f are thermal conductivity of matrix and CNT, respectively. This equation is valid at a reasonably low volume fraction (φ) of CNT, less than 0.02. However, the important nature, namely, the geometry of CNT such as diameter and length which can be represented as the aspect ratio is not included. Therefore, the model equation was further modified by considering the aspect ratio, diameter, and interface thermal resistance [13]

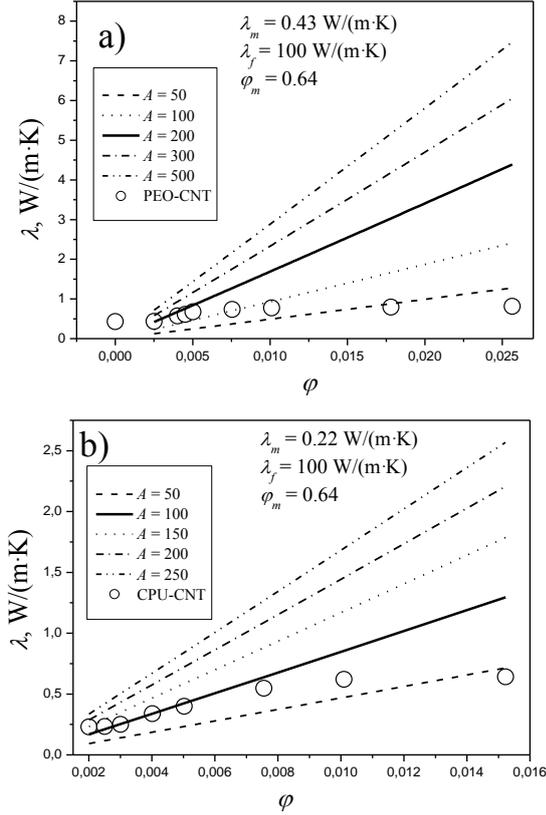


Fig. 2 – The experimental data simulated using equation (2) for nanofilled systems based on PEO (a) and CPU (b). Solid lines are the Lewis-Nielsen model

$$\frac{\lambda}{\lambda_m} = 1 + \frac{fp}{3} \frac{\lambda_f / \lambda_m}{p + \frac{2\alpha_K \lambda_f}{d \lambda_m}}, \quad (4)$$

where α_K is Kapiza radius. Also d , p , and ϕ are the diameter, aspect ratio, and volume fraction of CNT, respectively. The Kapiza radius α_K is defined by for nanotube composites, α_K is 16-40 nm when λ_m is 0.2-0.5 W/(m·K). This eq. (4) holds for a diluted concentration of CNT with $\phi < 0.01$.

2.4 The Modified Lichtenecker's Model

Compliance with the calculation experiment can be achieved by the method of constructing functions, which is rarely used in the present. For structures of the type of closed inclusions in the matrix, Lichtenecker [14] recommends the function

$$\lambda = \frac{(\varphi_m \lambda_m + \varphi_f \lambda_f)^u}{\left(\frac{\varphi_m}{\lambda_m} + \frac{\varphi_f}{\lambda_f}\right)^{1-u}}, \quad (5)$$

where λ_m , λ_f , φ_m and φ_f are thermal conductivities and volume fraction of matrix and CNT, respectively; u is the frequency of the sequential arrangement of particles of inclusions relative to the heat flux; $1 - u$ is the contribution of the parallel configuration, $0 \leq u \leq 1$.

In the case of $\lambda_m \ll \lambda_f$, expression (5) is simplified to the equation

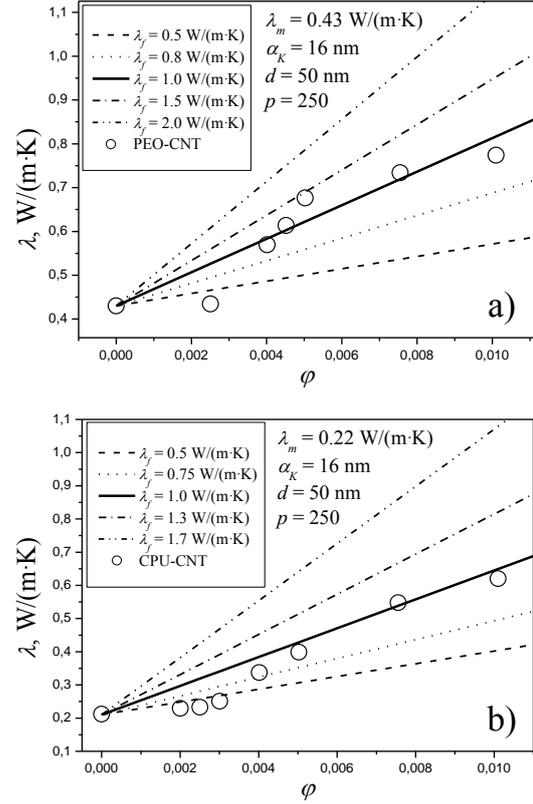


Fig. 3 – The experimental data simulated using equation (4) for nanofilled systems based on PEO (a) and CPU (b). Solid lines are the Nan's model

$$\lambda = \left(\frac{\varphi_f}{\varphi_m} \lambda_m \lambda_f \right)^u. \quad (6)$$

It can be noted that eq. (6) corresponds to the lower Schulgasser boundary for the thermal conductivity of two-phase composites with a cell structure with the same volume content of components 1 and 2 ($\varphi_1 = \varphi_2 = 0.5$)

$$\lambda > (\lambda_1 \lambda_2)^{\frac{1}{2}}. \quad (7)$$

The thermal resistance of the filler-matrix interface can be taken into account by replacing λ_f in (6) with $\lambda_f / (1 - B)$,

$$\lambda = \left(\frac{\varphi_f}{\varphi_m} \frac{\lambda_m \lambda_f}{1 + B} \right)^u, \quad (8)$$

In this equation, B is determined as $B = 2\lambda_f / (DG)$, where D is particle size and G is thermal conductivity of the filler-matrix interface.

2.5 The Percolation Model

When increasing the amount of filler per unit volume, one eventually reaches a point at which particles of filler begin to contact. Assuming that the filler is highly conductive, heat transfer is easier between two contacting particles than between the particle and the matrix. With increasing filler fraction, chains of connected conductive particles begin to appear (see the schematic in Fig. 5). These chains act as channels with increased heat conduction. Formation of such conductive

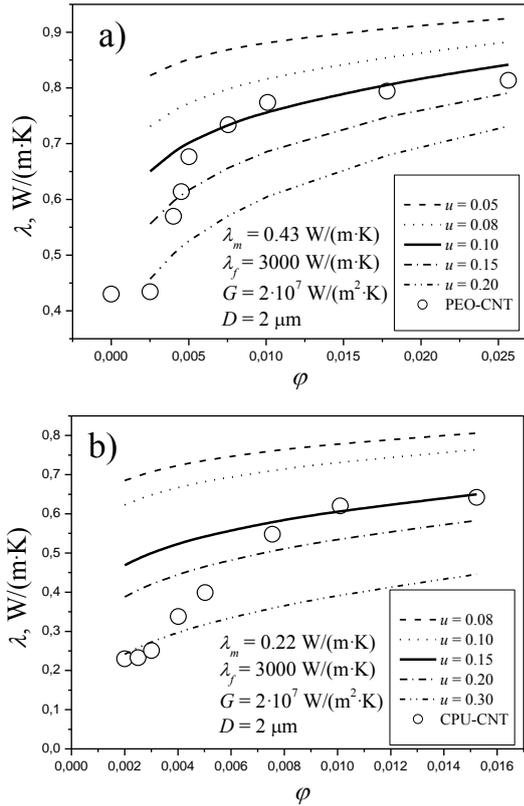


Fig. 4 – The experimental data simulated using equation (8) for nanofilled systems based on PEO (a) and CPU (b). Solid lines are the modified Lichtenecker's model

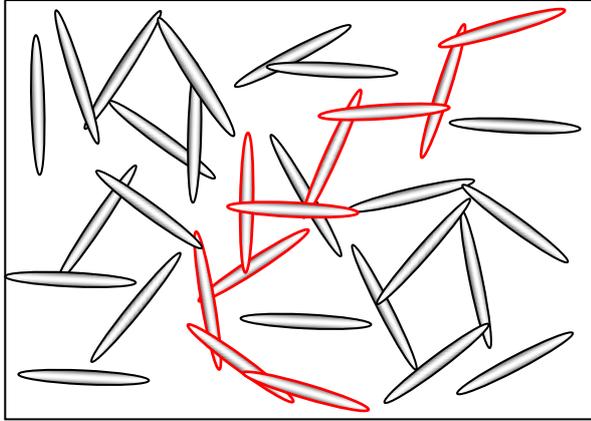


Fig. 5 – A scheme of heat transfer enhancement in polymer composite material due to percolation. Continuous percolation clusters of CNT are depicted as red. Other CNT do not form a continuous cluster

channels causes a significant increase in the effective thermal conductivity of the material. This effect is visible as a shift from a flat to a steep slope of the effective thermal conductivity plotted versus filler volume fraction. The point or volume fraction at which this shift occurs is known as the percolation threshold [15].

The term percolation was initially used to describe the passing of a liquid through a porous substance or small holes, but then its meaning was expanded to describe the phenomenon of formation of conducting channels in many types of transport problems, e.g., electric circuits, public transport or spread of a disease [3].

In general, effective medium approximations fail to predict the properties of a multiphase medium close to the percolation threshold. Efforts have been made to overcome this flaw. One of the most effective models, which allow to predict the percolation behavior of thermal conductivity, is a scaling model.

The scaling model assumes that the appearance of high thermal conductivity is explained by the probability of formation of the contact between the filler particles within the composite [15]. The basic equation of this model is the power law, which is written as:

$$\lambda \sim (\varphi - \varphi_c)^k, \quad (9)$$

where λ is the thermal conductivity of the nanocomposite, φ is the filler volume fraction, φ_c is the percolation threshold, i.e. the minimum filler content, at which a continuous cluster of particles is formed, k is the critical thermal conductivity index, which mainly depends on the topological dimension of the system and does not depend on the structure of particles, which form clusters, and their interaction.

However, eq. (9) allows to define the thermal conductivity only after the percolation threshold. To expand the application range of this model, Sun, et al. [16] for thermal conductivity have proposed to use not one scaling equation, but the system of equations of the type

$$\lambda = \begin{cases} \lambda_m (\varphi - \varphi_c)^k & \text{for } \varphi > \varphi_c \\ \lambda_f (\varphi_c - \varphi)^{-q} & \text{for } \varphi < \varphi_c \end{cases} \quad (10)$$

where λ , λ_m , λ_f are the thermal conductivities of the composite, matrix, and filler, respectively, q is the critical thermal conductivity index characterizing the number of particles, which form the percolation cluster. This system of equations is a universal one and allows to describe the thermal conductivity of the filled polymer systems in the vicinity of the percolation transition with a high degree of accuracy.

3. RESULTS OF SIMULATION

The experimental results of the concentration dependence of the thermal conductivity for polyethyleneoxide (PEO)-CNT (crystalline matrix) [17] and cross-linked polyurethane (CPU)-CNT (amorphous matrix) [18] systems were used to establish the correspondence between the theoretical models and the experiment. Selected systems are characterized by a sharp increase of thermal conductivity when reaching a critical concentration of CNT.

A comparison between the experimental data and the Russell's model is shown in Fig. 1. It shows that the thermal conductivity of the PEO-CNT and CPU-CNT systems increases with the increase in volume fraction of nanotubes. With low content of the filler, the model partially describes the experimental data. But, when φ reaches 0.005, the experimental curve lies above the theoretical curve. This is because the fillers in the theoretical curve are supposed to be identical cubes without mutual interaction, and the fillers in the experiment are unequal particles and have the mutual interaction with each other [19]. When $\varphi > 0.005$, the

mutual interaction among particles becomes stronger, which leads to a higher thermal conductivity. In general, the Russell's model qualitatively describes a jump-like change in heat conductivity. The fitting parameters of this model are the thermal conductivity of the matrix and the filler. However, even with the variation of these parameters in wide intervals, the Russell's model cannot describe the change in thermal conductivity with an increase in the content of the filler for systems filled with CNT.

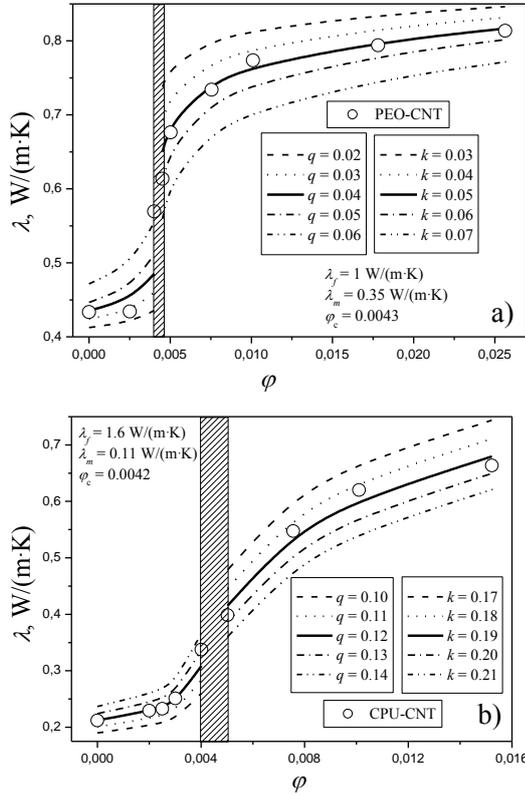


Fig. 6 – The experimental data simulated using equation (10) for nanofilled systems based on PEO (a) and CPU (b). Shaded area is the percolation threshold region and lines are the percolation model

A comparison between the experimental data and the Lewis-Nielsen model is shown in Fig. 2. It shows that calculated thermal conductivity increases with the increase in volume fraction of nanotubes and demonstrates the linear behavior. Such behavior of the theoretical curve does not correspond to the jump-like dependence of the thermal conductivity obtained from the experiment. The fitting parameters of the model are the thermal conductivity of the matrix and the filler, the maximum packing fractions of the filler in the system, which for the studying systems is 0.64, and the form factor A . Theoretical curves with different values of the parameter A are presented in Fig. 2. From the results of fitting, it is clear that the parameter A is greater than 50. This indicates a large anisotropy of the form of the filler's particles. However, even with the variation of these parameters in wide intervals, the Lewis-Nielsen model cannot describe the change in thermal conductivity with an increase in the content of the filler for systems filled with CNT.

Unlike Russell and Lewis-Nielsen models, the Nan's model takes into account the size of the filler particles and the interface thermal resistance. Fig. 3 presents a comparison between the experimental data and the Nan's model. It is shown that the model partially describes the experimental data. The model has many fitting parameters, most of which are constants for a certain type of filler. However, the theoretical curve shows a linear behavior that does not allow to accurately describe the experimental results. It was possible to obtain the theoretical values of the thermal conductivity as close as possible to the experiment only with the decrease in the value of the thermal conductivity of the filler. However, the values of λ_f are very low, even taking into account the high thermal resistance at the matrix-filler interface. Consequently, using the Nan's model, it is impossible to accurately describe the experimental results of the thermal conductivity of the selected systems.

Like the previous models, the modified Lichtenecker's model also takes into account the thermal resistance of the interface and the size of the filler particles. Fig. 4 presents a comparison between the experimental data and the modified Lichtenecker's model. It is seen that the theoretical curves coincide with the experimental ones in form. By changing the fitting parameters of the model, it is possible to obtain a partial agreement of the theoretical curve with the experimental results. The values of thermal conductivity of the matrix and the filler correspond to the real values. The diameter of the filler particles is 2 μm , which corresponds to the size of the aggregates of CNT. The thermal resistance lies within the range of possible values, which for G is 10^4 - 10^8 W/(m²·K) [20]. Thus, using the Lichtenecker's equation with allowance for the thermal resistance of the interface (8), one can partly describe the experimental data obtained. The disadvantage of this model is quite phenomenological. So, it is not quite clear how to justify the choice of a specific value of the parameter u .

Fig. 6 illustrates the simulation of the experimental data for the polymer-CNT system by using the percolation model. As seen from the analysis of functions (10) (see Fig. 6), the thermal conductivity of the system increases with decreasing critical index k , and a decrease in the critical index q leads to the decrease in the system thermal conductivity. After analyzing the system of equations (10), we can say that change in the value of the critical index k does not lead to the change in the maximum thermal conductivity of the polymer composite, which is specified only by the filler thermal conductivity. The change in the percolation threshold of the filler in the composite does not result in the change of the system thermal conductivity.

The percolation model demonstrates good correspondence with the experimental data of the thermal conductivity for the polymer-CNT systems (Fig. 6). Theoretically, percolation model assumes that the thermal conductivity critical indexes are universe for the systems with the same dimensions. However, the critical indexes differ from the theoretical values for the studied polymer-CNT systems. This fact does not indicate the decrease in the system dimension, and, probably, is the consequence of a large degree of aggregation of nanotubes in the system [15].

4. CONCLUSIONS

As a result of this work, we have analyzed the basic theoretical models of thermal conductivity of polymer nanocomposites and their application for the description of the experimental data on polymer-CNT systems. It is established that the models based on the provisions of the effective medium theory (Russell's and Lewis-Nielsen's models) describe poorly the experimental data. In these models, heterogeneous materials are considered as being macroscopically homogeneous. Due to their nature, effective medium approximations are unable to accurately predict the properties of heterogenic material beyond the percolation threshold.

It is revealed that the Nan's model takes into account the size of the filler particles and the interface thermal resistance. However, the theoretical curve shows a linear behavior that does not allow to accurately describe the experimental results, which demonstrate percolation behavior.

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Теоретичний аналіз теплопровідності полімерних систем, наповнених вуглецевими нанотрубками

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Використовуючи методи математичного моделювання, проаналізовано основні теоретичні моделі теплопровідності полімерних нанокомпозитів (моделі Расселла, Льюїса-Нільсена, Нана, Ліхтенекера та перколяції) та їх відповідність експериментальним результатам для систем полімер-вуглецеві нанотрубки (ВНТ). Для встановлення відповідності між теоретичними моделями та експериментом були використані експериментальні результати концентраційної залежності теплопровідності для систем поліетиленоксид-ВНТ (кристалічна матриця) та сітчастий поліуретан-ВНТ (аморфна матриця). Встановлено, що модель Расселла частково описує експериментальні дані, лише при низькому вмісті наповнювача. Проте ця модель не може описати зміну теплопровідності зі збільшенням вмісту наповнювача для систем, наповнених ВНТ. Модель Льюїса-Нільсена передбачає лінійну залежність між теплопровідністю і вмістом наповнювача. Але така поведінка теоретичної кривої не відповідає стрибкоподібній зміні теплопровідності, отриманої в результаті експерименту. Встановлено, що з використанням моделі Нана неможливо точно описати експериментальні результати теплопровідності обраних систем. Використовуючи модифіковану модель Ліхтенекера, можна отримати часткове узгодження теоретичної кривої з експериментальними результатами. Ця модель дозволила визначити величину теплового опору досліджуваних систем полімер-ВНТ, який дорівнює $2 \cdot 10^7$ Вт/(м²·К). Виявлено, що перколяційна модель демонструє гарну відповідність з експериментальними даними теплопровідності для систем полімер-ВНТ. Ця модель враховує наявність порога перколяції. Перевагою цієї моделі є врахування структурних особливостей формування перколяційного кластера, які виражаються через універсальні критичні індекси k і q . Однак критичні показники для досліджуваних систем полімер-ВНТ, визначені з використанням даної моделі, виявилися нижчими, ніж теоретичні, що пов'язано з високим ступенем агрегації ВНТ.

Ключові слова: Теплопровідність, Полімерні нанокомпозити, Вуглецеві нанотрубки, Моделі теплопровідності, Перколяція.