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THERMAL CONDUCTION IN POLYSTYRENE/CARBON NANOTUBES: EFFECTS OF NANOFILLER ORIENTATION AND PERCOLATION PROCESS

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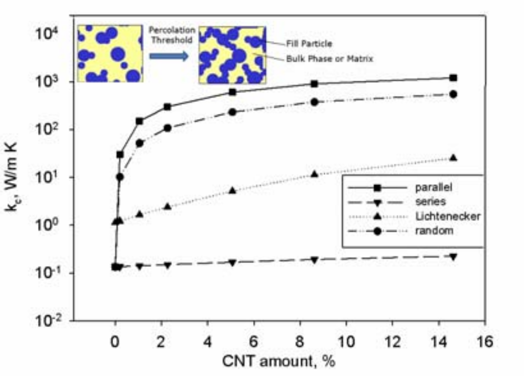
Polymer nanocomposites based on polystyrene and carbon nanotubes were investigated from the point of view of their thermal conduction properties. The thermal flux and temperature gradient were evaluated by using the finite element method. Starting from these parameters the thermal conductivity was determined for two cases. The first one considers the carbon nanotube is oriented along the heat flux direction, while the second case refers to the carbon nanotube that is perpendicular to the heat flux. To ascertain the effects on nanocomposite thermal conduction induced by the percolation process, various concentrations of nanofiller were considered. Thermal conductivity was evaluated by applying several theoretical models. The obtained results are important in designing polymer nanocomposites for high power electronics where heat dissipation is essential for maintaining the devices reliability.



INTRODUCTION

Polymer composites exhibiting high thermal conductivity offer new perspectives for replacing metal parts in several applications, including power electronics, electric motors and generators, heat exchangers, owing to the polymer advantages such as light weight, corrosion resistance and ease of processing.[1] Current interest to enhance the thermal conductivity of polymers is focused on the introduction of nanofillers with high thermal conductivity.[2] The most promising candidate material for thermally conductive composites is carbon nanotube (CNT) due to its unusually high thermal conductivity*, i.e.* 3000 W/m·K along the nanotube axis.[3] However, the thermal conductivities of polymer/CNT nanocomposites are relatively low in regard with the intrinsic thermal conductivity of CNTs. This is the result of the large interfacial thermal resistance between the CNT and polymer matrix which impedes the transfer of phonon dominating heat conduction in polymer and CNT.

The thermal conduction in such materials could be improved by inducing the alignment of CNT or by their functionalization.[4,5] Literature reports various methods for obtaining a good orientation of the CNT in polymers, such as mechanical stretching, magnetic or electric fields, fracture, uniaxial pressure, filtration or fiber drawing,

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acoustic waves, and pulling a substrate from CNT solution.[6] Another route for enhancing the thermal conduction is related to the changes in the reinforced polymer micro- and nano-structure, like formation of a percolation network.[7,8]

On the other hand, the properties of the polymer nanocomposites are influenced by both nanofiller characteristics (chemical structure and size) and polymer physical features. Among the matrices used for nanocomposites preparation, polystyrene is one of the most studied due to its excellent mechanical resistance, high adhesion and good transparency.[9,10]

In this work, a system of polymer nanocomposites based on CNT and polystyrene (PS) is analyzed with respect to the thermal conduction properties. The thermal flux and temperature gradient were evaluated by using the finite element method. The simulations are performed in such manner that they include the effect of the nanofiller orientation process. Various concentrations of CNT are considered for taking into account the percolation process influence on thermal conductivity.

RESULTS AND DISCUSSION

The heat transfer involves the transport of energy from one place to another by energy carriers. In solids, thermal energy is transported by phonons, electrons, or photons – quantized modes of vibration occurring in a rigid crystal lattice. The latter represent the main mechanism of heat conduction in most polymers because free movement of electrons is not possible.[1] In the case of unidimensional heat flux the heat transfer in polymer materials can be described by Fourier law for thermal conduction, as shown by equation (1):

$$q = -k\frac{dT}{dx} \tag{1}$$

where q is the heat flux along x, dT/dx is the temperature gradient, and k is the thermal conductivity of the medium in the direction of heat flow.

The finite element method is applied through the ANSYS® software (Ansys, Inc., demo). The analysis type settings used for the solution processing of the steady state response to the thermal boundary conditions is steady state. Thermal preference in this program is selected, which activates the capability to create thermal boundaries, and enables the user to select elements designed to process thermal calculations. The boundary conditions are imposed to limit the heat flow to the one axis. Using proper tools in the analysis package, thermal heat flux and thermal gradient at each node of the meshed volume is collected. The volume average of heat flux and the thermal gradient is calculated for two cases, namely when the heat flux is applied along the CNT axis or perpendicular to the CNT radius direction. Fig. 1 shows heat flux and the thermal gradient for the considered situations, when the matrix contains only one CNT.

The values of the thermal conductivity of polymer composites (k_c) are influenced by the positioning of the CNT with regard to the heat flux direction. The obtained data using the finite element method are displayed in Table 1. When the CNT axis is parallel to the applied heat, one can notice that the thermal conduction in the reinforced PS is enhanced, whereas for perpendicular (radial) CNT orientation the increment is not so high.

These results are further extended to higher concentrations of CNT in PS matrix in order to investigate the effect of the changes occurring in the sample micro- and nano-structure under the form of percolation networks. For this reason it is necessary to perform first an evaluation of the thermal conduction abilities for the polymer matrix (k_m). In case of PS, the method developed by Bicerano[11] that starts from the connectivity index formalism, is used:

$$k_m = 0.135614 + 0.126611 \cdot {}^1\chi^{BB} / N + 0.108563(N_N + N_O - 0.125N_H)/N \tag{2}$$

where ${}^1\chi^{BB}$ is the fraction of first order connectivity index that contributes to the bonding among the backbone atoms; N_N, N_O, N_H are the number of nitrogen, oxygen, and hydrogen atoms in the structural unit, and N is the number of non-hydrogen atoms.

By applying the relation (2) one obtains for PS a thermal conductivity of 0.135 W/ m·K. Knowing that CNT present a thermal conductivity[1] of 3000 W/ m·K, the heat transport characteristics of the PS with different degrees of reinforcement is evaluated. Several theoretical models are used for predicting the thermal conductivity of the PS/CNT nanocomposites.[12-14]

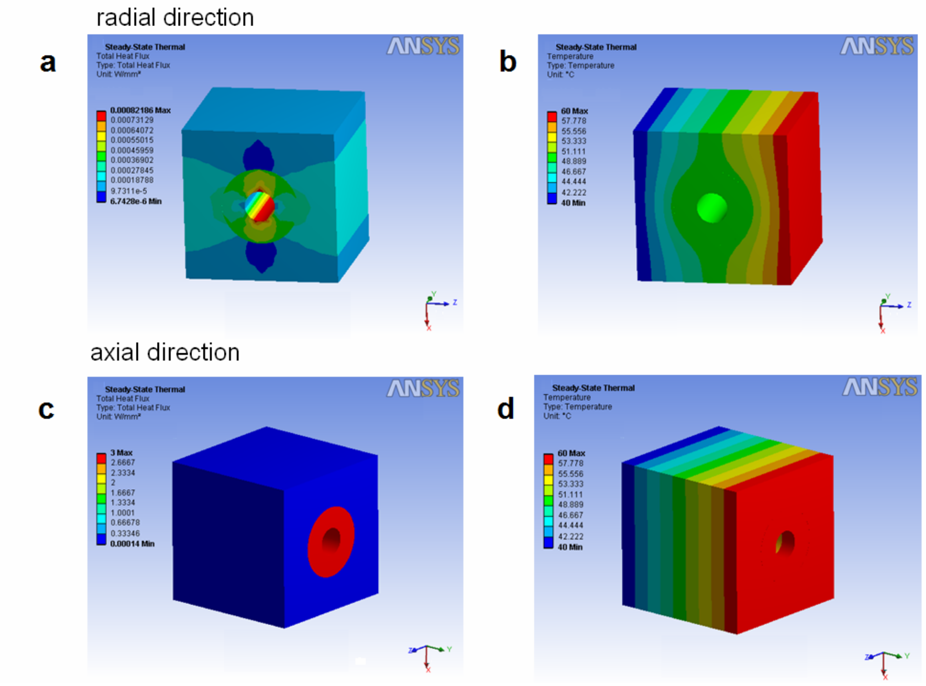

Fig. 1 – The heat flux and the thermal gradient for PS containing a CNT oriented radial (a), (b) and axial (parallel) to the applied heat (c), (d), respectively.

Table 1

Heat flux, temperature gradient and thermal conductivity values for PS/CNT

Sample	q, W/m^2	dT/dx	k$_c$, W/ m·K
PS/CNT - axial	$1.5 \cdot 10^6$	15.56	$5.196 \cdot 10^3$
PS/CNT - radial	414.301	15.56	1.435

In the rule of mixture model, also known as the parallel model, each phase is assumed to contribute independently to the overall conductivity, proportionally to its volume fraction:

$$k_c = k_m \phi_m + k_p \phi_p \tag{3}$$

where the index “c” is for composite, “m” is for matrix and “p” is for nanoparticle (CNT in this case), while the symbol ϕ is the volume fraction.

The conductivity of composites accordingly with the series model, that assumes no contact between particles and thus the contribution of particles is confined in the region of matrix embedding the particle, is predicted by relation (4):

$$k_c = \frac{1}{(\phi_m / k_m) + (\phi_p / k_p)} \tag{4}$$

The Lichtenecker model represents an intermediary approach between the parallel and series models being bases on the geometric mean of the components conductivity:

$$k_c = k_m^{\phi_m} + k_p^{\phi_p} \tag{5}$$

An analytic model has been developed to calculate the thermal conductivity enhancement of nanocomposites of randomly dispersed CNT throughout the composite, as defined by equation (6):

$$k_c = k_m \frac{3 + \dfrac{\phi_p k_p}{k_m}}{3 - 2\phi_p} \tag{6}$$

The dependence of thermal conductivity on the CNT amount is graphically represented in Fig. 2. For a better visualization of the differences given by the applied theoretical models the y-axis is represented in logarithmic scale.

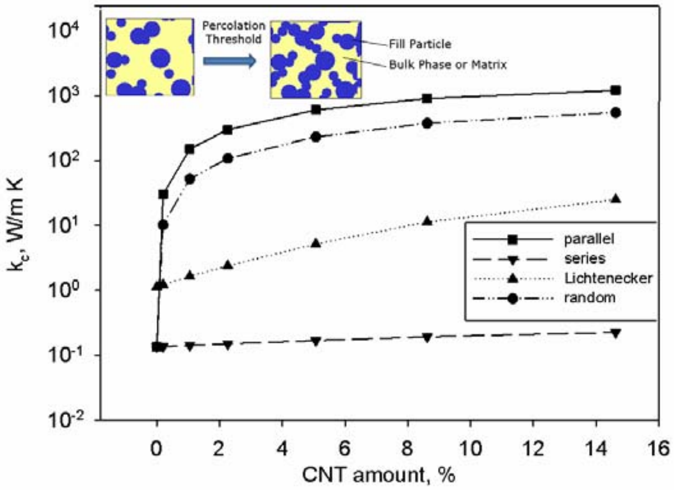

Fig. 2 – Thermal conductivity dependence on CNT amount for PS/CNT determined from equations (3)-(6).

All models reveal that the introduction of CNT increases the heat transfer in the considered matrix. The series model leads to the lowest increment of thermal conductivity whatever the CNT percent in PS. The Lichtenecker approach leads to intermediary values, but it does not describe accurately the thermal behavior at low CNT amounts if one considers that at zero percents of nanofiller the thermal conductivity of the PS should be obtained. The highest values of thermal conductivity are obtained from parallel and analytic models. In both cases a sudden increase of thermal conductivity is noticed. This is the results of the changes occurring in the sample microstructure as a result of percolation process. Percolation threshold is that minimum filler content in the polymer matrix after which there is no significant change in the conduction properties of the composites. Once the concentration of inclusions or filler exceeds a critical value conductivity increases sharply (by several orders of magnitude). This is also related with the percolation network formation within the matrix for the conduction. Percolation threshold is an important phenomenon for the polymer matrix composites which shows that at which minimum weight % of the filler the conductivity of the polymer matrix composite increased. In our case, the percolation threshold is considered the critical filler amount after which the thermal conductivity changes with one order of magnitude. The parallel model leads to a threshold of 0.056%, while for the analytical model this value is slightly higher, namely 0.126%. After this critical value the heat conduction in PS/CNT is considerably improved. Taking into account that the equations (3) and (6) lead to similar values it can be assumed that these are the results that describe closer to reality the thermal behavior of the nanocomposites here under analysis.

CONCLUSIONS

This paper is focused on evaluation of the thermal conductivity of some nanocomposites based on PS and CNT. The results derived from finite element method reveal that the orientation of the nanofiller along with the heat flux direction leads to an enhancement of the conduction properties, comparatively with the case of the radial orientation of the CNT. For the prediction of heat conduction at different reinforcement percents four models are used, allowing to asses the percolation threshold. It can be noticed that after this critical value the thermal conductivity increases considerably. The obtained data are important in processing polymer nanocomposites based on CNT with elevated heat dissipation abilities that maintain the reliability of devices in high power electronics.

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