Thermal Conductivity of Phase Changing Materials Doped with Carbon Nanotubes

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Abstract. Phase changing materials (PCM) can accumulate and release a great quantity of energy at changing the temperature in result of the phase transition. This permits one to use PCMs as a basis of thermal accumulators storing the thermal energy at elevated temperatures and releasing it at lowering the temperature below the phase transition point. Worldwide usage of PCMs in building technology and other fields is hindered by a rather low thermal conductivity coefficient of the most PCMs which makes the response of the relevant thermal accumulators too slow and limits the possibilities of application of such devices. This drawback can be overcome through doping a PCM with particles having high thermal conduction coefficient. The present article contains results of experimental and theoretical investigations of heat propagation in PCM doped with carbon nanotubes the thermal conduction coefficient of which exceeds that of the most PCM by 4 – 5 orders of magnitude. Paraffin П-2 have been used as PCM. The experiments performed demonstrate a 2 – 3 times enhancement of thermal conductivity and 16 orders of magnitude enhancement of the electric conductivity because of doping paraffin with 10% multi-walled nanotubes. The propagation of both heat and electric current has a percolation character, so that nanotubes form conductive paths at exceeding some concentration of the dopant. The heat propagation process was modelled through the solution of the non-stationary heat conduction equation with taking into account the sorption of heat due to the phase transition. The calculations performed for composite materials with the varied thermal characteristics of a material imply that the characteristic heating time is proportional to the value of the melting enthalpy and inversely proportional to the value of the heat conduction coefficient.

1. Introduction

Phase changing materials (PCM) permit accumulation and release a considerable quantity of the thermal energy due to the phase transition at changing the temperature. Estimations imply that the worldwide application of heat accumulators based on PCM in the building industry offers a possibility for decrease of the world energy consumption by about 10%. Besides of that, thermal accumulators on the basis of PCMs can be utilized for energy storing on solar and wind energy plants as well as for thermal stabilization of electronic apparatus. However, the most of PCM are characterized by a rather low thermal conductivity, which hinders the wide spread of such materials in technologies. This peculiarity causes the response of PCM-based thermal accumulators too slow which limits possibilities of the usage of such devices. Therefore, the problem of the enhancement...
of the thermal conductivity of PCM seems to be very topical. An effective approach to overcoming this problem is based on doping a PCM with highly conductive particles. Carbon nanoparticles (nanotubes, graphene etc.) are obviously the most suitable dopant for this aim [1 – 10]. The thermal conduction coefficient of carbon nanotubes (CNTs) accounts about $10^3$ W/m [11] which exceeds a characteristic value for PCM by 4 orders of magnitude. Even higher the thermal conduction coefficient of graphene [12] which reaches 5000 W/m K. Therefore, doping a small quantity of carbon nanoparticles is sufficient to enhance notably the thermal conductivity of a PCM. The present article contains results of experimental and theoretical investigations of heat and electrical current propagation through a PCM doped with CNTs of various type at different concentration of the dopant.

Inserting a small quantity CNTs into a PCM results in formation of a composite material with percolation electric and thermal conduction. Both electric current and heat propagate along paths formed by contacting nanotubes in such a material. The electric and thermal conduction have a threshold character, so that the value of electric and thermal conductivity is experienced to a jump at exceeding some threshold value of the concentration of the dopant. One of the purposes of the present work is experimental determination of the position of the percolation threshold in the composite material under investigation.

2. Experiment.

Paraffin П-2 characterized by the melting temperature of 52°C, density of 870 g/m³, specific heat capacity of 2.2 J/(g K), melting enthalpy of 157 J/g, electric conductivity of ~ $10^{-19}$ S/m and heat conduction coefficient of 0.267 W/m K have been used as PCM. Two types of carbon nanotubes were used as a dopant: single walled CNTs TUBALL™ of about 5 μm in an average length and of 1.6 ± 0.4 nm in an outer diameter and multi-walled CNTs DEALTOM of 3 μm in length and 50 and 72 nm in the average outer diameter. The measured dependence of the electric conductivity on the dopant concentration was used as an indicator of reaching the percolation threshold. Two approaches to the preparation of the composite Paraffin + CNTs were applied. In the first approach the nanotubes are inserted into the melted paraffin under long time stirring. Unfortunately, such an approach did not result in any changing both electric and thermal conductivity because of a strong trend of CNTs to the aggregation. Despite of a long-time stirring, it is hard to provide homogeneous distribution of nanotubes over the volume of the material. In the second approach a preliminary prepared 3D nanotube network is filled with melted paraffin. This approach resulted in formation of a percolation conducting structure. The samples of the composite Paraffin + CNT of about 25x15x2 mm³ were prepared for the measurement of the electric conductivity and thermal conductivity. The electric measurements were performed using the standard apparatus (multi-meter Щ4313.2 and voltmeter В7-38). The thermal diffusivity of samples was measured by the laser flash method using the apparatus NETZSCH LFA 457. The thermal conductivity was calculated in the standard manner using the measured values of the thermal diffusivity and the data on density and heat capacity of the material.

Table 1. Electric conductivity of composites Paraffin + CNTs measured at various CNT concentrations.

| №  | CNT concentration, % by weight | Electric conductivity, $\text{S} \cdot \text{m}$ |
|----|-------------------------------|-----------------------------------------------|
| 1  | 5,2                           | $\sim 10^{-19}$                               |
| 2  | 10,4                          | 4,04 $10^{-3}$                                |
| 3  | 17,2                          | 9,49 $10^{-3}$                                |
A notable influence of CNT doping on electric conductance and thermal conductivity of paraffin was observed in the case of the usage a network of multi-walled CNTs DEALTOM filled with melted paraffin. Table 1 presents the dependence of the electric conductivity of such a composite on the CNT concentration. The measurements demonstrate that an increase of CNT concentration from 5% to 10% results in enhancement of the electric conductivity by 16 orders of magnitude. Such a behavior is inherent to the percolation conduction. One can believe that the percolation threshold for the electric conduction lies between 5 and 10%.

The measurements performed indicate non-linear electric properties of conducting composites Paraffin + CNTs. These properties manifest themselves in an increasing dependence of the conductivity on the applied voltage. Some examples of such dependences are presented on Fig. 1. Such a behavior is inherent to composites with the percolation conduction and relates to non-perfect contacts between neighboring conducting particles [13, 14]. In such contacts the charge transfer takes place due to the electron tunneling through the barrier formed by the electrical field between the adjacent particles. The tunneling probability depends critically on the distance between the contacting particles which results in an increasing dependence of the conductivity of the applied voltage.

![Fig.1](image.jpg)

**Fig.1.** Dependences of the conductivity of composites Paraffin + CNTs on the applied voltage measured for different samples. 1: CNT content is 17.5%, mixing duration is 20 min; 2: CNT content 17.5%, mixing duration is 30 min; 3: CNT content is 10.4%, mixing duration is 20 min.; 4: CNT content is 10.4%, mixing duration is 20 min. The thermal conductivity of the composites Paraffin+CNTs enhances at exceeding the percolation threshold for the electric conduction. At the CNT content of 10% the enhancement in the thermal conductivity accounts about 100%, which is in accordance with the data of [2].

### 3. Modelling the heat propagation in PCM

The heat propagation through PCM was simulated using the code COMSOL in dependence of the heat conduction coefficient and the phase transition enthalpy. The non-stationary heat equation was resolved with taking into account the jump in the specific heat capacity at the point of the phase transition. The rate of the heat propagation was by the characteristic heating time, i. e. the time required for the enhancement of at the distance of 10 cm from the origin by 30%. The calculation results are presented on Fig. 2 and Fig. 3 which show the dependence of the characteristic heating
time on the inversed the heat conduction coefficient, calculated at the phase transition enthalpy of 157 J/g and the dependence of the characteristic heating time on the phase transition enthalpy calculated at the heat conduction coefficient of 0.2 W/m K. As is seen, the characteristic heating time is proportional to the phase transition enthalpy and inversely proportional to the heat conduction coefficient of the material.

Fig. 2. Dependence of the characteristic heating time on the inversed the heat conduction coefficient, calculated at the phase transition enthalpy of 157 J/g

Fig. 3. Dependence of the characteristic heating time on the phase transition enthalpy calculated at the heat conduction coefficient of 0.2 W/m K

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