Thermal conductivity of PCM materials based on a composite consisting of $n$-alkane and nanoscale additives

A K Borisov, V M Egorov, V A Marikhin and L P Myasnikova
Ioffe Institute, 26 Polytechnicheskaya, St. Petersburg, 194021, Russia

Abstract. Composites based on $n$-alkane and nanoscale additives were investigated to determine the efficiency of heat transfer during phase transitions in phase change materials. It was found that the thermal conductivity of composite materials is several times higher than the thermal conductivity of the initial $n$-alkane. The observed effect is due to the specificity of the supramolecular nanostructure of the composite, which differs from the supramolecular structure of the nonadecane.

1. Introduction
One of the most relevant and promising directions for the green energy is the development of phase change materials (PCM) capable of absorbing, storing and transforming thermal energy flows due to their own thermal effects, including phase transitions (PT). Homologous series of aliphatic hydrocarbons and their derivatives, primarily normal $n$-alkanes, are considered as the most promising PCM in this respect [1, 2]. In addition to the most important characteristic of PCM – their energy content, the thermal conductivity of these materials, which determines the power of the energy absorbed or released in the form of heat, is of great importance.

2. Samples and experiment
In this work, to clarify the efficiency of heat transfer during phase transitions, composites based on $n$-alkane (nonadecane) and nanoscale additives (aluminum powders with a particle size of 50-70 nm and 90-110 nm; silver powder with a particle size of 50-70 nm) were investigated: 1) initial nonadecane – sample I, 2) nonadecane with the addition of 50-70 nm Al particles – sample II, 3) nonadecane with the addition of 90-110 nm Al particles – sample III, 4) nonadecane with the addition of 50-70 nm Ag particles – sample IV. Composite samples were prepared in a nonadecane/powder weight ratio of 95/5. For uniform distribution of additives over the volume, the samples in the molten state were treated with an ultrasonic disperser UZD1-0.1/22 (St.Petersburg, Russia).

The thermodynamic parameters of the composites were determined on a DSC 500 calorimeter (OOO “Spezpribor”, Samara, Russia) in a nitrogen atmosphere at a scanning rate of 1 K/min. The temperature scale is calibrated with respect to the melting points of ice (273.1K) and indium (429.7K). The heat flow scale was calibrated with respect to the heat capacity of sapphire. The measurements were carried out in the temperature range 270-320K. The weight of the test pieces was 5 mg.

Figure 1 shows the DSC curves obtained by heating the samples under study in the temperature range containing the range of the first-order structural PT ~ 290-294K. It can be seen from the figure 1, that the shape of the endothermic peaks on the DSC curves corresponding to nonadecane (curve 1) and composites (curves 2-4) are significantly different. In the latter, the amplitudes of the peaks ($\Delta C_{\text{max}}$) significantly increased, melting peak positions change, and the temperature ranges of the PT decreased.
$\Delta C_p = 25 \text{ J g}^{-1} \text{K}^{-1}$

![Image of endothermic peaks corresponding to solid-state PT in samples I-IV. Bold lines are the experimental data; dotted lines are the baselines; thin lines are linear extrapolations of the leading edge of the peaks.]

3. Theoretical calculations

In [3], we developed a method for determining the thermal conductivity coefficient by analyzing the shape of the PT endothermic peak. It turned out that the slope of the peak on the experimental DSC curve and the shift of the temperature of the peak maximum $T_0$ to higher temperatures (the so-called "thermal lag") are due to the thermal resistance $R$. The value of the latter is inversely proportional to the thermal conductivity of the material under investigation and is determined by the relation $R = \frac{\lambda}{k} \phi$, where $\phi$ is the angle of inclination of the leading edge of the peak (see figure 1). The value of $R$ with an accuracy up to a factor $k$, which takes into account the geometric dimensions of the sample, determines the coefficient of thermal conductivity $\lambda$ of the sample material according to the ratio $\lambda = \frac{k}{R}$ [3]. When testing samples of the same geometric shape, the factor $k$ remains constant. This makes it possible to find comparative characteristics of the thermal conductivity of the samples. If the coefficient of thermal conductivity of one of the samples is known, then the value of $R$ defined for it can be used to establish the value of $k$, which can then be used to determine the coefficient $\lambda$ of other samples.

Figure 1 shows that the linearity of the leading edge of endotherms with increasing temperature is largely preserved for all samples and, therefore, the thermal resistance during the phase transition remains constant. From the angle of inclination of the leading edge $\phi$ for all the samples under study, the values of $R$ were determined, which are given in table 1.

As noted above, to determine the $\lambda$ coefficients of all samples, it is sufficient to find the $k$ value of one of the tested samples. Indeed, since the thermal conductivity coefficient for paraffins is well known ($\lambda = 0.1264 \text{ W K}^{-1} \text{m}^{-1}$ [4]), it is easy to determine the value of the factor considering the geometric dimensions of the sample, which for nonadecane turned out to be equal to $k = 112 \text{ m}^{-1}$. And using this value, it is possible to determine the value of the thermal conductivity coefficient for the studied composites. The values of $\lambda$ calculated in this way are shown in table 1.
The greatest effect from the introduction of nanoscale particles was observed in a study [5] under study significantly exceeds the thermal conductivity of the most amorphous-crystalline polymers. The thermal conductivity coefficient \( \lambda \) of the two symmetric peaks. By varying the parameters in which \( \approx 10\% \) of graphene was embedded in paraffin. The thermal conductivity coefficient in the composite is apparently associated with a change in the structure of paraffin when small particles are introduced into it. This fact manifests itself in the change in the thermal conductivity coefficient in the composite is apparently associated with a change in the structure of paraffin when small particles are introduced into it. This fact manifests itself in the change in the thermodynamic parameters of the solid-state PT.

Table 1. Thermal conductivity coefficient \( \lambda \) in nonadecane with additives and parameters of heat capacity peaks during solid-state phase transition.

| Sample | \( R \) (KW\(^{-1}\)) | \( \lambda \) (WK\(^{-1}\)m\(^{-1}\)) | Calculation peak \( T_0 \) (K) | \( \Delta C_{\text{max}} \) (J/gK) | \( q_0 \) (J/g) | \( q_0/(q_0+q_\omega) \) (%) | \( B \) | \( \omega \) (nm\(^3\)) |
|--------|----------------------|--------------------------|--------------------------|--------------------------|--------------|--------------------------|--------|--------------------------|
| I      | 888                  | 0.1264 [4]               | 1                        | 291.60                   | 18.0         | 35.1                     | 77     | 580                      | 84    |
| II     | 208                  | 0.5376                   | 1                        | 292.50                   | 15.0         | 17.5                     | 44     | 1000                     | 290   |
| III    | 226                  | 0.4928                   | 1                        | 292.50                   | 16.0         | 18.7                     | 40     | 1000                     | 280   |
| IV     | 273                  | 0.4032                   | 1                        | 291.75                   | 10.0         | 11.7                     | 38     | 1000                     | 430   |

Where \( R \) is the thermal resistance, \( T_0 \) is the peak temperature, \( \Delta C_{\text{max}} \) is the peak amplitude, \( q_0 \) is the quantity of transition heat, \( B \) is the athermal parameter and \( \omega \) is the elementary volume of transformation.

From the data given in the table 1, it follows that the thermal conductivity \( \lambda \) of the composites under study significantly exceeds the thermal conductivity of the most amorphous-crystalline polymers. The greatest effect from the introduction of nanoscale particles was observed in a study [5] in which \( \approx 10\% \) of graphene was embedded in paraffin. The thermal conductivity coefficient according to the results of this work was \( \approx 0.9362 \) WK\(^{-1}\)m\(^{-1}\). Since the thermal conductivity of solids has a different nature depending on the type of substance, it can be assumed that by adding particles of aluminum and silver to the paraffin, which have a much higher conductivity (for Al\(_2\)O\(_3\) \( \approx 25-30 \) WK\(^{-1}\)m\(^{-1}\); for Ag \( \approx 400 \) WK\(^{-1}\)m\(^{-1}\)), an increase in thermal conductivity in the composite can also be expected. Thermal resistance as an additive value consists of the thermal resistance of paraffin and additive. Taking the latter as a value close to zero, one can expect an increase in thermal conductivity by the value of \( \lambda \) of the additive. Our estimates show that the effect of such an increase cannot exceed 5-10\%. Therefore, it can be assumed that the observed effect of a multiple increase in the thermal conductivity coefficient in the composite is apparently associated with a change in the structure of paraffin when small particles are introduced into it. This fact manifests itself in the change in the thermodynamic parameters of the solid-state PT.

Figure 1 shows that the shape of the PT peaks is asymmetric. This may be due to the presence of at least two components. To identify these components, the peaks were analyzed in the framework of the thermodynamic theory of a self-consistent field [6] as applied to the \( A \)-shaped diffuse first order phase transitions. The main idea of the theory is that in the volume of the old phase, localization of numerous fluctuations occurs in a limited volume in the form of stable nuclei of a new phase, the so-called elementary transition volume \( \omega \). Subsequently, as the transition develops, the motion of the interphase boundary is carried out by successive additions of nuclei with a volume \( \omega \) to the resulting phase boundary. The sizes of stable nuclei \( \omega \) can be determined from the shape of the heat capacity peaks. In [7], a relation was obtained for the temperature dependence of the heat capacity at a diffuse phase transition in the form

\[
\Delta C_p(T) = 4\Delta C_m \cdot \exp[B(T-T_0)/T_0] \cdot [1+\exp[B(T-T_0)/T_0]]^2,
\]

where \( T_0 \) is the temperature of the first-order PT, \( \Delta C_m \) is the maximum value of the heat capacity at \( T = T_0 \), \( B \) is the athermal parameter.

In asymmetric peaks, separation into two peaks of a symmetric \( A \)-shape was carried out under the condition that the enthalpy of the experimentally obtained peak was equal to the sum of the enthalpies of the two symmetric peaks. By varying the parameters \( T_0 \), \( \Delta C_m \), and \( B \) for each of the symmetric peaks, it was possible to obtain a coincidence with the right (high-temperature) or left (low-temperature) shoulder of the peak. The best agreement between the calculated and experimental
dependences was observed for the values of the parameters given in table 1. Figure 2 shows the results of calculating the $\Lambda$-shaped peaks by relation (1) and the experimental dependences of the heat capacity $\Delta C_p(T)$.

Parameter $B$ in the above relation (1) contains the most interesting information on the physical nature of the phase transition, since it is associated with the magnitude of the heat capacity peak $\Delta C_m$

$$\Delta C_m = q_0 \times B / 4 T_0,$$

(2)

where $q_0$ is the quantity of transition heat, and the elementary volume of transformation $\omega$

$$B = \omega \rho q_0 / k T_0,$$

(3)

where $k$ is the Boltzmann constant and $\rho$ is the density.

Parameter $B$ is a structurally sensitive parameter, since it determines the volumes of nuclei of a new phase in materials with diffuse PT. From relation (2) it is possible to determine the values of the specific heat (enthalpy) of transformation, and from relation (3) one can estimate the elementary volume of transformation $\omega$ (assuming in the first approximation that the density of paraffin crystals is $\rho \sim 0.8$ g·cm$^{-3}$ [8]). The calculation results for these ratios are shown in table 1.

$$\int \Delta C_p = 25 \text{ J/g·K}^{-1}$$

Figure 2. Endothermic peaks corresponding to first-order solid-state phase transitions in samples I-IV. Bold lines are the experimental data; thin lines are the result of calculation by dependence (2).

Indeed, the solid-phase transition in nonadecane occurs in two stages. As can be seen from figure 2, in the initial nonadecane, the phase transformation in most of the crystal occurs at the first stage. In this case, the nucleation of domains of a new phase with a size of $\omega = 84$ nm$^3$ is initiated (this follows from the ratio of the heats of transformation at the first and second stages; see table 1). The phase transformation leads to the depletion of the defect-free regions of the crystal and an increase in the surface energy due to the accumulation or appearance of obstacles in the remaining (not undergoing phase transformation) part of the crystal. At the second stage of the PT in the initial nonadecane, the phase transformation occurs in the smaller, remaining part of the crystal, but with an increase in the nucleus volume to $\omega = 570$ nm$^3$.

As can be seen from table 1, in contrast to the initial nonadecane, the phase transformation in composites occurs in the main part of the crystal in defect-free regions with larger $\omega = 500-600$ nm$^3$. Since the interfaces between elementary volumes are the predominant defects in $n$-alkane polycrystals,
Lack of interfaces provides increased thermal conductivity of the composite crystals. Therefore, an increase in $\omega$ will lead to a decrease in the volume defectiveness and, accordingly, to a decrease in phonon scattering, which will contribute to an increase in the thermal conductivity of the composite crystals as compared to the initial nonadecane [4].

4. Conclusion
It was found that a significant increase in thermal conductivity of the composite materials investigated is not due to the "additive" dopant of a more heat-conducting material, but to the rearrangement of the supramolecular structure of nonadecane due to the presence of additional crystallization centers and the formation of a specific supramolecular structure of $n$-alkane in the composite.

References
[1] Egorov V M, Borisov A K and Marikhin V A 2019 *Letters ZhTF* **45** 38
[2] Borisov A K, Egorov V M and Marikhin V A 2019 *J. Phys.: Conf. Ser.* **1236** 012010
[3] Bershtein V A and Egorov V M 1994 *Differential Scanning Calorimetry of Polymers: Physics, Chemistry, Analysis, Technology* (New York: Ellis Horwood)
[4] Godowsky Yu K 1982 *Thermophysics of polymers* (Moscow: Publishing house "Chemistry")
[5] Li M 2013 *Appl. Energy* **106** 23
[6] Fisher M 1968 *The nature of the critical state* (Moscow: Mir)
[7] Malygin G A 2001 *Solid state physics* **43** 1911
[8] Small D M 1986 *The Physical Chemistry of Lipids* (New York: Plenum Press)