This paper reports a series of experimental studies to establish regularities of the integrated effect exerted on the specific heat capacity of polymer nanocomposites by such factors as the temperature regime of their production, the value of the mass fraction of the filler, and the temperature of the composite material. The studies were conducted for nanocomposites based on polypropylene filled with carbon nanotubes. When obtaining composites, the method of mixing the components in the melt of the polymer was used. During the studies, the temperature of nanocomposites varied from 295 to 455 K, the mass fraction of the filler—from 0.3 to 10 %. The basic parameter of the technological mode for obtaining composite materials, the value of overheating the polymer melt relative to its melting point, varied in the range of 10...75 K.

It is shown that the temperature dependence of the specific heat capacity of the considered composites is sensitive to changes in the overheating of the polymer melt only in the region maximum values of the specific heat capacity. Concentration dependences of the specific heat capacity of the considered nanocomposites at different values of their temperature and the level of overheating of the polymer melt have been built.

The studies have been carried out to identify the effects of the influence of the above parameters on the coefficient of thermal diffusivity of nanocomposites. It has been established, in particular, that an increase in the level of overheating the polymer could lead to a very significant increase in the coefficient of thermal diffusivity, which is all the more significant the higher the proportion of filler and the lower the temperature of the composite material. It is shown that the level of overheating the polymer melt relative to its melting point is a parameter that can be used as the basis for the creation of polymer composite materials with specified thermophysical properties.

Keywords: polymer nano-composites, heat capacity of nanocomposites, thermal diffusivity of nanocomposites, carbon nanotubes, temperature regimes
The widespread use of polymer composites requires a large value of knowledge regarding their thermophysical properties. At the same time, detailed information on the noted properties is needed, which includes, in particular, their dependence on temperature, filler concentration, parameters of the technological mode for obtaining composites, etc. This predetermines the relevance of research aimed at a comprehensive study of these dependences for various thermophysical properties of polymer nanocomposites.

2. Literature review and problem statement

The results of studies into the heat capacity of polymer micro- and nanocomposites are reported in many papers [1–5]. In those cases, experimental and theoretical research methods are used. Thus, the authors of [1] acquired a large value of experimental data on the specific heat capacity \( c_p \) of new nanocomposites based on a binary salt melt (NaNO\(_3\)–KNO\(_3\)), filled with hexagonal boron nitride (hBN) nanoparticles. However, the cited paper is limited to the study of \( c_p \) average values in the solid and liquid phases. Work [2] provides data from experimental studies of the temperature dependence of the heat capacity of polymer composites based on polycarbonate when it is filled with aluminum microparticles or carbon nanotubes (CNT). An analysis of the influence of the mass fraction of the filler on the value of the heat capacity of the composite materials under consideration is given. At the same time, the work lacks a technological aspect of research concerning the effects of the influence of technological factors on the magnitude of the specific heat capacity of the polymer nanocomposites under study. Paper [3] reports the results of experimental studies to determine the heat capacity of nanocomposites used for devising a new method for separating the components of the mobile and rigid amorphous fractions. That is, the study of the specific heat capacity of polymer composites is of a service nature and concerns only the justification of the specified method. The data from experiments to study the effect of filler dispersion on the heat capacity and thermal stability of nanocomposites made of low-density polyethylene filled with regenerated clay are reported in [4]. The obtained heat capacity data were used to analyze changes in thermal characteristics associated with the nanomorphology of materials. The results of heat capacity studies play a supporting role in the cited work and are used mainly for the specified analysis. Paper [5] reports a theoretical study into the effective thermal properties of polymer nanocomposites based on high-density polyethylene and single-layer carbon nanotubes as a matrix and filler, respectively. Using the Mori-Tanaka scheme, the heat capacity of nanocomposites has been shown to decrease with increasing volume fraction of CNT. The cited paper deals mainly with the theoretical prediction of the heat capacity of nanocomposites and there are no studies of its dependence on the totality of defining parameters.

In several works [6, 7], the studies into the specific heat capacity of polymer composites are accompanied by the examination of their other thermomechanical properties. Thus, paper [6] defines the temperature dependences of the most important physical and mechanical parameters of nanocomposites – the modulus of elasticity, yield strength, density, specific heat capacity, etc. That is, the specific heat capacity of nanocomposites is studied along with their other physical characteristics, and, consequently, relatively little attention is paid to its study. In work [7], along with the study into the thermal stability of composite materials, the results of investigating their specific heat capacity are considered. At the same time, the latter play a service role in the cited study.

Our review of studies into the heat capacity of polymer nanocomposites indicates that the available publications relate only to certain aspects of the influence of various parameters on the heat capacity of nanocomposites. They do not exhaust the need for a comprehensive analysis of the dependence of this property of composites on a set of defining factors (temperature, filler concentration, the technological mode for obtaining composite material, etc.).

As regards the coefficient of thermal diffusivity of polymer nanocomposites, which is responsible for their thermal inertial properties, and is essential for non-stationary thermal processes, research into this thermophysical parameter is very limited. An example is work [8], in which the thermal conductivity coefficients for two series of polymer nanocomposites are considered in terms of heat transfer mechanisms in these composite materials. In [9], based on modeling molecular dynamics, the effect of aluminum oxide nanoparticles on the thermal diffusivity of isotactic polymethyl methacrylate is investigated.

Thus, it is important to study the specific heat capacity and thermal diffusivity of polymer nanocomposites in terms of a comprehensive investigation of their concentration, temperature, and technological dependences.

3. The aim and objectives of the study

The purpose of this work is to establish the regularities of influence exerted on the specific heat and thermal diffusivity of polymer nanocomposites by such factors as the temperature regime of their production, the value of the mass fraction of the filler, and the temperature of the composite material. The results to be obtained could be used as the basis for the creation of composite materials with the specified thermophysical properties necessary for engineering practice.

To accomplish the aim, the following tasks have been set:
- to perform a set of experimental studies to establish, for the specific heat capacity of the studied polymer composites, its temperature, concentration, and technological dependences;
- to identify the regularities of influence exerted on the coefficient of thermal diffusivity of the studied composites by the level of overheating the melt of polymer \( \Delta T \), the temperature of the composite, and the mass fraction of the filler.

4. The study materials and methods

We have considered polymer nanocomposites based on polypropylene filled with CNT. The production of nanocomposites involved a method based on mixing the components in the polymer melt using a disk extruder. A description of the procedure for implementing the method and the corresponding equipment is given in [10]. In terms
of the influence of the temperature regime for obtaining composites, we investigated the dependence of their thermophysical properties on one of the most important technological parameters – the level of overheating the polymer melt $\Delta T$ relative to its melting point.

Standard and improved procedures were used to determine the specific heat capacity and thermal diffusivity of the resulting composite materials.

The specific mass heat capacity of the resulting composite materials $c_p$ was determined using the method of differential scanning calorimetry at the Perkin-Elmer DSC-2 unit employing the software from IFA GmbUlm.

The thermal diffusivity coefficient $\alpha$ of composite materials, which is a measure of its heat inertial properties, was calculated from the dependence $\alpha=\lambda/(c_p\rho)$. In this formula, the heat conductivity coefficient of composites $\lambda$ was determined using the modified IT$\lambda$-400 device; their density $\rho$ was determined using the hydrostatic method.

An experimental study into the thermophysical properties of polymer composites was carried out with a variation in the mass fraction of the filler from 0.3 to 10 %. The polymer melt overheating level $\Delta T$ relative to the melting point of the polymer varied in the range of 10...75 K. The temperature of the resulting composite varied within 295...455 K.

5. Results of studying the properties of polymer nanocomposites based on polypropylene filled with carbon nanotubes

5.1. Results of determining the specific heat capacity of polymer nanocomposites

Fig. 1 shows the results of experimental studies into the specific heat capacity of the considered composites depending on their temperature at different values of the level of overheating $\Delta T$ for the mass concentration of the filler $\omega$ equal to 3%.

![Fig. 1. Dependence of the specific heat capacity $c_p$ of the polymer nanocomposite based on polypropylene filled with carbon nanotubes on the composite temperature $T$ for a mass concentration of filler equal to 3 %, at different values of the overheating level of the polymer melt $\Delta T$.

$1 - \Delta T=10 K; 2 - 30 K; 3 - 50 K$

Fig. 2 illustrates experimental dependences of the specific heat capacity of polymer composites on the value of overheating the melt of polymer $\Delta T$ at different temperatures of the composite and different mass fractions of the filler.

![Fig. 2. Dependence of the specific heat capacity $c_p$ of the polymer nanocomposite based on polypropylene filled with carbon nanotubes on overheating of the polymer melt $\Delta T$, at different temperatures of the composite $T$:

$1 - 390 K; 2 - 410 K; 420 - 3 K; 4 - 430 K; 5 - 440 K$, and different values of the mass fraction of filler $\omega$:

$\omega=0.3 %; b = 3.0 %; c = 10.0 %$

The effect of the mass fraction of the filler on the specific heat capacity of composites is demonstrated in Fig. 3.

This figure shows the results for different values of overheating $\Delta T$ and temperature of the composite.

![Fig. 3. Dependence of the specific heat capacity $c_p$ of the polymer nanocomposite based on polypropylene filled with carbon nanotubes on overheating of the polymer melt $\Delta T$, at different temperatures of the composite $T$ and different mass fractions of filler $\omega$.

$1 - 390 K; 2 - 410 K; 3 - 420 K; 4 - 430 K; 5 - 440 K$, and different values of the mass fraction of filler $\omega$:

$\omega=0.3 %; b = 3.0 %; c = 10.0 %$]
corresponding to the melting point of the polymer, it does not change with increasing the polymer melt overheating level $\Delta T$.

Our studies also indicate that the nature of the effect of overheating $\Delta T$ on the values of the specific heat capacity of composites $c_p$ is preserved at different values of the mass fraction of the filler – CNT.

It follows from the data shown in Fig. 2 that at polymer nanocomposite temperatures of 440 K and 430 K, a noticeable decrease in its heat capacity is observed only with an increase in the level of overheating the polymer melt $\Delta T$ from 10 to 50 K. A further increase in $\Delta T$ almost does not affect the value of the heat capacity of the composite. At lower temperatures of the polymer composite (420, 410, 390 K), there is a slight drop in its heat capacity in the region of change in $\Delta T$ from 10 to 50 K, and a practical constancy of $c_p$, with a further increase in $\Delta T$. As can be seen from Fig. 2, $a$ – $b$, the described regularities are characteristic of all the values considered.

According to the data obtained, the dependences of the heat capacity of polymer nanocomposites on the mass fraction of the filler for different temperatures of composites and levels of overheating of the melt of polymer $\Delta T$ are of a similar nature (Fig. 3). Namely, an increase in the mass fraction of CNT from 0.3 to 3.0 % leads to a decrease in heat capacity. At the same time, the lower the temperature of the composite, the less significant the drop in the value of $c_p$. With a decrease in the temperature of the nanocomposite, the effect of the melt temperature of the polymer $\Delta T$ on the heat capacity of the nanocomposite would also decrease.

It follows from the data shown in Fig. 2, 3 that when implementing different temperature regimes for obtaining nanocomposites corresponding to different values of $\Delta T$ differences in the values of their specific heat capacity could reach about 20 %.

The obtained values of the calculated coefficients of thermal diffusivity $a$ of the nanocomposites under consideration indicate that with an increase in overheating the melt of polymer $\Delta T$ relative to its melting point, the values of $a$ increase. This increase occurs over the entire range of temperature change $T$ of the composite and the mass fraction of the filler $\omega$ (Table 1). At the same time, this increase in the thermal diffusivity coefficient is the more significant the higher the value of $\omega$. Thus, at $T=390$ K, for $\omega=0.3$ %, with an increase in $\Delta T$ from 10 K to 50 K, the thermal diffusivity coefficient increases by 1.21 m²/s, and, at $\omega=10.0$ %, this increase is 2,193.19 m²/s.

It follows from the data given in Table 1 that the increase in the thermal diffusivity coefficient with an increase in $\Delta T$ is somewhat smaller with an increase in the temperature of the composite. For example, at $\omega=10.0$ %, with an increase in $\Delta T$ from 10 K to 50 K, the thermal diffusivity coefficient of composite materials increases by 2,240.50 m²/s for $T=380$ K, and by 2,106.2 m²/s for $T=400$ K.

According to our data, at a fixed value of overheating of polymer $\Delta T$ and the set temperature of the composite, its thermal diffusivity significantly depends on the mass fraction of the filler $\omega$. Thus, at $\Delta T=30$ K and temperature $T=400$ K, for $\omega=0.3$ %, the value of the thermal diffusivity coefficient is 8.87 m²/s, at $\omega=3.0$ % – 548.28 m²/s, and, at $\omega=10.0$ %, it reaches 1,187.37 m²/s.

6. Discussion of results of studying the thermophysical properties of polymer nanocomposites when they are filled with carbon nanotubes

According to our data, the heat capacity value $c_p$ of the polymer nanocomposites under consideration may significantly depend on the polymer melt overheating level $\Delta T$ (Fig. 1). With the growth of $\Delta T$, there is a slight drop in the values of heat capacity. At the same time, this drop is significant only in the region of the maximum of the curve $c_p=f(T)$. As regards the position of this maximum

$$\Delta T = 50 \text{ K}$$

$$\omega = 0.3, 1, 2, 3, 4, 5, 6, 7, 8, 9$$

$$\Delta T = 10 \text{ K}$$

$$\Delta T = 30 \text{ K}$$

$$\Delta T = 40 \text{ K}$$

$$\Delta T = 50 \text{ K}$$

Table 1

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<tr>
<th>T, K</th>
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<th>$\Delta T, K$</th>
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<tr>
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The data given in Table 1 correspond to different values of overheating $\Delta T$, different values of the mass fraction of the filler $\omega$, and the temperature of the composite $T$. 

Fig. 3. Dependence of the specific heat capacity $c_p$ of the polymer nanocomposite based on polypropylene filled with carbon nanotubes on the mass concentration of the filler $\omega$, at different values of the polymer melt overheating level $\Delta T$: 1, 4, 7 – $\Delta T=10 \text{ K}$; 2, 5, 8 – $\Delta T=30 \text{ K}$; 3, 6, 9 – $\Delta T=50 \text{ K}$, and different values of the temperature of the composite $T$: 1, 2, 3 – $T=440 \text{ K}$; 4, 5, 6 – $T=430 \text{ K}$; 7, 8, 9 – $T=400 \text{ K}$.

5.2. Results of calculating the thermal diffusivity of polymer nanocomposites

Table 1 gives the results of calculations of the thermal diffusivity coefficient for the composites under consideration.
For the predefined value of $\omega$ at a fixed value of $\Delta T$, the thermal diffusivity of composites decreases with increasing temperature. For example, at $\omega=10.0$ % and $\Delta T=50$ K, the value of $a$ is $2.592.18$ m$^2$/s at $T=380$ K, and $2.424.08$ m$^2$/s at $T=400$ K.

Worth noting is that the effect of the value of overheating the melt of polymer $\Delta T$ can be significantly larger for the coefficient of thermal diffusivity of composites in comparison with their heat capacity. As already noted, an increase in $\Delta T$ leads to an increase in the heat capacity of composites, which reaches about 20 %. At the same time, the coefficient of thermal diffusivity can increase by 14.3 times.

Thus, the level of overheating the melt of polymer $\Delta T$ relative to its melting point can be considered as a parameter by which it is possible to control the value of the heat capacity and thermal diffusivity of nanocomposites.

The study reported here considers only one type of polymer composites. In addition, it is limited to investigating the thermophysical properties of composite materials. Further research could explore the thermophysical properties of a wide range of practically important polymer composite materials. In addition, it must cover a set of various physical and mechanical properties of composites.

7. Conclusions

1. We have investigated, for polymer nanocomposites based on polypropylene filled with CNT, the regularities of changes in their specific heat capacity in terms of its concentration, temperature, and technological dependences. The experiments were performed at a temperature change $T$ of nanocomposites from 295 to 455 K for conditions of varying the mass fraction of CNT from 0.3 to 10 %. At the same time, in the process of obtaining composites, the level of overheating the polymer melt $\Delta T$ relative to its melting point changed in the range from 10 to 75 K. The dependences of the specific heat capacity of the considered composites on the temperature at different values of overheating $\Delta T$ and the mass fraction of the filler $\omega$ were determined. It is shown that for all values of $\omega$ with an increase in $\Delta T$, there is a decrease in the value of the heat capacity, which is significant only in the region of the maximum of the curve $c_p=\text{f}(T)$. The experimental dependences of the specific heat capacity of the considered nanocomposites on the level of overheating the polymer $\Delta T$ at different temperatures of the composites and fractions of the filler $\omega$ have been obtained. It is shown that at composite temperatures close to the melting point of the polymer, a significant change in the heat capacity of the nanocomposite material is observed only when the value of $\Delta T$ changes from 10 to 50 K. At temperatures corresponding to regions distant from the maximum of the curve $c_p=\text{f}(T)$, the drop in $c_p$ with an increase in $\Delta T$ is insignificant. We have obtained concentration dependences of the specific heat capacity of the studied nanocomposites for various values of its temperature and overheating $\Delta T$. The fact of a significant dependence of $c_p$ on the value of $\omega$ is established only in the region of its change from 0.3 to 3.0 %.

2. A set of necessary studies was carried out, which made it possible to calculate the coefficient of thermal diffusivity of the nanocomposites under consideration and to identify the influence exerted on it by the level of overheating the melt of the polymer $\Delta T$, the temperature of the composite $T$, and the mass fraction of the filler $\omega$. It is shown that an increase in the level of overheating $\Delta T$ can lead to a significant (more than 14 times) increase in the coefficient of thermal diffusivity of the composite, which is the more significant the higher the value of $\omega$ and the lower the temperature of the composite. It has been established that there is a significant dependence of the coefficient of thermal diffusivity of the composite $a$ on the mass fraction of the filler $\omega$. It is shown that the value of $a$ can increase by more than 260 times with an increase in $\omega$ from 0.3 to 10 %. At the same time, the level of this increase slightly depends on the temperature of the nanocomposite and increases with increasing the overheating $\Delta T$. It is concluded that the polymer melt overheating level $\Delta T$ is a parameter of the technological mode for obtaining composites, with the help of which the values of the specific heat capacity and thermal diffusivity of the nanocomposites under consideration can be controlled.

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