INFLUENCE ON THE THERMOPHYSICAL PROPERTIES OF NANOCOMPOSITES OF THE DURATION OF MIXING OF COMPONENTS IN THE POLYMER MELT

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1. Introduction

Modern trends in the development of technology, which are global in nature, include the widespread use of polymer composite materials. The latter have a combination of a number of important physical and mechanical characteristics, such as low specific weight, increased corrosion resistance and fatigue strength, a wide range of thermophysical proper-
ties, etc. Within the framework of this trend, the use of polymer nanocomposites stands out, characterized by the possibility of achieving record indicators important for promising areas of their use. This necessitates in-depth studies into the properties of polymer nanocomposites in these areas.

Among the many areas of application of polymer nanocomposite materials, their use for the manufacture of heat sinks in electrical or electronic systems, heat exchange surfaces in the thermal power industry, etc. In view of this, the task of studying the set of thermophysical properties of polymer nanocomposites depending on various parameters is relevant. Particular attention should be paid to studies relating to the analysis of the influence exerted on the thermophysical properties of composites by the parameters of the technological mode of their production. Such parameters, which largely determine these properties, include the duration of mixing of components in the melt of the polymer.

2. Literature review and problem statement

A large body of research addresses the thermophysical properties of polymeric micro-and nanocomposite materials. Thus, papers [1–6] highlight the results of experimental and theoretical studies into the thermal conductivity of polymer composites. In works [3, 7, 8], their heat capacity is investigated.

Many of the available studies of the thermophysical properties of polymeric micro-and nanocomposite materials concern the study of the effects exerted on these properties by various parameters. The main ones include the type of filler, its proportion and geometric characteristics, temperature, method of obtaining composites, etc. However, in the cited works, the dependence of a particular property of polymer nanocomposites on individual factors is typically considered without analyzing their complex influence. In addition, several works investigate relatively small ranges of changes in these parameters. Thus, paper [1] reports the results of experimental studies to establish the relationship between the thermal conductivity of polymer nanocomposites and the dimensions of the filler – graphene nanoplatelets. It is shown that an increase in the lateral size and thickness of the plates leads to a significant increase in the thermal conductivity of the composite materials under consideration. That is, the cited study is practically limited only to varying the size of the filler particles. Work [2] tackles the analysis of the effect of the mass fraction of the filler, TiO₂ or Al₂O₃ nanoparticles, on the thermal conductivity of nanocomposites based on epoxy resin. The results indicate that in the range of changes in the proportion of filler from 0.5 to 2 %, its increase more significantly affects the increase in the thermal conductivity of composites when using Al₂O₃ nanoparticles. Here, attention is drawn to a rather narrow range of changes in the proportion of filler and, accordingly, a very slight increase in the thermal conductivity of the materials in question. In work [3], based on the implementation of the Moore-Tanaka scheme, the thermally conductive properties of polymer nanocomposites based on high-density polyethylene filled with single-walled carbon nanotubes are predicted. Based on the results of the simulation, the presence of linear dependence of thermal conductivity on the volume fraction of the filler was established. The cited work also belongs to the group of studies in which the influence of only one parameter on the thermally conductive properties of polymers is subject to consideration. In [4], the authors devised an original computational approach to determining the thermal conductivity of polymer nanocomposite materials. As a representative example of the use of this approach, the results of modeling the thermally conductive properties of the epoxy resin-carbon nanotubes composite are reported. Data on the influence on the thermal conductivity of composites of such factors as the degree of solidification of epoxy resin, and the length and volume fraction of carbon nanotubes are also given. That study is mainly methodological in nature in terms of modeling the mechanisms of heat transfer in polymer composites. Work [5] reports experimental studies into the thermal conductivity of micro-and nanocomposites using various methods of their production. It is shown that the considered methods based on the mixing of components in dry form and in the melt of the polymer have significantly different efficiency in terms of the possibility of obtaining composites with high thermal conductive properties. The cited study concerns only two types of filler, although it is performed in a wide range of changes in their mass fraction. Paper [6] describes the features of the proposed method of preparing foams “polyvinyl formaldehyde-multilayer hydrocarbon nanotubes”. The results of studies of their thermal conductivity in a wide range of temperature changes (25...200 °C) with a variation in the mass fraction of the filler from 1 % to 4 % are given. Here, the emphasis is primarily on demonstrating the possibilities of a new method for obtaining nanocomposites, and not on a detailed study of their properties.

Works related to the study of the influence of various parameters on the heat capacity of polymer composites are significantly less numerous than the corresponding studies of their thermal conductivity. In addition, as a rule, they are more limited in terms of the completeness of research. Thus, in [3], the theoretical analysis of the specific heat capacity of nanocomposites “high-density polyethylene – single-walled carbon nanotubes” concerns the effect on their heat capacity of only the volume fraction of the filler. Work [7] reports experimental studies into the specific heat capacity of nanocomposites “binary salt solution (NaNO₃-KNO₃)-particles of hexagonal boron nitride”. It also considers the effects on the heat capacity of composite materials only of the concentration of filler nanoparticles. Paper [8] reports the results of experimental studies of the heat capacity of nanocomposites based on low-density polyethylene filled with regenerated clay. In the cited study, data on the heat capacity of nanocomposites are used to determine their thermal characteristics and, accordingly, have an auxiliary value.

It follows from our review of papers reporting studies into the influence of various parameters on the thermophysical properties of nanocomposites that the studies concerning the parameters of the technological regime for obtaining composites are very limited. As an example of such studies, there are works [9, 10], which provide the results of experiments to establish patterns of influence on the thermal conductivity and heat capacity of polymer nanocomposites of the temperature regime of their production. That is, in those works, the dependences of thermal conductivity [9] and heat capacity [10] of nanocomposites on only one technological parameter are considered. Although the thermophysical properties of these materials, as is known, are determined by a set of various regime parameters for their production.

Thus, our review reveals that available papers do not pay due attention to studies into the dependence of the thermophysical properties of nanocomposites on the set of parameters that determine these properties. Of particular interest are studies aimed at analyzing the effects of the technology for obtaining composites on their thermophysical characteristics.
3. The aim and objectives of the study

The aim of this work is to establish the regularities of influence exerted on the thermal conductivity, heat capacity, and density of polymer nanocomposites by the duration of mixing of components in the polymer melt when obtaining these composite materials. The results of the experimental studies could be used as the basis for devising a highly efficient energy-saving technology for obtaining these materials. To accomplish the aim, the following tasks have been set:

– to determine the thermal conductivity of polymer nanocomposite materials depending on the mixing time of components \( \tau \) in the polymer melt in the process of obtaining these materials and, on this basis, to justify the choice of a rational value for this parameter;

– to determine the specific heat capacity and density of the polymer nanocomposites obtained at different mixing durations of components in a wide range of temperature changes of the materials under study.

4. The study materials and methods

Polymer nanocomposite materials based on polypropylene when it was filled with carbon nanotubes (CNTs) were to be considered. The carbon nanotubes used were manufactured by the CVD (chemical vapor deposition) method. The content of mineral impurities in them was 0.1 %. The specific surface area of CNTs, determined by N\(_2\) adsorption, was 190 m\(^2\)/g. The outer diameter of CNTs, found using the method of small-angle scattering of X-rays, was 20 nm, the length – 1...5 \( \mu \)m, and the wall thickness – 5 nm. They were manufactured by OOO Spetsmash. As for the initial thermoplastic polymer matrix, isotactic polypropylene (type F401, melt flow index ITP=8.5 g/10 min) was used in the studies. To obtain these nanocomposites, a method based on mixing the components in the melt of the polymer was used. A description of this method is given in [9]. The thermophysical properties of nanocomposite materials were determined depending on the mixing time of components \( \tau \) in the polymer melt.

To find the thermal conductivity of the materials under study, the modified IT-\( \lambda \)-400 device was used. We determined the specific mass heat capacity of composites based on the method of differential scanning calorimetry implemented at the Perkin-Elmer DSC-2 unit. The density of the materials under study was determined using the hydrostatic method.

During our experimental studies, the mixing time \( \tau \) of the components of composite materials varied from 10 to 52 min. The mass fraction of filler \( \omega \) varied from 0.3 to 10 %. The thermophysical properties of the studied composites were determined in the temperature range of 290...475 K.

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

5.1. Results of studies to determine the coefficient of thermal conductivity of polymer nanocomposites

Fig. 1 illustrates the results of experimental studies to determine the coefficients of thermal conductivity of the examined nanocomposite materials as a function of the mass fraction of CNTs at different values of the mixing time \( \tau \). The data in Fig. 1, \( a \) correspond to the linear ordinate scale, in Fig. 1, \( b \) – logarithmic.

![Dependence on the mass fraction of the filler \( \omega \) of the coefficient of thermal conductivity \( \lambda \) of nanocomposite materials based on polypropylene filled with carbon nanotubes, at different values of the mixing time \( \tau \) of components in the melt of the polymer: 1 – \( \tau=52 \) min; 2 – \( \tau=27 \) min; 3 – \( \tau=20 \) min; 4 – \( \tau=16 \) min; 5 – \( \tau=10 \) min; 6 – \( \tau=5 \) min; \( a \) – linear ordinate scale; \( b \) – logarithmic]

Table 1 gives the values of the first and second percolation thresholds for polypropylene-based polymer nanocomposites filled with carbon nanotubes, with different durations \( \tau \) of mixing of their components.

<table>
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<th>Percolation threshold No.</th>
<th>Mixing duration ( \tau ), min</th>
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<tr>
<td>1</td>
<td>5 10 16 20 27 52</td>
</tr>
<tr>
<td>1</td>
<td>0.46 0.45 0.43 0.42 0.40 0.39</td>
</tr>
<tr>
<td>2</td>
<td>2.29 2.21 2.18 2.13 2.10 2.08</td>
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</table>

Table 1

Values of percolation thresholds (%) for polymer nanocomposites at different mixing durations \( \tau \) of components.
Percolation thresholds were defined as CNT mass fraction values corresponding to jumps in the thermal conductivity coefficient at the respective concentration dependences.

5. 2. Results of studies to determine the specific heat capacity and density of the obtained nanocomposites
The data on our experimental studies of dependence on the temperature of the specific heat capacity of nanocomposites for different values of the mixing time τ at fixed values of the mass fraction of the filler are given in Table 2. The results of experimental studies to determine the change in the maximum value of the heat capacity of the polymer \( C_{p,m}^\text{max} \), corresponding to the melting point, depending on the mixing time τ of the components at different values of the mass fraction of the filler ω are illustrated in Fig. 2. Fig. 3 shows the experimental dependences of the density of the nanocomposites under consideration on the temperature at different values of the mixing time of their components for ω=3.0 %.

| Table 2 | Temperature dependence of heat capacity \( c_p \), kJ/(kg·K) at a different mass fraction of filler ω and mixing time τ |
|---|---|---|---|---|---|---|
| ω=0.3 % | τ, min | 390 | 400 | 410 | 420 | 430 |
| | 5 | 2.88 | 3.05 | 3.35 | 3.98 | 5.46 | 7.50 | 6.89 |
| | 10 | 2.87 | 3.04 | 3.32 | 3.91 | 5.21 | 7.03 | 6.48 |
| | 16 | 2.86 | 3.03 | 3.27 | 3.78 | 4.96 | 6.60 | 6.11 |
| | 20 | 2.73 | 2.86 | 3.09 | 3.56 | 4.68 | 6.22 | 5.76 |
| | 27 | 2.62 | 2.73 | 2.94 | 3.37 | 4.38 | 5.77 | 5.35 |
| | 50 | 2.57 | 2.68 | 2.88 | 3.31 | 4.29 | 5.66 | 5.25 |

<table>
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<tr>
<th>ω=3 %</th>
<th>τ, min</th>
<th>390</th>
<th>400</th>
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For the purpose of comparative analysis, Fig. 3 also shows the temperature dependence of the density of polypropylene (line 1).

6. Discussion of results of studying the thermophysical properties of polymer nanocomposite materials
The thermal conductivity of polymer nanocomposites, as is known, significantly depends on the degree of uniformity of the distribution of the filler in the polymer matrix. The more uniform this distribution, the more branched the percolation structures of filler particles responsible for the thermally conductive properties of nanocomposites.

When using a method based on mixing components in a polymer melt to obtain nanocomposites, the uniformity of the distribution of nanoparticles in the volume of the matrix, and, consequently, the thermal conductivity of the materials, is largely determined by the mixing time τ.
It follows from the data of our experimental studies that the thermal conductivity of the polymer nanocomposite materials under consideration increases with increasing mixing time $\tau$ (Fig. 1). In this case, the manifestation of this trend depends on the value of the mass fraction of the filler $\omega$. Larger values of $\omega$ correspond to a more significant effect of the mixing time of the components $\tau$ on the thermal conductivity of nanocomposites. For example, with an increase in $\tau$ from 5 to 50 minutes, the thermal conductivity coefficient increases from 0.8 to 60.7 W/(m·K) at $\omega=10\%$ and only from 0.21 to 0.23 W/(m·K) at $\omega=0.3\%$. As can be seen from Fig. 1, in the specified range of change in $\tau$, its effect on the thermal conductivity of composites is noticeable only at $\omega=2\%$.

According to the data obtained, an increase in the mixing time $\tau$ from 5 to 16 minutes leads to a relatively slight increase in the thermal conductivity of the composite $\lambda$ in the entire study range of change $\omega$. A further increase in the mixing time $\tau$ to 27 minutes corresponds to a rather sharp increase in $\lambda$. With an increase in $\tau$ from 27 to 52 minutes, a very slight increase in the thermal conductivity coefficient of composites is observed. That is, the role of mixing time in increasing the thermally conductive properties of the materials under consideration is practically limited to its specific value $\tau_{\text{m}}$. The choice of the latter should be carried out taking into consideration the need to implement energy-saving technology for obtaining nanocomposite materials. The mixing time for energy-saving purposes obviously should not include a region in which its increase does not lead to a significant increase in the thermal conductivity coefficient of the nanocomposite. As follows from the data of our experiments, the time $\tau_{\text{m}}$ can be taken to be equal to 27 min. At this value, a high degree of uniformity of the distribution of nanoparticles in the polymer matrix is ensured, at which the thermally conductive properties of composite materials close to the maximum for a given physical situation are achieved.

Our data also indicate that the value of $\tau$ affects the values of percolation thresholds (Table 1). As can be seen, an increase in the mixing time $\tau$ leads to a slight decrease in the values of both thresholds. This decrease is one of the factors in the formation of more branched percolation structures from filler particles and, accordingly, an increase in the thermal conductivity of nanocomposite materials.

According to the results of our experimental studies, the specific heat capacity $c_p$ of the nanocomposite materials under consideration decreases with an increase in the mixing time $\tau$ of their components (Table 2). This pattern is observed in the entire study range of changes in the temperature of composites $T_p$ and the mass fraction of the filler $\omega$.

The degree of influence of the value $\tau$ on the heat capacity $c_p$ depends significantly on the temperature level of the nanocomposite materials. As can be seen from Table 2, the drop in heat capacity $c_p$ with an increase in $\tau$ is most significant in the region of temperatures close to the melting point of the polymer ($T_m=442$ K) and for all values of the mass fraction of the filler. Further away from this region, the effect of mixing time on the heat capacity of nanocomposites decreases markedly. Thus, at $\omega=3\%$, an increase in $\tau$ from 5 to 50 minutes leads to a decrease in $c_p$ by 1.64 kJ/(kg·K) and 0.28 kJ/(kg·K) at a temperature of 440 K and 390 K, respectively.

As evidenced by the results of our experimental studies, in the entire range of changes in $\tau$ and $\omega$ under consideration, the maximum values of the heat capacity of polymer nanocomposites $c_{p,\text{max}}$ correspond to the melting point of the polymer. At the same time, the dependence of heat capacity $c_{p,\text{max}}$ on the mixing time $\tau$ at different values of the mass fraction of the filler $\omega$ is of a similar nature (Fig. 2). An increase in $\tau$ from 5 to 27 minutes leads to a rather sharp decrease in values $c_{p,\text{max}}$. This dependence $c_{p,\text{max}}=f(T)$ in this interval of change in $\tau$ is close to linear. A further increase in the mixing time to 50 minutes does not significantly affect the value of the maximum heat capacity of nanocomposite materials. Thus, for $\omega=3\%$, at an increase in $\tau$ from 5 to 27 min, the decrease $c_{p,\text{max}}$ is 1.6 kJ/(kg·K) (or 23%), and with an increase in $\tau$ from 27 to 50 minutes, only 0.1 kJ/(kg·K) (or 2%).

As can be seen from Fig. 2, the smaller the mass fraction of the filler $\omega$, the lower the heat capacity value $c_{p,\text{max}}$ over the entire range of time variation $\tau$. The noted pattern is maintained for heat capacity $c_p$ at different temperatures of composites. Although it is most pronounced in the region of temperatures close to the melting point of the polymer matrix.

Our data also indicate that the mixing time of the components $\tau$ has a noticeable effect on the density of the polymer nanocomposite materials under study. With an increase in time $\tau$, an increase in the density of composites for all values of their temperature is observed (Fig. 3). This increase is due to an increase in the efficiency of the formation of percolation structures from filler particles and, accordingly, an increase in the electromagnetic interaction between them and the matrix.

The increase in the density of the composite materials under consideration, associated with the increase in time $\tau$, under the analyzed conditions is relatively small. For example, for $T=400$ K at $\tau=5$ min, the density of $\rho=858.9$ kg/m$^3$, and at $\tau=52$ min – increases to $927.5$ kg/m$^3$, that is the increase is approximately 8%.

Attention is also drawn to the fact that the increase in the density of nanocomposites with an increase in time $\tau$ occurs very unevenly. Namely, with an increase in $\tau$ from 5 to 20 minutes, there is a relatively small increase in density. With a further increase in $\tau$ to 27 min, there is a rather sharp increase in the density $\rho$. Finally, with an increase in the mixing time of the components $\tau$ from 27 to 52 minutes, the density of nanocomposites changes very slightly.

As can be seen from Fig. 3, the temperature dependence of the density $\rho$ of nanocomposite materials is similar for all values of time $\tau$. It decreases significantly with increasing temperature. Thus, at $\tau=52$ min, the density of the nanocomposite material drops from 980 kg/m$^3$ at a temperature of $T=290$ K to 818 kg/m$^3$ at $T=475$ K. At all values of $\tau$, this decrease in density occurs most intensively near the melting point of the polymer matrix ($T_m=442$ K).

Our work reports studies relating to only one type of polymer nanocomposites. In addition, it is limited to the study of the influence on the thermophysical properties of the materials under consideration of only one technological parameter of their production.

Possible directions for further research may be related to the study of the thermophysical properties of a wide range of practically important polymer nanocomposites. Of interest are also studies aimed at analyzing the influence of various technological parameters to produce polymer nanocomposites on their thermophysical properties.

### 7. Conclusions

1. The coefficients of thermal conductivity of nanocomposites based on polypropylene filled with CNTs have been
determined, depending on the important technological parameter of their production – the mixing time of components $\tau$ in the melt of the polymer matrix. Our studies were conducted for conditions corresponding to the change in the duration of mixing of composite components from 5 to 52 minutes for different values of the mass fraction of the filler (0.3...10 %). It is shown that the thermal conductivity of the nanocomposites under consideration increases with the increasing mixing time of its components. At the same time, the manifestation of this trend is all the more significant the higher the value of the mass fraction of the filler. It was found that in the considered range of changes in the duration of mixing of components, its increase can provide an increase in the thermal conductivity of nanocomposites by more than 70 times. It is shown that the effect of the mixing time of components $\tau$ on the thermal conductivity of the materials under study is practically limited to some value $\tau_{p}$ above which this effect is insignificant. Under the considered conditions, the time $\tau_{p}$ value, which meets the energy-saving scenario for the implementation of the technology for obtaining nanocomposites, is 27 min. Data on the dependence of percolation threshold values on the mixing time components $\tau$ are obtained. An interpretation of this dependence is given in the context of the efficiency of the formation of percolation structures from nanoparticles in a polymer matrix.

2. For the polymer nanocomposites under study, the effects of the effect of the mixing time $\tau$ of their components on the specific heat $c_{p}$ and the density $\rho$ of these composite materials were investigated. Corresponding temperature dependences were obtained when the temperature of nanocomposites changes from 290 K to 475 K. It was shown that with an increase in the duration of mixing of components $\tau$, a decrease in the heat capacity of composites is observed. In this case, the latter is significant only in the region of temperatures close to the melting point of the polymer matrix $T_{m}=442$ K for all values of the mass fraction of the filler. It is found that, in general, the dependence of the heat capacity $c_{p}$ on time $\tau$ is less significant than the corresponding dependence for the thermal conductivity of nanocomposites. The decrease in the $c_{p}$ values with the growth of $\tau$ does not exceed 27 %. Data have been obtained indicating that in the range of time change $\tau$ from 27 to 50 minutes, the value $c_{p}$ changes insignificantly with all the studied values of the mass fraction of the filler $\omega$ and the temperature of nanocomposites $T$. It has been established that the mixing time $\tau$ has a noticeable effect on the density of the nanocomposite materials under study. At the same time, in qualitative terms, the nature of this influence is similar to that of the thermal conductivity of nanocomposites. However, the increase in density $\rho$ due to the increase in time $\tau$ is relatively small and does not exceed 10 % under the considered conditions.

References

1. Kim, H. S., Bae, H. S., Yu, J., Kim, S. Y. (2016). Thermal conductivity of polymer composites with the geometrical characteristics of graphene nanoplatelets. Scientific Reports, 6 (1). doi: https://doi.org/10.1038/srep26825


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