SECTION 5. ENERGY AND ENERGY ENGINEERING AND TECHNOLOGIES

5.1 Thermophysical properties of polymer micro- and nanocomposites when they are obtained by different methods

The increasing use of polymer micro- and nanocomposites is known to be associated with their improved properties compared to unfilled polymers. The needs of further development of this direction necessitate an in-depth study of the influence of various factors on the main characteristics of these composites [53 – 60]. According to the results of a number of studies, these characteristics significantly depend on the methods for obtaining composite materials [61 – 67]. Said circumstance determines the relevance of a comparative analysis of methods for obtaining composites to establish the regularities of their influence on the structure and properties of composites. Of particular interest is the conduct of relevant studies for high-heat-conductive composites, the prospects for the use of which are associated with the manufacture of parts for heat power equipment, installations for the chemical, food, processing industries, etc.

This article is mainly devoted to experimental and theoretical studies of the regularities of the influence of methods for obtaining high heat conductivity polymer micro- and nanocomposites on their thermophysical characteristics.

During the experiments, the two most widely used methods for obtaining polymer composites in engineering practice were used:

- method A, based on mixing dry components using a magnetic stirrer and an ultrasonic disperser with further hot pressing of the resulting composition;

- method B, based on mixing the components in a polymer melt using an extruder, with further giving the composite the required shape by hot pressing.

As for the second of these methods, within the framework of this study, one of its modifications was used, in which the so-called disk extruders are applied, which are

characterized by a number of well-known advantages in comparison with traditional screw devices.

The considered methods were used to obtain composites based on polypropylene filled with CNTs or aluminum particles. When conducting research, the mass fraction of fillers ω varied from 0.3% to 10%. A description of the methods for manufacturing these fillers and their characteristics is given in [68]. In this article there are also the technics used to determine the thermophysical properties of the resulting composites.

Let us first consider the results of experimental studies of the dependence of the heat conductivity coefficients λ of polymer composites on the mass fraction of fillers (CNTs or aluminum microparticles) when using methods based on mixing components in dry form and in a polymer melt to obtain these composites. According to those shown in Table 1 data, the use of the second of these methods makes it possible to obtain polymer composites with significantly higher heat-conducting properties than in the case of the first method.

Table 1. Dependence of the heat conductivity coefficient λ of polymer composites based on polypropylene, obtained using the methods of mixing components in dry form (Method A) and in a polymer melt (Method B) when filling the polymer matrix with CNT and aluminum microparticles

ω, %	Method A		Method B	
	Al	CNT	AL	CNT
0.0				
0.3	0.22	0.24	0.23	0.23
0.5	0.22	0.25	0.30	0.30
0.55	0.224	0.26	0.33	0.34
0.8	0.23	0.27	0.35	0.37
1.0	0.32	0.33	0.36	0.38
1.15	0.38	0.39	0.40	0.43
1.5	0.42	0.49	0.47	0.49

Continuation of table 1

2.0	0.45	0.56	2.45	3.15
2.5	1.05	2.11	11.42	16.78
2.85	1.78	2.79	15.45	26.15
3.0	2.10	3.99	18.47	31.11
3.15	2.98	4.52	20.23	33.14
4.0	5.48	10.41	23.08	41.63
4.2	6.01	12.52	23.9	42.21
4.6	8.40	15.90	24.50	44.01
5.0	10.68	17.40	25.39	45.82
7.0	19.44	27.82	27.03	54.56
9.0	23.90	32.11	28.56	57.69
10.0	24.91	32.55	28.92	58.73

It is also noteworthy that the increase in the values of λ associated with the use of method B is more significant for a polymer composite filled with CNTs than for a microcomposite filled with aluminum particles. Thus, the differences in the values of λ for the two considered methods with a mass fraction of fillers of 5.0% are 28.4 W/(m K) when CNTs are used as a filler, and only 14.7 W/(m K) when the polymer is filled with aluminum microparticles.

As can be seen from Table 1, the discrepancies in the heat conductivity coefficients of polymer composites obtained by various methods depend significantly on the mass fraction of the filler ω. For both considered composites, these deviations are insignificant in the range of ω from 0.3% to 2%. With an increase in ω, they increase, reaching a maximum value at a mass fraction of fillers equal to 4%. At the same time, the heat conductivity coefficients of composites obtained by method B exceed the corresponding values for composites obtained on the basis of method A, in the case of filling the polymer with CNT and aluminum by 4.0 and 4.2 times, respectively. Further, with an increase in the mass fraction of fillers from 4% to 10%, there is a tendency to reduce the discrepancies in the values of λ corresponding to

different methods of obtaining composites. Moreover, this trend is much more expressed for aluminum-filled microcomposites. Here, the indicated discrepancies decrease from 17.6 W/(m K) at ω = 4% to 4.1 W/(m K) at ω = 10%. For composites filled with CNTs, this decrease is not so significant, from 31.2 W/(m K) to 26.2 W/(m K).

Let us briefly consider the features of the influence of methods for obtaining composites on the effects of a sharp change in the value of their thermal conductivity coefficients at certain values of the proportion of fillers ω. As can be seen from Table 1 for both considered composites, two jumps in the thermal conductivity coefficient are observed. The first of them corresponds to the formation of percolation clusters from filler particles, which are a kind of heat-conducting channels, the second - to the formation of a percolation network, which is a highly thermally conductive medium. As for the position of these jumps, it follows from the data presented that it varies depending on the method of obtaining the composite. In this case, the values of ω corresponding to these jumps, the so-called percolation thresholds, for method B are shifted to the region of lower filler concentrations. Thus, for both considered composites, the first percolation threshold is 1.15% and 0.55%, respectively, when these composites are obtained by methods A and B. The second percolation threshold corresponds to a concentration of CNTs equal to 4.2%, and aluminum microparticles, 4.6% method A. This threshold decreases when using method B to 3.15% particals and to 2.85% when the polymer is filled with CNTs and aluminum microparticles.

The described picture of the influence of methods for obtaining polymer composites on their heat-conducting properties is associated with the following circumstances. As the results of the performed studies have shown, the use of method B for obtaining composites provides a more uniform distribution of the filler in the polymer matrix. This, in turn, leads to a higher efficiency of the formation of continuous percolation clusters and percolation networks from filler particles, which are responsible for increasing the heat conductivity of materials.

Regarding the established fact of greater sensitivity of the composite filled with CNTs to the method of its preparation, it is explained by a more significant effect of

the degree of uniformity of the filler distribution in the polymer volume on the formation of the indicated percolation structures. Indeed, due to the fact that the length of a carbon nanotube significantly exceeds its diameter, and the forces of electromagnetic interaction between the tubes are significantly less than between aluminum microparticles, the formation of percolation structures from CNTs with an increase in the uniformity of their distribution in the polymer matrix occurs more efficiently in comparison with aluminum microparticles.

Let us proceed to consider the results of experimental studies to determine the specific heat capacity c_p of polymer micro- and nanocomposites obtained by different methods. As can be seen from Fig. 1, differences in the values of c_p corresponding to method A and method B ($\Delta c_p = c_{pA} - c_{pB}$), are significant only in the region of polymer melting. In this case, the values of c_p for the composites obtained by method B are lower in this region for all values of the mass fraction of fillers ω. The data presented also indicate that the effect of the method of obtaining a composite on the values of its specific heat capacity is more significant when the polymer is filled with CNTs.

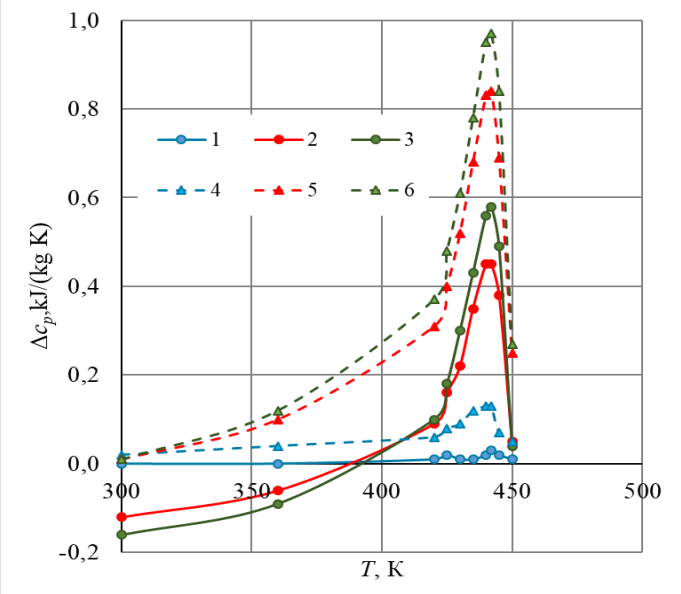

Figure 1. Temperature dependence of differences in specific heat capacity Δav (kJ/(kg K)) of polymer composites based on polypropylene, obtained using the method of mixing components in dry form (method A) and in a polymer melt (method B), for different mass fraction of fillers ω: 1, 4 - ω = 0.3%; 2, 5 - ω = 3.0%; 3, 6 - ω = 10.0%; when filling the composite with aluminum microparticles (1, 2, 3) and carbon nanotubes (4, 5, 6).

Based on the results of studies of the temperature dependence of the heat capacity c_p, the degree of polymer crystallinity χ in composite materials obtained by various methods was estimated. The value of χ was determined using these data according to the formula [69].

$$\chi = \frac{\Delta H_m}{\Delta H_{mc}} \cdot 100\% . \quad (1)$$

where ΔH_m, ΔH_{mc} – enthalpy of melting of the composite and fully crystalline polymer, J/kg

The results of calculations of the degree of crystallinity of polypropylene are shown in fig. 2. As follows from the presented data, for the considered polymer composites, the degree of crystallinity of polypropylene decreases with an increase in the mass fraction of fillers. Moreover, this decrease is more significant for composites obtained by method B. As for the degree of crystallinity of polypropylene filled with CNTs and aluminum microparticles, it turns out to be lower in the entire studied range of ω when polypropylene is filled with CNTs for both considered methods of obtaining composites.

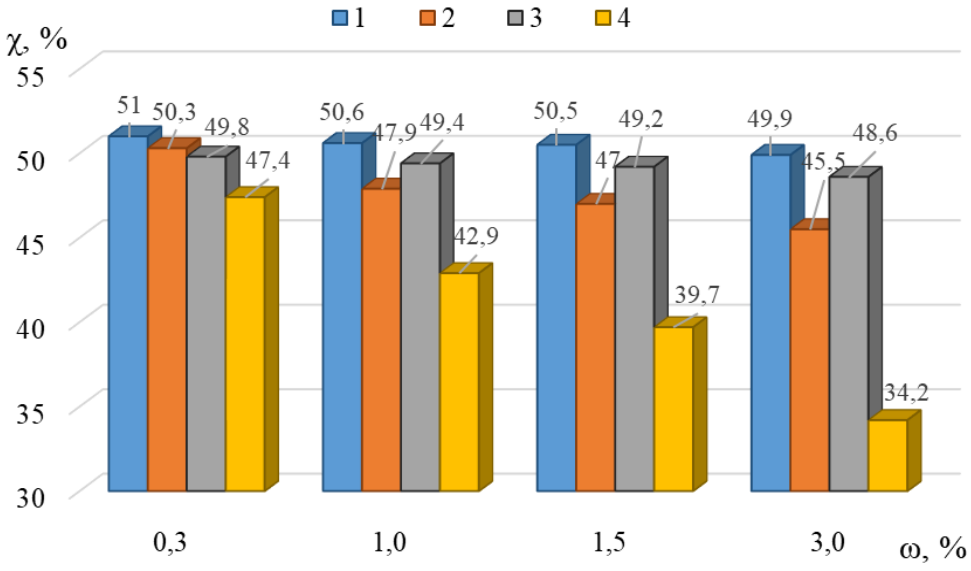

Figure 2. Dependence of the degree of crystallinity of polypropylene on the mass fraction of filler in composites obtained using the method of mixing components in dry form (1, 3) and in a polymer melt (2, 4), when polypropylene is filled with aluminum microparticles (1, 2) and CNTs (3, 4).

The established patterns of the influence of the method of obtaining composites on the degree of crystallinity of the polymer matrix are directly related to the level of uniformity of the filler distribution in polimer matrix. As already noted, a higher level of this uniformity occurs when method B is used. Under these conditions, a higher efficiency of the formation of percolation clusters and networks, which are steric obstacles to the formation of crystalline structures in the polymer matrix, is observed. In other words, the lower level of crystallization of the polymer matrix for composites obtained by method B is explained by the formation of more branched percolation systems from the filler particles due to the greater uniformity of the distribution of these particles in the volume of the matrix. It is the noted high branching that complicates the process of polymer crystallization.

On Figure 3 presents the results of experimental studies to determine the temperature dependence of the density of the polymer composites under consideration, obtained by various methods, at a fixed mass fraction of the filler ω = 3%.

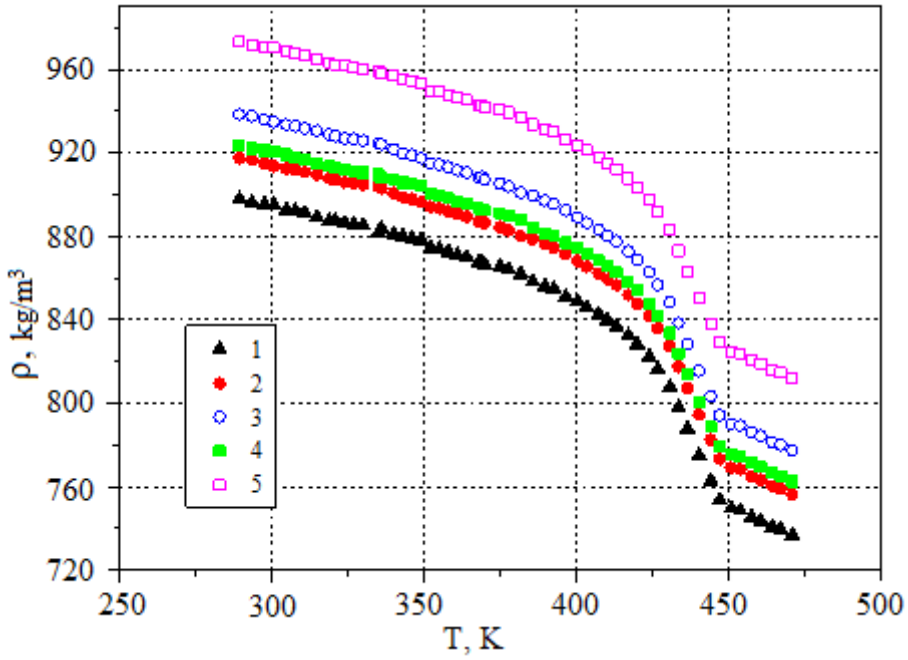

Figure 3. Temperature dependence of the density of polypropylene (1) and composite materials based on it, obtained using the method of mixing components in dry form (2, 4) and in a polymer melt (3, 5), when polypropylene is filled with CNTs (4, 5) and aluminum particles (2, 3) for ω = 3%.

As can be seen, for both methods under study, over the entire temperature range, the density of composites filled with CNTs turns out to be higher than the corresponding density values when the polymer is filled with aluminum microparticles. In this case, however, the ratio of the densities of the considered fillers is opposite, namely, the density of CNTs is 2200 kg/m^3, and that of aluminum microparticles is 2700 kg/m^3. Thus, the high density of composites with CNTs is determined not by the level of filler density, but by the mechanisms of formation of these composite materials. Indeed, under the conditions under consideration, in the amorphous zones of the polymer, due to the electromagnetic interaction of the filler particles with the polymer matrix, the material as a whole is compacted. Moreover, such densification occurs somewhat more intensively when the CNT polymer is filled, since these forces in this case turn out to be more significant due to the peculiarities of the shape of the tubes and their huge specific surface area (190 m^2/g).

As for the influence of the methods of their preparation on the density of composites, method B corresponds to a higher density. This is due to the above-described picture of an increase in the level of uniformity of the distribution of fillers in the matrix and, as a result, with a greater branching of the percolation structures formed during the implementation of this method. The presence of such structures determines the strengthening of the electromagnetic interaction between the fillers and the polymer matrix, which leads to the compaction of the material.

It is also important to note that, according to the experimental data, the differences in the density of composites obtained by different methods turn out to be more significant for composites filled with CNTs.

Figure 4 illustrates the dependence on the mass fraction of the filler of the increase in the porosity of composites $\Delta\Pi$, which is due to the introduction of the filler into the polymer matrix ($\Delta\Pi = \Pi - \Pi_{pm}$). Here, the values of Π were determined in accordance with [70] by the formula

$$\Pi = 1 - \frac{\rho - \left[\frac{\rho_f}{\rho_p}(1-\omega)\right]\rho_p}{\left[1 - \frac{\rho_f}{\rho_p(1-\omega)}\right]\rho_f}. \quad (2)$$

Where Π, Π_{pm} – porosity of composites and polymer matrix, %;

ρ_p, ρ_f – density of the polymer matrix and filler, kg/m^3.

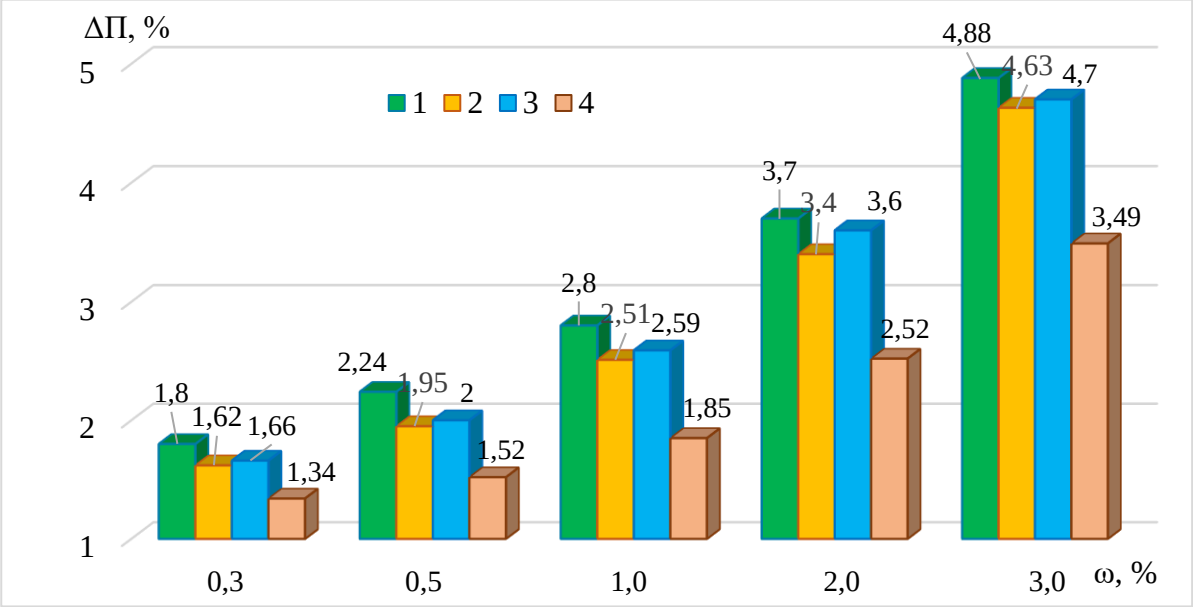

Figure 4. Dependence on the mass fraction of fillers of the increment in porosity ΔΠ of polymer composites obtained using the method of mixing components in dry form (1, 3) and in the polymer melt (2, 4), when filling the composite with CNT (3, 4) and aluminum particles (1, 2).

The data obtained indicate that the porosity of the composites increases with an increase in the mass fraction of the filler. At the same time, this increase is somewhat more significant for composites filled with aluminum microparticles, and it manifests itself to a greater extent when implementing the first of the considered methods for obtaining composite materials - the method of mixing components in a dry form.