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THERMOPHYSICAL PROPERTIES AND STRUCTURE OF THE POLYMER MATRIX OF MICRO- AND NANO-COMPOSITES BASED ON POLYETHYLENE

Summary. *The results of studies of thermal conductivity and the degree of crystallinity of the polymer matrix for polymer micro- and nanocomposites "polyethylene - carbon nanotubes and aluminum particles" are presented. The existence of a correlation dependence between the specified characteristics of composites was revealed and its explanation was given based on the theory of crystallinity and its explanation was given based on the theory of percolation.*

Key words: *polymer micro- and nanocomposites, degree of crystallinity, heat conductivity, aluminum microparticles, carbon nanotubes.*

The prospects for the use of high heat conductivity polymer micro- and nanocomposites are directly related to the study of their thermophysical properties and structure [1–15]. The creation of this modification of polymer composite materials involves the use of various fillers with high heat conductivity. Along with this, it is important to study the characteristics of such materials when using a wide range of polymer matrices.

Of great interest are also studies aimed at establishing a relationship between the thermophysical properties of high heat conductivity polymer materials and their structure.

The object of the work is to establish the patterns of changes in the heat conductivity of polymer micro- and nanocomposites based on polyethylene or polycarbonate from the mass fraction of different high heat conductivity fillers - CNTs or Al microparticles, as well as to analyze the relationship between the heat conductivity properties of these composites and the crystallinity degree of their polymer matrix.

To achieve the set aim, the following tasks were to be solved:

- perform a complex of experimental studies to establish the dependence of the heat conductivity properties of the obtained composites on the mass fraction of the fillers;

- based on the results of experimental studies of the temperature dependence of the materials under consideration, to reveal the regularities of the relationship between the heat conductivity properties of composites and the degree of crystallinity of their matrix.

Polymer micro- and nanocomposite materials based on polyethylene when filled with CNTs or aluminum microparticles were subject to consideration. These composites were produced using a method based on mixing components in the polymer melt using a special disk extruder [5].

The thermophysical properties of the investigated composite materials were determined taking into account standard methodological approaches. The improved IT-λ-400 device was used to determine their heat conductivity, and the mass specific heat capacity was determined by the method of differential scanning calorimetry on a DSC-2 unit with modified software.

In the course of research, the mass fraction of fillers ω varied from 0,3 to 10%. Methods of obtaining and characteristics of fillers used are given in [9].

The crystallinity degree χ of the obtained composite materials was determined based on the experimental dependence of the composites heat capacity on the temperature according to the formula [7]

$$\chi = \frac{\Delta I_m}{\Delta I_{mc}} \cdot 100\% \quad (1)$$

The characteristic results of the performed studies are presented in fig. 1 – 2 and in table. 1.

Let us first consider the experimental data for polymer micro- and nanocomposites based on polyethylene. Fig. 1 illustrates the change in heat conductivity λ of the studied composites depending on the content of fillers. As can be seen, the values of heat conductivity coefficients of composites significantly depend on the mass fraction of the filler ω. With an increase in the filler content, an increase in λ values is observed.

At the same time, in the entire analyzed range of changes in ω, the heat conductivity of the composites is higher when used as a CNT filler in comparison with the use of Al microparticles. Thus, the maximum achievable levels of λ (at ω=10%) are 45.4 W/(m·K) and 26.7 W/(m·K) when filling polyethylene with CNTs and Al, respectively.

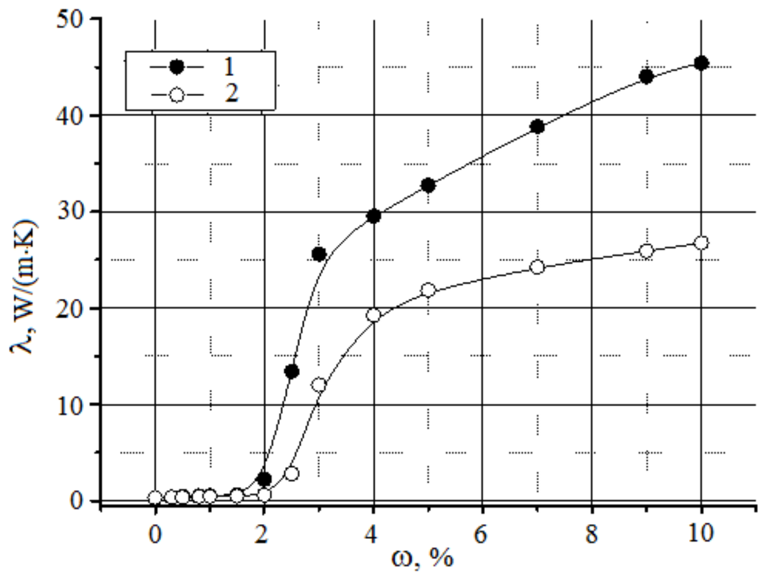

Fig. 1. Dependence of λ=λ(ω) for micro- and nanocomposites based on polyethylene filled with various fillers: 1 - carbon nanotubes; 2 - aluminum microparticles

Attention is drawn to the fact that the pattern of the change in the heat conductivity λ of the composites in different regions of the change in ω turns out to be different. As can be seen, three zones of change in ω can be distinguished, corresponding to different rates of increase in the coefficient of heat conductivity of composites.

The first zone corresponds to the range of filler content change from 0 to 2%. In this zone, the coefficient of heat conductivity of the analyzed composites does not undergo significant changes. It is important that this range contains the values of the first and second percolation thresholds (Table 1). Accordingly, after reaching these thresholds, there is a noticeable relative increase in heat conductivity of composites. However, in absolute terms, these changes are relatively small.

Table 1

Values of percolation thresholds (%) for polymer micro- and nanocomposites based on polyethylene, filled with CNTs and aluminum particles

CNT		Al	
Percolation threshold number			
1	2	1	2
0.40	1.55	0.55	1.98

The second zone of change in ω is characterized by a significant increase in the heat conductivity coefficient of composites, which indicates the intensive formation of percolation structures responsible for the heat conductivity properties of the materials under consideration. As for the boundaries of this zone, they are varied when using different fillers. Thus, in the case of filling polyethylene with CNTs, it covers the range of ω change from approximately 2% to 3%, when it is filled with Al microparticles - from 2% to 4%.

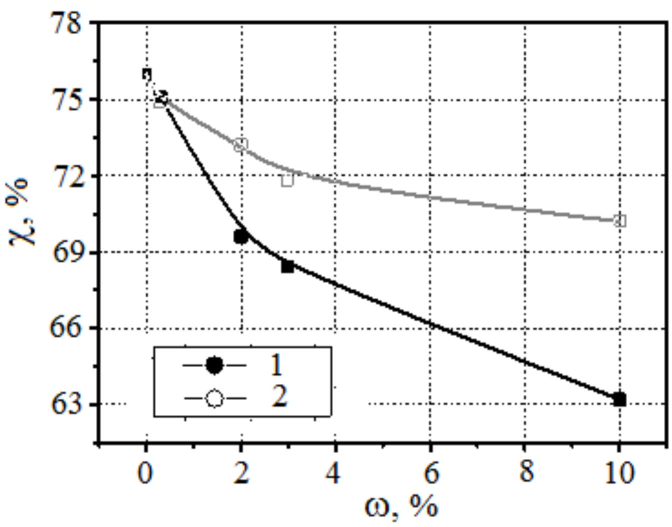

Fig. 2. Dependence χ=χ(ω) for micro- and nanocomposites based on polyethylene filled with CNTs (1) and aluminum microparticles (2)

In the third zone (which corresponds to ω values of 3-10% when used as CNT filler, and 4-10% - Al microparticles), the growth rate of the heat conductivity of composites decreases sharply. This fact indicates that the further branching of percolation structures with increasing ω leads to less intensive formation of heat conductivity channels from filler particles.

As can be seen from fig. 2, as ω increases, the degree of crystallinity χ of the polymer matrix of the composite decreases. At the same time, this decrease turns out to be much more significant when polyethylene is filled with CNTs than with Al microparticles. Thus, in the first of these situations, when ω increases from 0 to 10%, the degree of crystallinity of the matrix drops from 74% to 63.2%, and in the second - only to 70.2%.

As in the case of the dependence λ= λ(ω), the intensity of the decrease in the degree of crystallinity χ is varied in different regions of the change in the mass fraction of the filler. Comparison of data in fig. 1 and fig. 2 shows that the above three zones of change in ω also correspond to different rates of decrease in the degree of crystallinity χ.

In the first zone, the increase in the content of filler significantly affects the degree of crystallinity of the polymer matrix of the composites. That is, here the degree of crystallinity is very sensitive to an increase in the mass fraction of the filler. Under these conditions, the filler particles are significant steric obstacles for the formation of crystalline structures in the polymer matrix.

In the second zone of change in ω, the rate of decrease in the degree of crystallinity of the polymer matrix decreases significantly, remaining higher for the polymer filled with CNTs.

The third zone is characterized by the fact that here the degree of crystallinity continues to decrease with an increase in the mass fraction of the filler, although the rate of this drop decreases somewhat.

Therefore, the obtained data indicate the presence of a certain relationship between the heat conductive properties of the considered polymer micro- and nanocomposites and the degree of crystallinity of their polymer matrix. For the second and third of the considered zones of change in the mass fraction of the filler, this relationship can be expressed by the dependence.

$$\lambda = a - b \cdot \chi \qquad (2)$$

In the table 2 shows the values of the equation coefficients (2) for polyethylene-based composites.

Table 2

Values of the coefficients a and b in dependence (2) for micro- and nanocomposites based on polyethylene for different zones of change in the mass fraction of the filler ω

The number of the change zone ω	Coefficient	Filler	
		CNT	Al
2	*a*	1357.7	837.24
	б	19.47	11.43
3	*a*	286.4	411.6
	б	3.813	5.482

The conducted studies showed the presence of a relationship between heat conductivity and the degree of crystallinity of a polymer matrix based on polyethylene when it is filled with carbon nanotubes and aluminum particles.

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