Studies were carried out to establish the mechanisms of structure formation during crystallization of polymer composites based on polyethylene, polypropylene or polycarbonate filled with copper microparticles. The researches were executed using a technique, the first stage of which consisted in the experimental determination of crystallization exotherms of composites, and the second – in the theoretical analysis based on the obtained exotherms of the structure formation characteristics. A complex of studies on determination of crystallization exotherms for investigated microcomposites was carried out. The regularities of the cooling rate influence of composites, the method of their production and the mass fraction of filler on the temperature level of the beginning and ending of crystallization, the maximum value of the reduced heat flux, etc. were established. It is shown that for the applied methods of obtaining composites the increase of their cooling rate causes the decrease of the indicated temperatures and heat flux. It is established that the value of the mass fraction of the filler has a less significant effect on the characteristics of the crystallization process.

The regularities of structure formation of polymer composites at the initial stage of crystallization with the involvement of data on crystallization exotherms and nucleation equations are investigated. The presence of planar and three-dimensional mechanisms of structure formation at this stage has been established. It is shown that the ratio of these mechanisms is influenced by the type of polymer matrix and the method of obtaining composites.

For the second stage of crystallization, which occurs in the entire volume of the composite, the results of experiments on crystallization exotherms were analyzed on the basis of the Kolmogorov-Avrami equation. It is shown that the structure formation of polyethylene-based composites occurs by the three-dimensional mechanism, and on the basis of polypropylene and polycarbonate – by the mechanism of the stressed matrix

Keywords: polymer composites, copper microparticles, mechanisms of structure formation, polyethylene, polypropylene, polycarbonate

IDENTIFYING THE INFLUENCE OF THE POLYMER MATRIX TYPE ON THE STRUCTURE FORMATION OF MICROCOMPOSITES WHEN THEY ARE FILLED WITH COPPER PARTICLES

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1. Introduction

Polymeric micro- and nanocomposites occupy an important place among synthetic materials, which successfully replace traditional natural materials. This is largely due to the complex of unique physical and technological properties of such composites.

The possibility of obtaining new polymer composite materials by varying their components – such as polymer matrix and filler – deserves special attention.

The development of polymer composite materials with the necessary complex of properties involves conducting systematic researches on the choice of polymer matrix and type of filler, analysis of the patterns of structure formation of composites and more. Promising uses of polymer microcomposites are associated with the application of their highly heat conductive modifications. Thus, the latter can be used to replace metal elements in electric motors and generators for the manufacture of heat exchange surfaces for various purposes and so on. For example, the high efficiency of using these composite materials to create heat exchangers is associated with such characteristics as the required thermophysical and anti-corrosion properties, relatively low specific gravity, and so on.

2. Analysis of literature data and problem statement

The beginning of systematic studies of various aspects of the kinetics of non-isothermal crystallization of polymer micro- and nanocomposites filled with metals dates back to about 2000. Works [1–14] made a significant contribution to the development of scientific and technical bases for the creation of these materials. Thus, the article [1] presents the study results of the kinetics of composite isothermal crystallization a based on nylon 6 and aerosil of different series. The use of the Kolmogorov-Avrami mathematical model for obtaining thermodynamic parameters of crystallization is proposed. It is shown that this mathematical model reliably describes the kinetics of crystallization for a pure polymer matrix at its insignificant filling with aerosil. In [2] it is found that the proposed model reliably describes the crystallization processes for monomers and metals. The limit cases when it is possible to use this model to describe the kinetics of isothermal crystallization for a thermoplastic polymer matrix are presented. The article [3] considers the results of studies of the kinetics of isothermal crystallization of a metal alloy and notes that the Kolmogorov-Avrami equation adequately describes the process of crystallization from the melt. Articles [1–3] are mainly of methodological importance for establishing the adequacy of the Kolmogorov-Avrami model and do not contain the results of extensive parametric studies. In [4], the influence of molecular weight on the crystallization temperature and velocity of crystallites growth is studied on the example of commercial polyethylene glycol. The article [5] presents the results of studies of the kinetics of non-isothermal crystallization of polypropylene reinforced with multilayer carbon nanotubes and short glass fibers. The fact of increasing the crystallization velocity and decreasing the half-life of polypropylene crystallization in the presence of micro- and nanofillers has been established. It is shown that the Kolmogorov-Avrami model reliably describes the behavior of polypropylene only if the share of its crystallization does not exceed 70 %. Beyond this level, there is a significant discrepancy between experimental results and theoretical calculations. Article [5], as well as the above works, is largely methodical in nature, it, in particular, sets the limits of application of the Kolmogorov-Avrami equation for the studied composites. The results of studies of the kinetics of non-isothermal crystallization of pure polyvinyl alcohol and its nanocomposite based on nanocrystals of NaX zeolite are presented in [6]. Based on the results of studies of crystallization kinetics, which are grounded on data from differential scanning calorimetry, it was shown that NaX nanocrystals play the role of nucleation centers during crystallization. This was taken into account in the theoretical model, which significantly improved the

mathematical description of the experimental results. That is, in [6] the idea of the mechanisms of crystallization of polymer composites was developed. However, there are practically no studies of this process on the influence of determining factors on its main characteristics. The work [7] is devoted to the study of the influence of the amount of reinforcement and cooling rate on the kinetics of non-isothermal crystallization of nanocomposites based on polyamide 6. Two methods of nanocomposite preparation are used. It is shown that the structure formation and thermophysical properties of such composites significantly depend on the method of preparation. Work [7], however, is limited to studies of polymer composites based on a single polymer matrix. In [8], the regularities of the influence of carbon nanotubes (CNTs) on the kinetics of nonisothermal crystallization of polymer composites using the isoconversion method with differential scanning calorimetry and the method of optical microscopy in polarized light are investigated. In this study, the range of fillers used is somewhat expanded, which remains, however, insignificant. Namely, the peculiarities of crystallization of composites for some variants of CNT functionalization are considered. The article [9] is devoted to the analysis of the peculiarities of polymer composites crystallization filled with copper nanoparticles at different mass fractions of filler (0.5; 1.0; 2.0 and 4.0) %. The work concerns a number of issues related to the process of crystallization of polymer composites under consideration. However, there are virtually no studies on the influence of different determinants on the characteristics of the structure of composite materials (except for the mass fraction of filler). Much attention is paid to the comparative analysis of crystallization models in the presence and absence of CNT functionalization. In the study [10] considered only a few options for combinations of polymer matrix and filler. In [11] the results of researches of structure formation mechanisms at crystallization of polymeric composites on the basis of polycarbonate filled with microparticles of aluminum or carbon nanotubes are resulted. The study [12] is devoted to establishing the patterns of the structure formation of polymer composites filled with carbon nanotubes. In it, in particular, the data of the comparative analysis of structure formation characteristics at application of various polymeric matrices – from polycarbonate and polyethylene are resulted. Peculiarities of the influence of methods of obtaining polymer composites on the mechanisms of their structure formation are analyzed in studies [13, 14]. They consider composites based on polyethylene, filled with aluminum and CNT, respectively. In [11–14], detailed studies of the influence on the characteristics of the structure formation of composites of such factors as the mass fraction of filler and their cooling rate from the melt were performed. However, all of them are characterized by the absence of a certain complexity of research on many combinations of polymers and fillers, different methods of obtaining composites and so on.

Therefore, the available studies of the patterns of structure formation of polymer microcomposites, however, do not cover a wide range of issues, the solution of which is necessary for the development of these composites with given characteristics. In particular, further development is necessary to study the patterns of the structure formation of polymer microcomposites for different combinations of polymer matrices and fillers, using different methods of obtaining these composites and the like. It is also important for these conditions to study the influence of such factors as their cooling rate from the melt, the mass fraction of filler, etc. on the features of the structure formation of polymer microcomposites.

3. The aim and objectives of research

The aim of research is to establish the regularities of the formation of the structure of polymer microcomposites based on polyethylene, polypropylene and polycarbonate when they are filled with copper particles with varying in a wide range of the main defining parameters. This will make it possible to obtain the information needed to control the properties of these materials by changing their structure when creating composites with predetermined characteristics for different areas of their application.

To achieve this aim, the following objectives are solved:

– to perform a complex of experimental studies to determine the crystallization exotherms of composites during their cooling from the melt in a relatively wide range of changes in the mass fraction of filler and cooling rate for different methods of obtaining composites;

– to determine the characteristics of the structure formation of the studied polymer microcomposites.

4. Materials and methods of research of structure formation mechanisms of polymeric microcomposites

The experimental-theoretical technique of establishing the mechanisms of structure formation of polymer composites, which included two stages, was used in the work. The first of them was to experimentally determine the crystallization exotherms of the composite when it was cooled from the melt at a given constant rate. At the second stage of the technique, the characteristics of the structure formation of composites were theoretically determined using the obtained experimental data.

With regard to the experimental preparation of polymer microcomposites, two methods were used in the work, based on mixing the components, respectively, in dry form and in the polymer melt.

4. 1. Experimental methods for obtaining microcomposites

The first of the applied methods (method I) for obtaining microcomposites is based on mixing the components, which are in dry form, using a magnetic stirrer and an ultrasonic dispersant. A measuring beaker with a suitable granular polymer and filler microparticles is placed in a magnetic stirrer (Velp scientifica F2052). In the beaker inside the mixture of components are installed two anchors that rotate in a magnetic field around their axes. In addition, the glass contains the rod of the ultrasonic dispersant (UZDN-A150). Depending on the type of polymer, the mixing time (9–23 min) and the rotation velocity of the armatures in the magnetic field (29 r/s), as well as the power (30–45 W) and the operating time of the ultrasonic disperser (7–21 min) are set. The second method (method II) is based on mixing the components in the polymer melt using a disk extruder. The mixture of the composite material components in the mold of the extruder is compacted using a hydraulic press. Next, the mixture is heated in the mold to a temperature that exceeds the melting point (glass transition) of the polymer by 20–70 °C, depending on the type of polymer. The rotation of the metal piston, which gradually descends into the region of the polymer melt, provides mixing of the composite components. At a certain time, the composite material passes through a hole in the lower part of the mold.

The finishing operation of both methods is hot pressing of the resulting composition. The latter is carried out in a special installation, in which the composite is heated at normal pressure to a temperature that is 20 °C higher than the melting (glass transition) temperature of the polymer. After holding at the specified temperature, which lasts 15–20 minutes, the samples of the composite material are pressed while giving them the desired shape.

The copper microparticles used as a filler were obtained from copper sawdust by grinding them in a ball mill also to form particles with a size of 0.5... 1.0 µm. The geometric characteristics of the particles were determined by optical microscopy. The particles were spherical and flattened.

4. 2. Experimental determination of crystallization exotherms of polymer microcomposites

The construction of experimental crystallization exotherms of the composite during its cooling from the melt at a given constant rate was carried out as follows. The sample placed in the cell was heated to a temperature exceeding the melting point of the polymer by 50 K, kept at a given temperature of 180 s and then cooled at a fixed cooling rate (V_t=0.5...20.0 K/min). The specific heat flow Q_s removed from the composite was determined in an atmosphere of dry nitrogen by differential scanning calorimetry using a Perkin-Elmer DSC-2 device with modified software from IFA GmbUlm.

4. 3. Theoretical determination of the structure characteristics of polymer microcomposites

The obtained experimental data on the kinetics of crystallization of composites, as already mentioned, were the basis for the theoretical determination of the corresponding parameters of structure formation. Two stages of structure formation were considered – the initial stage of crystallization (nucleation stage) and the stage of crystallization in the whole volume of the composite. In the first of these situations, the main characteristics of crystal formation, such as the reduced nucleation parameter a_m and the reduced transport barrier K_m, were to be determined.

$$a_m = Z/k\left(\Delta H_m^o\right)^m, \quad K_m = A\exp\left(\Delta E/kT_N\right), \qquad (1)$$

where Z is the nucleation energy; k is the Boltzmann table; ΔH_m^o – melting enthalpy; m is the dimensionless parameter of the form; T_N – temperature of the crystallization beginning; ΔE – activation energy; A – numerical coefficient.

In addition, it was necessary to analyze the dimension of crystal formation associated with the parameter m.

The nucleation equation was used to determine the values of a_m and K_m [15]

$$\ln\left\{V_t\left[(m+1)T_N - T_M\right](T_M)^m/T_N^2(\Delta T)^{m+1}\right\} =$$
$$= \ln\left(K_m/a_m\right) - a_m(T_M)^m/T_N(\Delta T)^m, \qquad (2)$$

where V_t – cooling rate; T_M – melt temperature corresponding to the maximum value of specific heat flow; ΔT – temperature range of crystallization.

The solution of this equation was carried out using the least squares method and using the values of T_N, T_M and ΔT obtained as a result of experimental studies. In order to analyze the dimensionality of crystal formation, equation (2) was solved for m=1 and m=2.

Regarding the second stage of crystallization (crystallization in the entire volume of the composite), the experimental exotherms of crystallization were considered under the assump-

tion of two mechanisms of crystal formation, the first of which is associated with the crystallization of the polymer matrix (realized on polymer density fluctuations), and the second – with crystallization, in which the role of its centers is played by filler particles. The results of experiments on the kinetics of crystallization were analyzed according to the modified Kolmogorov-Avrami equation

$$\alpha(\tau) = f\left[1 - \exp\left(-K'_n \tau^{n'}\right)\right] + \\ + (1-f)\cdot\left[1 - \exp\left(-K''_n\tau^{n''}\right)\right], \qquad (3)$$

where f – relative share of the crystallization mechanism associated with the crystallization of the actual polymer matrix; K_n – effective rate constant; n – pseudoparameter of the form; α – relative volume fraction of the crystalline phase; τ – reduced time, $\tau = V_t \cdot t$; t – time; superscript indices «'» and «"» refer to the first and second of these mechanisms.

5. Research results of the structure formation patterns of polymer microcomposites filled with copper particles

5. 1. Research results to determine the crystallization exotherms of polymer microcomposites

Experimental studies of the characteristics of the crystallization process of polymer microcomposites during their cooling from the melt were performed when the mass fraction ω of copper microparticles changed from 0.2 % to 4.0 % and when the cooling rate varied from 0.5 K/min to 20.0 K/min (Fig. 1). Composites obtained by the two methods described above, which are based on the mixing of the components in dry form and in the polymer melt, respectively, were subjected to this study.

Table 1 shows the corresponding studies results of the crystallization process characteristics. Research data on the influence of the mass fraction of filler ω on the parameters of the crystallization process of polymer microcomposites are given in Table 2.

The following tables present data on the main characteristics of the crystallization process, such as the temperature of the beginning T_N, the end T_k of crystallization and the temperature interval of crystallization ΔT, as well as the maximum value of specific heat flow Q_s^{max} and the corresponding temperature T_M. The results are obtained for cooling conditions of dispersed microcomposites with different matrices – polyethylene, polypropylene and polycarbonate.

Data on the values of the specific heat flow for the studied composites are shown in Fig. 2, and according to the level of

characteristic temperatures of the crystallization of composites – in Fig. 3.

The research results presented in Tables 1, 2 and in Fig. 2 correspond to the two investigated methods of obtaining polymer composites.

Table 1

Characteristics of the crystallization process of polymer microcomposites based on polyethylene, polypropylene and polycarbonate filled with copper particles, with different methods of obtaining them for ω=4.0 %

V_t, K/min	T_N, K	T_M, K	T_k, K	ΔT, K	Q_s^{max}, W/kg	V_t, K/min	T_N, K	T_M, K	T_k, K	ΔT, K	Q_s^{max}, W/kg
Method I						Method II					
Polyethylene matrix											
0.5	379.2	373.7	368.8	10.4	12.8	0.5	379.0	373.3	367.7	11.3	16.2
2.0	378.2	372.2	367.2	11.0	9.2	2.0	378.0	372.4	366.7	11.3	12.6
5.0	375.1	368.2	361.7	13.3	5.8	5.0	374.7	369.0	363.3	11.4	9.0
20.0	364.8	357.2	350.2	14.6	2.7	20.0	364.7	358.9	353.2	11.5	5.6
Polypropylene matrix											
0.5	408.4	404.9	401.4	7.0	11.91	0.5	408.5	405.1	401.7	6.8	10.2
2.0	402.6	398.3	394	8.6	6.89	2.0	402.1	397.9	393.7	8.4	9.4
5.0	399.1	394.1; 389.3	390.2	8.9	5.07; 2.54	5.0	400.2	395.4	390.7	9.5	7.9
20.0	392.1	387.0; 386.2	381.9	10.2	3.08; 2.00	20.0	392.6	386.2; 379.1	381.7	10.9	3.17; 2.43
Polycarbonate matrix											
0.5	468.6	464.5; 465.4	460.4	8.2	1.82; 1.75	0.5	468.9	464.5; 463.6	463.0	5.9	2.28; 2.27
2.0	466.2	461.7; 463.0	457.3	8.9	1.30; 1.28	2.0	466.3	457.3; 459.4	459.6	6.7	1.56; 1.34
5.0	462.5	455.1; 458.6	451.8	10.7	0.85; 0.77	5.0	462.4	453.9; 456.6	455.5	6.9	1.04; 0.86
20.0	457.9	447.5; 452.4	440.4	17.5	0.38; 0.37	20.0	457.8	443.8; 448.1	443.9	13.9	0.51; 0.27

Table 2

Characteristics of the crystallization process of polymer microcomposites based on polyethylene, polypropylene and polycarbonate filled with copper particles, with different methods of obtaining them for V_t=5.0 K/min

ω, %	T_N, K	T_M, K	T_k, K	ΔT, K	Q_s^{max}, W/kg	ω, %	T_N, K	T_M, K	T_k, K	ΔT, K	Q_s^{max}, W/kg
Method I						Method II					
Polyethylene matrix											
0.2	376.0	369.3	362.9	13.1	6.2	0.2	375.8	369.3	362.5	13.3	10.1
0.3	375.5	368.7	361.9	13.6	5.9	0.3	375.1	369.2	363.4	11.7	9.1
1.0	375.2	368.4	361.7	13.5	5.8	1.0	374.9	369.1	363.4	11.5	9.0
4.0	375.1	368.2	361.7	13.3	5.8	4.0	374.7	369.0	363.3	11.4	9.0
Polypropylene matrix											
0.2	400.2	395.1	389.9	10.3	7.20	0.2	400.0	394.7	389.4	10.6	9.3
0.3	400.4	395.5; 394.1	390.7	9.7	7.00; 6.25	0.3	400.1	395.0	389.9	10.2	8.5
1.0	401.8	393.7; 390.0	392.5	9.3	6.50; 5.20	1.0	400.8	395.8	390.9	9.9	8.1
4.0	399.1	394.1; 389.3	390.2	8.9	5.07; 2.54	4.0	400.2	395.4	390.7	9.5	7.9
Polycarbonate matrix											
0.2	461.5	456.1	452.0	9.5	1.39	0.2	461.3	455.5	451.8	9.4	2.00
0.3	461.5	455.9	452.1	9.4	1.32	0.3	461.4	455.4	452.1	9.3	1.60
1.0	462.2	456.9; 455.5	451.7	10.5	1.19; 1.05	1.0	462.2	456.3; 455.6	454.3	7.1	1.20; 1.05
4.0	462.5	455.1; 458.6	451.8	10.7	0.85; 0.77	4.0	462.4	458.9; 457.6	455.5	6.9	1.04; 0.86
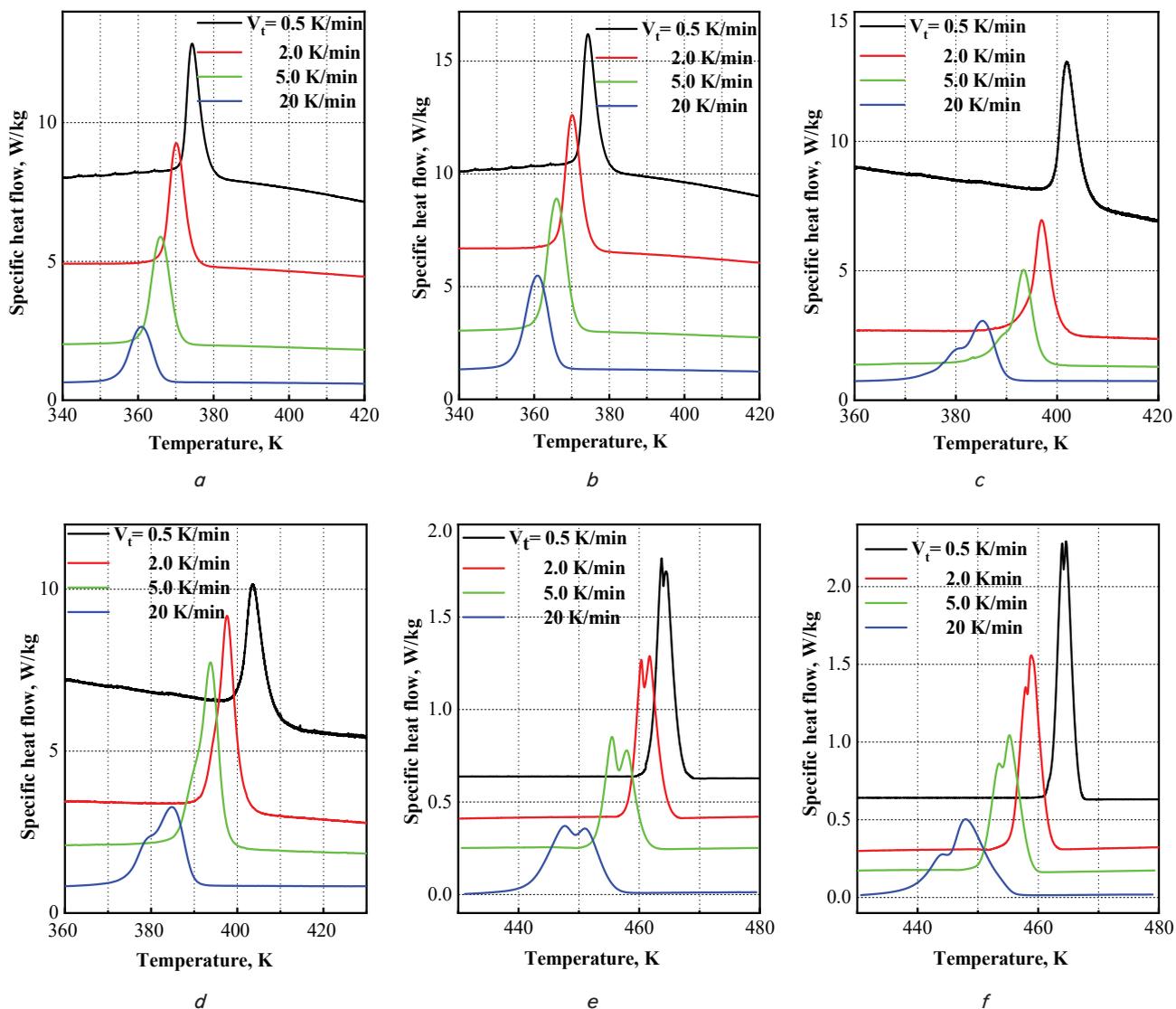
Fig. 1. Crystal exotherms for polymer microcomposites filled with copper particles, at a filler content ω=4.0 % for fixed cooling rates of the melt composite V_t, obtained by two methods based on different polymer matrices: a − polyethylene matrix, method I; b − polypropylene matrix, method I; c −polycarbonate matrix, method I; d − polyethylene matrix, method II; e − polypropylene matrix, method II; f − polycarbonate matrix, method II
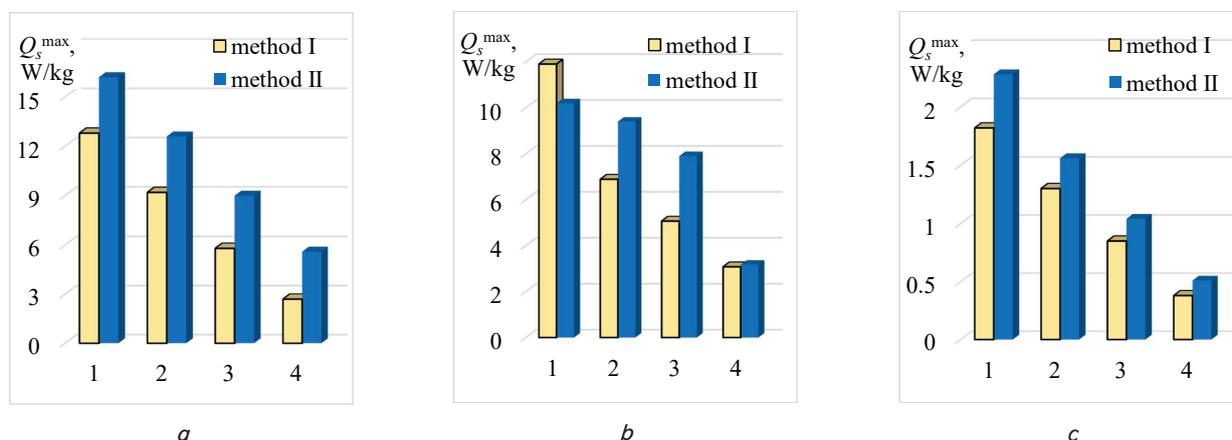
Fig. 2. Maximum values of specific heat flow Q_s^{max} for polymer composites filled with copper microparticles, at a filler content ω=4.0 % for fixed cooling rates of the melt composite V_t using two methods of obtaining them and different polymer matrices: a − polyethylene matrix; b − polypropylene matrix; c −polycarbonate matrix; 1 − V_t=0.5 K/min; 2 − V_t=2.0 K/min; 3 − V_t=5.0 K/min; 4 − V_t=20.0 K/min
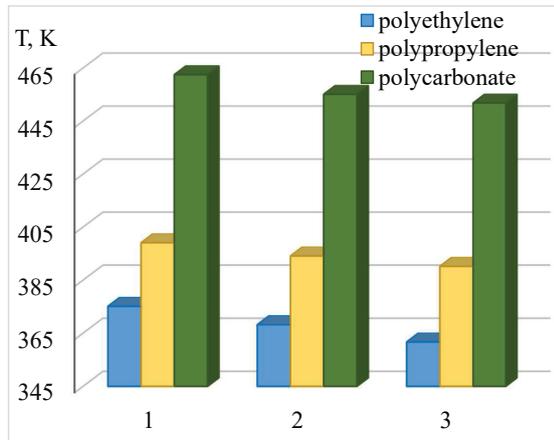
Fig. 3. Temperature characteristics of the crystallization process of polymer composites filled with copper microparticles for ω=4.0 %, V_f=5.0 K/min when using method I, to obtain composites based on different polymer matrices: 1 — temperature of the beginning T_N of crystallization; 2 — melt temperature T_M, which corresponds to the maximum value of the specific heat flow; 3 — temperature of the end T_k of crystallization

5. 2. The results of theoretical studies to determine the characteristics of the structure formation of polymer microcomposites

Using the obtained experimental data on crystallization exotherms at the second stage of research, as already noted, the characteristics of structure formation for the two crystallization stages of polymer composites were theoretically determined.

In the Table 3 to the example the corresponding data for the initial stage of crystallization – the stage of nucleation of individual structurally ordered subdomains for V_t=2.0 K/min are shown. The presented results were obtained using equation (2) for two values of the form parameter m (m=1 and m=2). The value of R in Table 3 denotes the correlation coefficient of experimental and calculated data.

Fig. 4 illustrates the results of studies on the values of the reduced nucleation parameter a_m for the studied polymer microcomposites.

Table 4 illustrates the research results for the second stage of structure formation – the stage of crystallization in the entire volume of the composite for ω=4.0 %.

a

b
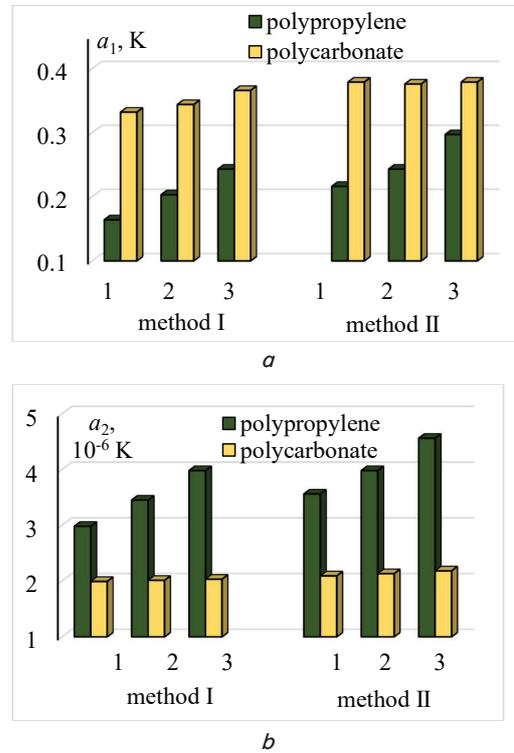
Fig. 4. The values of the above nucleation parameters am for polymer composites based on polypropylene and polycarbonate filled with copper microparticles at V_f=2.0 K/min for two methods of obtaining the studied polymer composite materials and different mass fractions of filler ω:
1 — ω=0.3 %; 2 — ω=1.0 %; 3 — ω=4.0 %; a — the nucleation parameter a_1; b — the nucleation parameter a_2

Table 3

Structure formation parameters at the initial stage of crystallization of polymer microcomposites based on polyethylene, polypropylene and polycarbonate filled with copper particles, with different methods of their production for V_f=2.0 K/min

ω, %	a_1, K	K_1, 1/c	R_1	a_2, 10⁻⁶ K	K_2, 1/c	R_2	a_1, K	K_1, 1/c	R_1	a_2, 10⁻⁶ K	K_2, 1/c	R_2
			Method I							Method II		
					Polyethylene matrix							
0.2	0.164	0.053	0.80	2.94	0.102	0.96	0.179	0.052	0.81	2.94	0.101	0.95
0.3	0.189	0.050	0.85	3.21	0.092	0.97	0.195	0.049	0.82	3.02	0.061	0.94
1.0	0.195	0.039	0.88	3.34	0.056	0.95	0.223	0.038	0.82	3.12	0.059	0.93
4.0	0.231	0.031	0.89	3.97	0.052	0.98	0.246	0.029	0.81	4.32	0.051	0.97
					Polypropylene matrix							
0.2	0.162	0.074	0.85	2.86	0.109	0.95	0.169	0.071	0.88	2.98	0.098	0.97
0.3	0.164	0.069	0.82	2.98	0.101	0.92	0.216	0.064	0.89	3.56	0.092	0.95
1.0	0.203	0.062	0.84	3.45	0.081	0.93	0.243	0.058	0.85	3.98	0.056	0.92
4.0	0.243	0.058	0.85	3.98	0.069	0.97	0.297	0.055	0.85	4.56	0.045	0.92
					Polycarbonate matrix							
0.2	0.324	0.049	0.83	1.86	0.94	0.991	0.349	0.048	0.92	2.05	0.97	0.96
0.3	0.332	0.042	0.84	1.99	0.92	0.992	0.356	0.039	0.93	2.09	0.93	0.95
1.0	0.344	0.037	0.83	2.01	0.75	0.996	0.376	0.034	0.92	2.13	0.79	0.92
4.0	0.366	0.035	0.81	2.03	0.73	0.997	0.379	0.030	0.92	2.18	0.77	0.90

Table 4

The parameters of structure formation at the stage of crystallization in the volume of polymer microcomposites based on polyethylene, polypropylene and polycarbonate filled with copper particles, with different methods of obtaining them for ω=4.0 %

V_t, K/min	f	n'	K_n', 10^{-5} $K^{-n'}$	n''	K_n'', 10^{-5} $K^{-n''}$	χ^2, 10^{-5}	f	n'	K_n', 10^{-5} $K^{-n'}$	n''	K_n'', 10^{-5} $K^{-n''}$	χ^2, 10^{-5}
			Method I						Method II			
				Polyethylene matrix								
0.5	0.80	3.0	99	3.2	145	8	0.81	3.2	96	2.9	155	3
2	0.78	3.1	97	3.1	176	4	0.81	3.1	85	2.9	166	3
5	0.77	3.0	104	3.1	207	7	0.80	3.2	84	3.0	207	3
20	0.79	3.1	107	3.2	278	4	0.79	3.1	73	3.1	232	7
				Polypropylene matrix								
0.5	0.80	5.2	129	4.4	356	8	0.84	5.0	56	4.6	182	7
2	0.82	5.0	134	4.5	348	2	0.83	5.0	94	4.5	162	6
5	0.82	4.8	129	4.5	356	7	0.82	5.1	97	4.6	166	5
20	0.83	4.9	142	4.4	324	6	0.84	4.8	67	4.3	154	8
				Polycarbonate matrix								
0.5	0.82	4.4	310	4.0	362	6	0.83	4.5	93	3.8	345	2
2	0.83	4.6	316	4.0	372	7	0.83	4.7	85	3.8	349	5
5	0.84	4.4	323	3.9	382	5	0.84	4.6	86	3.9	351	6
20	0.85	4.5	345	4.1	385	9	0.85	4.6	91	4.0	362	8

The data on the relative fraction f of the mechanism of structure formation associated with the crystallization of the actual polymer matrix, the value of the parameter of form n and the effective rate constant K_n for the two mechanisms of crystallization are presented here. The first of them is realized on fluctuations of polymer density, and in the second the role of crystallization centers is played by filler particles. The value of χ^2 in Table 4 denotes the variance.

The data presented in Fig. 5 illustrate the values of the parameter of form n with respect to the investigated conditions.
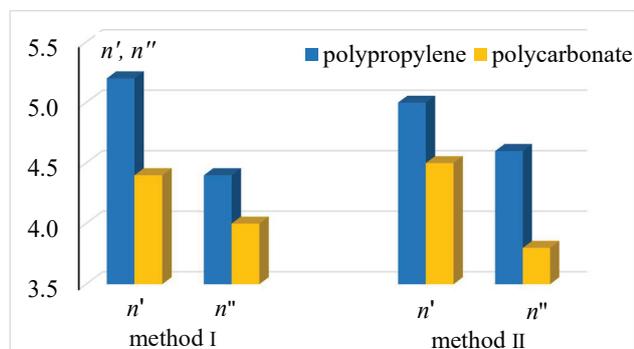
Fig. 5. Values of parameters of form n' and n'' for polymer composites based on polypropylene and polycarbonate filled with copper particles at V_t=5.0 K/min, ω=4.0 % for the two considered methods of obtaining the investigated materials

The results are given in Table 4 and in Fig. 5, is obtained on the basis of the modified Kolmogorov-Avrami equation (3).

6. Discussion of researches results of structure formation pattern of polymer microcomposites at their filling by copper particles

6. 1. Discussion of research results to determine the crystallization exotherms of polymer microcomposites

According to the obtained data (Table 1) for all studied composites with different polymer matrices when using both methods of obtaining them, the increase in cooling rate V_t causes a decrease in the temperatures of T_N, end T_K of the crystallization process and temperature T_M, which corresponds to the maximum specific heat flow Q_s^{max}. The value Q_s^{max} decreases significantly. Also noteworthy is the fact that, other things being equal, higher values Q_s^{max} correspond to composites obtained by method II (Fig. 2).

According to the research results, the above characteristics of the crystallization process at the same values of V_t differ significantly for composites based on different polymer matrices (Fig. 3). The largest values of temperatures T_N, T_K and T_M correspond to composites based on polycarbonate, slightly smaller – polypropylene and the smallest – polyethylene. For example, at =4.0 % and V_t=20.0 K/min, the temperature of crystallization beginning is 364.8 K and 457.9 K for composite materials with a matrix of polyethylene and polycarbonate. That is, the difference between these temperatures is 93.1 K. The difference in temperature of the crystallization end under these conditions is 90.2 K.

As for the value of the maximum heat flow Q_s^{max}, according to the obtained data, it also significantly depends on the type of polymer matrix. At the same time, there is a tendency to decrease the values Q_s^{max} during the transition from the polyethylene matrix to the polypropylene matrix and then – to polycarbonate matrix. This trend is fully realized for polymer composites obtained by method II, and with some exceptions for materials obtained by method I. Namely, at V_t=20,0 K/min the value Q_s^{max} for the composite based on polypropylene exceeds the corresponding value for polyethylene (Fig. 2).

The research results also indicate that the type of polymer matrix has a significant effect on the nature of crystallization exotherms for the corresponding polymer composites. As can be seen from Fig. 1, a, d, when using a polymer matrix made of polyethylene in the investigated range of changes in the cooling rate V_t, the crystallization exotherms have only a unimodal peak for composites obtained by both method I and method II. For composites based on polypropylene with increasing V_t, the unimodal peak on the curve Q_s=$f(T)$ is transformed into a bimodal one (Fig. 1, b, e). However, the

values of V_t at which this transformation is observed differ significantly for different methods of obtaining the studied polymer composites. Namely, in the case of method I, the bimodal peak appears at V_t=5.0 K/min, and in the case of method II – only at V_t=20. K/min.

With regard to polymer composites based on polycarbonate, according to the experimental results, the corresponding exotherms of crystallization are characterized by the presence of a bimodal peak on the curve Q_s=$f(T)$ in the entire range of cooling rate V_t. This nature of crystallization exotherms occurs for both methods of obtaining polymeric composite materials. (Fig. 1, c, f).

According to the obtained data, the value of the mass fraction of filler ω has a less significant effect on the characteristics of the crystallization process than the cooling rate V_t of the melt composite. As can be seen from Table 2, an increase in ω from 0.2 to 4.0 % leads to relatively insignificant changes in the temperatures of the beginning and end of crystallization for all investigated polymer microcomposites in both methods of their production. At the same time, there is a tendency to decrease the value of the specific heat flow $Q_s^{\max}$. Its relative reductions are the largest for polycarbonate, slightly smaller – for polypropylene and the smallest – for polyethylene.

It is noteworthy that the value of ω differently affects the nature of crystallization exotherms for composites based on different polymer matrices. Thus, for composites based on a polyethylene matrix, the crystallization exotherms are characterized by the presence of a unimodal peak in the entire range of change ω. When using matrices made of polypropylene and polycarbonate for microcomposites obtained by method I, with increasing ω on the crystallization exotherm, the unimodal peak changes to bimodal. As for these composites obtained by method II, for composites based on polycarbonate this change is observed, and on the basis of polypropylene it is absent (Table 2).

6. 2. Discussion of the results of theoretical research to determine the structure characteristics of polymer microcomposites

On the basis of the crystallization exotherms obtained as a result of experimental researches, as already noted, the theoretical determination of the structure formation parameters was carried out. According to the data given in Table 3, at the first stage of crystallization – the stage of nucleation there are two mechanisms of structure formation: two-dimensional, planar (m=1) and three-dimensional, volumetric (m=2). This is evidenced by the values of the coefficients R_1 and R_2, which confirm a satisfactory correlation between the results of experiments and calculations.

The fact that under these conditions the values of R_2 are higher than R_1 indicates the advantage of the three-dimensional mechanism over the planar one. The only exception is the situation corresponding to the crystallization of polycarbonate-based microcomposites obtained by method II. As can be seen from Table 3, here the values of R_1 and R_2 are comparable in value. That is, under these conditions, there are similar in value fractions of planar and volumetric mechanisms of structure formation.

Regarding the changing of the nucleation parameter a_m, according to the obtained data, its values rise with increasing mass fraction of filler when using different polymer matrices for both methods of obtaining composites (Table 3, Fig. 4). The differences in the values of a_m for matrices made

of polyethylene and polypropylene are relatively small. The values of a_1 for polycarbonate matrices significantly exceed the corresponding values for these matrices, and the values of a_2 – on the contrary are significantly lower.

It should also be noted that there is a tendency to increase the values of the reduced nucleation parameter a_m for composites obtained by method II in comparison with method I. This trend is somewhat violated in the case of a polyethylene matrix relative to the value of a_2 (Table 3).

Studies have shown that the values of the reduced transport barrier K_n with increasing ω decrease for composites based on different polymer matrices. This indicates an increase in restrictions on the transport of matrix segments across the lamella-crystal surface. In this case, the values of K_n as a whole are slightly higher for composites obtained by method I. Exceptions are the values of K_2 relative to polymer composites based on polycarbonate.

Regarding the second stage of crystallization, which occurs throughout the volume of the composite material, here, as mentioned above, two mechanisms of crystal formation were studied. The first mechanism takes place on fluctuations in the density of the polymer, in the second mechanism centers of crystallization are microparticles of filler. As can be seen from Table 4, for polyethylene-based composites for these two mechanisms of structure formation, a parameter of the form n≈3 for all values of ω and both methods of obtaining these composite materials. This means that crystallization on fluctuations in polymer density and crystallization associated with copper microparticles occur by a three-dimensional mechanism.

These data also indicate that for composites based on polypropylene and polycarbonate, the parameter of form n varies in the range of 3.8...5.2. This indicates that the crystallization mechanism associated with both the polymer matrix and the filler has a stress matrix mechanism. It is noteworthy that this mechanism when using matrices made of polypropylene is slightly more pronounced than in the case of matrices made of polycarbonate (Table 4, Fig. 5).

The performed work concerns only the peculiarities of the structure formation of polymer microcomposites of a certain type. It does not contain studies on the relationship between structure formation and the properties of the resulting composite materials.

Further development of this study will be to establish the dependence of the properties of the studied composites on the characteristics of their structure. Of considerable interest will also be the analysis of the possibilities of controlling the properties of polymer composites by changing their structure.

7. Conclusions

1. Experimental data on crystallization exotherms for polymer composites filled with copper microparticles were obtained. The analysis of crystallization characteristics at application of various polymeric matrices – from polyethylene, polypropylene and polycarbonate is executed. The experiments were performed in a relatively wide range of changes in the mass fraction of filler (from 0.2 to 4.0 %) and the cooling rate of composite materials (from 0.5 to 20.0 K/min). The investigated composites were obtained on the basis of methods based on mixing the components in dry form (method I) and in the polymer melt (method II). The influ-

ence of the cooling rate V_t of composites from the melt, the mass fraction of filler ω and the method of obtaining composites on the main characteristics of the crystallization process are revealed. In particular, it is shown that in the studied range of change V_t the type of polymer matrix significantly affects the nature of crystallization exotherms in terms of the presence of unimodal or bimodal peak and its transformation when changing the value of V_t. It is also found that the value of the mass fraction of filler ω has a less significant effect on the characteristics of the crystallization process of composites than the cooling rate V_t.

2. Using the results of experimental studies of crystallization exotherms of polymer composites, the regularities of their structure formation at two stages of crystallization are established:

a) at the initial stage of crystallization – nucleation stage. In accordance with the nucleation equation, it is shown that

at this stage for all the composites under consideration, in both methods of their production there are two mechanisms of structure formation – planar and three-dimensional with some advantage of the latter;

b) in the second stage of crystallization, which occurs throughout the volume of the composite. Using the modified Kolmogorov-Avrami equation, two mechanisms of crystal formation were investigated, the first of which takes place on fluctuations in polymer density, and in the second the filler particles serve as centers of crystallization. It is shown that for polyethylene-based composites with two methods of their production, these mechanisms are three-dimensional. It is also established that when using polymer matrices made of polypropylene and polycarbonate, crystallization occurs by the mechanism of the stressed matrix on both the fluctuations of the polymer density and when it is initialized on the filler particles.

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