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ESTABLISHING PATTERNS IN THE STRUCTURE FORMATION OF POLYMER NANOCOMPOSITES BASED ON POLYAMIDE 6 DURING THEIR CRYSTALLIZATION PROCESSES

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This paper reports experimental and computational studies on patterns in the structure formation of polymer nanocomposites when different types of fillers are used. The study was conducted for nanocomposites based on polyamide 6 filled with carbon nanotubes or silicon dioxide nanoparticles. In the course of research, the mass fraction of the filler varied from 0.2 % to 4.0 %, and the cooling rate of the melt composite varied from 0.5 K/min up to 20 K/min.

Data on experimental and theoretical studies into the mechanisms of structure formation of composites according to the method, which includes two stages, are given. According to the first stage, crystallization exotherms of nanocomposites were experimentally obtained when they are cooled from the melt at a given constant rate. The dependence of various characteristics of the crystallization process on the mass fraction of the filler and the cooling rate of the composite was established.

At the second stage, based on the analysis of the obtained crystallization exotherms, theoretical studies were performed to determine the mechanisms of structure formation of nanocomposites at different stages of crystallization. For the initial stage, according to the nucleation equation, the presence of two mechanisms of structure formation – planar and volumetric – has been shown.

Within the framework of the Kolmogorov-Avrami equation, the mechanisms of structure formation at the next stage of crystallization were established, which corresponds to the formation of ordered structures in the material within the volume of the polymer composite as a whole. The research was carried out assuming the existence of a mechanism of crystallization of the polymer matrix itself, which is realized on fluctuations in the density of the polymer, and a mechanism of crystallization, the centers of which are filler particles.

The use of the proposed nanocomposites is promising for the manufacture of parts of energy equipment, electronic equipment, elements of chemical, processing, defense industry installations, etc.

Keywords: polymer nanocomposites, carbon nanotubes, silicon dioxide, crystallization exotherms, structure formation mechanisms

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1. Introduction

Polymer micro- and nanocomposites are promising structural materials for various technical applications. This is due, first of all, to the high level of their physical and mechanical characteristics. Expanding the use of polymer micro- and nanocomposites requires further development of research into the set of their properties. At the same time, it is important to study patterns in the structural formation of composites, which largely determine their main characteristics. In particular, the task of establishing the dependence of the characteristics of structure formation on a number of determining factors is an urgent one.

Studies of nanocomposites based on polyamide 6 are of considerable interest. This polymer has such advantages as high strength and wear resistance, a wide range of operating temperatures, etc. The use of nanocomposites based on it is meant to provide increased durability, reliability, and a reduction in the weight and size characteristics of parts made of these materials.

2. Literature review and problem statement

The results of studies on the kinetics of crystallization of polymer micro- and nanocomposites are covered in a large number of publications, for example [1–8]. In a number of studies, various kinetic models are considered for the analysis of patterns in the crystallization of polymer composite materials. For example, in [1], the results of a comparison of the data on experimental studies into the kinetics of isothermal crystallization of polyethylene terephthalate filled with nanoparticles of aluminum oxide and the corresponding calculation data obtained using a number of macrokinetic models are reported. It is shown that the Avrami, Malkin, Urbanovich-Segal models adequately describe the kinetics of isothermal crystallization. As for Tobin's model, it corresponds less satisfactorily to the results of experimental studies. In [2], several kinetic models were used to analyze the crystallization of the polyamide 12/polypropylene nanocomposite – multilayer carbon nanotubes. In particular, it was established that the Jeziorny model (modified by Avrami) and the Mo model successfully explain the studied crystallization process. The indicated kinetic models are also used in study [3] to analyze the crystallization of graphene/polyamide 10T composites. According to the research results, it is shown that the Jeziorny equation does not have a linear dependence in the entire range of crystallization. As for the Mo level, it provides a satisfactory linear approximation.

However, in papers [1–3], as well as in most other works aimed at researching the peculiarities of the mathematical description of the crystallization of polymer composites, the dependence of the characteristics of the crystallization process on a number of determining parameters is practically not considered. The results of studies on the kinetics of crystallization of a matrix of polyethylene oxide filled with nanoparticles of silicon dioxide grafted (grafted) with polyethylene glycol (PEG-g-SiO_2) and pure (bare) SiO_2 are given in [4]. According to research data, it has been established that (PEG-g-SiO_2) can significantly increase the crystallinity and crystallization temperature of the polyethylene oxide matrix in the process of non-isothermal crystallization. The paper assumes that the interphase structure of grafted PEG plays a key role in the formation of crystallization centers and thus ultimately determines the overall crystallization rate of the studied composites. Work [5] reports a study into the impact of polyether sulfone-modified graphene (f-GEi) on the kinetic characteristics of non-isothermal crystallization of polyether ketone composites. According to research results, the addition of f-GEi reduces the crystallinity of PEEK composites and shortens the total crystallization time. Study [6] analyzes the crystallization processes of polymer composites when they are filled with copper nanoparticles. In the cited literature, research data are given, which, as a rule, correspond to the use of only one polymer matrix and one filler. Work [7] reports a study on the characteristics of structure formation for three options for combining the polymer matrix and the filler. Namely, the patterns of structure formation for micro composites based on polyethylene, polypropylene, and polycarbonate are considered. Work [8] reports the results of studies into the crystallization processes of polymer composites when using several fillers (aluminum microparticles, and carbon nanotubes). According to research data [7, 8], the Kolmogorov-Avrami kinetic model and the corresponding modified model successfully explain the processes of structure formation in polymer composite materials.

Our review of the literature [1–8] reveals that the task to systematically investigate the structure formation of polymer composites needs to be solved, taking into account the dependence of the characteristics of their crystallization process on a number of determining factors, such as the rate of cooling from the polymer melt, the concentration of fillers, etc.

3. The aim and objectives of the study

The purpose of our work is to identify features in the structure formation of polymer nanocomposite materials based on polyamide filled with carbon nanotubes or silicon dioxide nanoparticles. The results could be used as a basis for designing nanocomposite materials for engineering practice.

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

– to perform experiments on the construction of crystallization exotherms of the studied composite materials while varying a number of determining parameters;

– to carry out theoretical studies on determining the characteristics of structure formation of polymer nanocomposites at various stages of crystallization of the polymer matrix.

4. The study materials and methods

4. 1. The object and hypothesis of the study

The object of our research is the mechanisms of structure formation in polymer nanocomposites during their cooling from the polymer melt under the conditions of using different types of fillers. The basic research hypothesis assumes the determination and analysis of two stages of the crystallization process, namely, the initial stage (nucleation stage) and the crystallization stage in the entire volume of the composite.

The experimental and computational procedure for analysis of crystallization processes, which was used in the work, involved the sequential execution of experimental and computational studies. Experimental studies implied the construction of crystallization exotherms, calculations – the theoretical determination of the characteristics of structure formation in composites based on the built crystallization exotherms.

4. 2. Methods for obtaining polymer nanocomposites and constructing their crystallization exotherms

To obtain polymer nanocomposites, a method based on mixing components in the polymer melt employing a disk extruder was used. A detailed description of the method and a schematic diagram of the extruder is given in [9]. The mixture of composite material components in the extruder mold is compacted using a hydraulic press. Next, the mixture is heated to a temperature that exceeds the melting (glass transition) temperature by 20–70 °C, depending on the type of polymer. The rotation of the metal piston, which gradually descends into the area of the polymer melt, provides mixing of the composite components. At the specified time, the composite material passes through the hole in the lower part of the mold. The final operation of the method is hot pressing of the resulting composition.

Regarding the construction of experimental exotherms of crystallization of nanocomposites upon their cooling from the melt, it was carried out as follows [7]. A sample was placed in the cell, which was heated to a temperature higher than the melting point of the polymer by 50 K. The sample was kept at this temperature for 180 s. Next, the temperature of the sample decreased at a given rate of its cooling. The determination of the specific heat flow Q_n, which is removed from the polymer nanocomposite material, was carried out in an atmosphere of dry nitrogen by the method of differential scanning calorimetry using a Perkin-Elmer DSC-2 device with modified software.

During the operation of the device, two cells are heated: one empty, the other with a test sample. At the initial stage, the same amount of heat is supplied to both cells and their temperatures differ insignificantly. Subsequently, the temperature of the cell with the test sample begins to decrease, and to compensate for this decrease, the amount of heat flow supplied to it increases until the temperatures of both cells become the same. The value of the compensating heat flow corresponds to the value of the flow diverted from the composite.

4. 3. Calculated determination of parameters for the structure formation in polymer nanocomposites

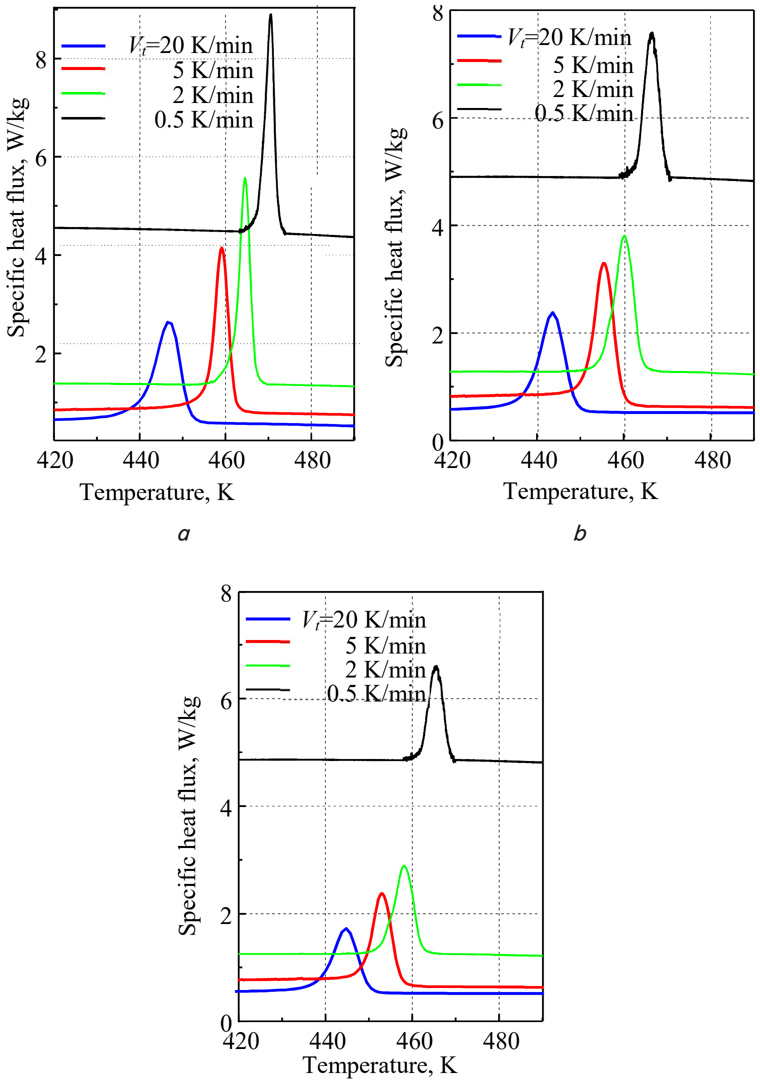
When calculating the parameters of structure formation, two stages of this process were considered – the initial stage of crystallization (nucleation stage) and the stage of crystallization in the entire volume of the composite. The general provisions of the relevant calculation procedure are outlined in [7]. At the first stage of structure formation, the reduced nucleation parameter a_m and the reduced transport barrier K_m were determined using the nucleation equation [10].

As for the second stage of crystallization – crystallization in the entire volume of the composite, the research was carried out based on the notion of the presence of two mechanisms of crystal formation. The first of these mechanisms is implemented on fluctuations in the density of the polymer, that is, it concerns the crystallization of the actual polymer matrix. The second of the mechanisms is related to crystallization, in which the centers of crystallization are nanoparticles of the filler. To analyze the kinetics of crystallization corresponding to the indicated physical situation, the modified Kolmogorov-Avrami equation was used. In order to compare the role of these mechanisms in the process of crystallization of composites, calculations were also carried out according to the Kolmogorov-Avrami equation, in which only the first of these mechanisms is taken into account.

5. Results of investigating the characteristics of structure formation in polymer nanocomposites

5. 1. Results of studies on the construction of crystallization exotherms of polymer nanocomposites

Fig. 1 shows the results of experiments on the construction of crystallization exotherms for the studied nanocomposites and polymer matrix. Table 1 gives relevant data on the temperature of the onset T_N, the end T_K, crystallization, the temperature interval of crystallization ΔT and the maximum value of the specific heat flux Q^{max} and the temperature T_M at which this value of the flux is reached.



a

b

c

Fig. 1. Crystallization exotherms of polyamide 6 and polymer composites based on it at filler content ω=4.0 % and fixed rates V_t of their cooling from the melt for the polymer matrix and various fillers: *a* – polyamide 6 matrix; *b* – carbon nanotube filler; *c* – SiO_2 nanoparticle filler

Fig. 2 illustrates the dependence on the cooling rate V_t of the indicated characteristics of the crystallization process, namely Q^{max}, T_M, T_N, T_K and ΔT for the investigated matrix and nanocomposites.

Table 2 gives the results of experimental studies on the characteristics of the crystallization process of polymer nanocomposites filled with CNTs and SiO_2 nanoparticles, with varying filler content.

Table 1

Characteristics of the crystallization process of polyamide 6 and polymer composites based on it, filled with carbon nanotubes and SiO_2 nanoparticles, with a filler content ω=4.0 % and different cooling rates from the melt V_t

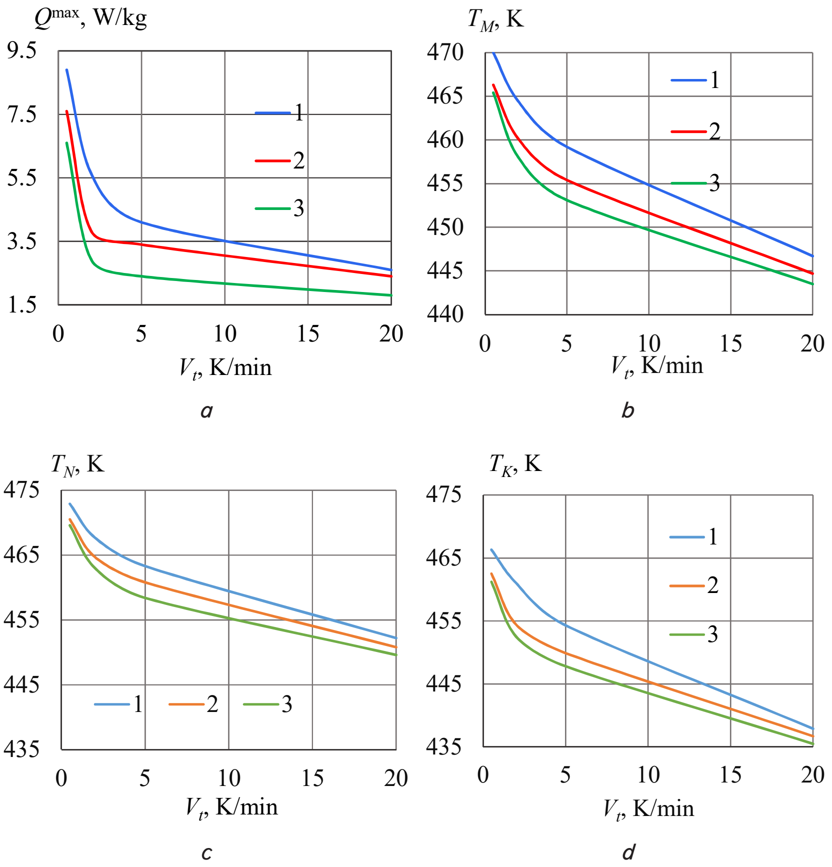
V_t, K/min	T_N, K	T_M, K	T_k, K	ΔT, K	Q^{max}, W/kg
Polyamide 6					
0.5	472.9	470.0	466.3	6.6	8.9
2.0	467.7	464.5	461.0	6.7	5.6
5.0	463.3	459.2	454.3	9.0	4.1
20.0	452.2 437.9	446.7	437.9	14.3	2.6
Polyamide 6 filled with carbon nanotubes					
0.5	470.5	466.3	462.5	8.0	7.6
2.0	464.7	460.2	454.4	10.3	3.8
5.0	460.8	455.4	449.9	10.9	3.4
20.0	450.8	444.7	436.7	14.1	2.4
Polyamide 6 filled with SiO_2 nanoparticles					
0.5	469.6	465.4	461.2	8.4	6.6
2.0	463.0	458.1	452.5	10.5	2.9
5.0	458.4	453.1	447.8	10.6	2.4
20.0	449.6	443.5	435.5	14.1	1.8

Table 2

Characteristics of the crystallization process of polymer composites based on polyamide 6, filled with carbon nanotubes and SiO_2 nanoparticles, for the cooling rate V_t=5 K/min at different filler contents ω

ω, %	T_N, K	T_M, K	T_k, K	ΔT, K	Q^{max}, W/kg
Polyamide 6 filled with carbon nanotubes					
0.2	463.1	459.0	454.2	8.9	4.10
0.3	462.9	458.6	453.6	9.3	4.02
1.0	461.5	457.2	452.1	9.4	3.89
4.0	460.8	455.4	449.9	10.9	3.40
Polyamide 6 filled with SiO_2 nanoparticles					
0.2	463.0	458.9	454.0	9.0	4.01
0.3	461.9	457.5	452.8	9.1	3.85
1.0	460.2	455.7	450.9	9.3	3.24
4.0	458.4	453.1	447.8	10.6	2.40

Experimental data in Tables 1, 2 and Fig. 1, 2 were obtained when the cooling rate varied from 0.5 K/min to 20.0 K/min and the filler mass fraction from 0.2 % to 4 %.



a b

c d

Fig. 2. Dependence of the characteristics of crystallization process of the polymer matrix and nanocomposites based on it on the rate of cooling from the melt V_t with a filler content ω=4 %: 1 – polyamide 6 matrix; 2 – carbon nanotube filler; 3 – SiO_2 nanoparticle filler: *a* – maximum value of heat flow Q^{max}; *b* – the temperature corresponding to the flow Q^{max}; *c* – temperature of the beginning of crystallization T_N; *d* – temperature of the end of crystallization T_K

5. 2. Results of calculation studies on determining the characteristics of structure formation in polymer nanocomposites

On the basis of our experimental studies on the construction of crystallization exotherms using calculation methods, the structure formation parameters for the nanocomposites under consideration were determined. At the same time, as already noted, two stages of crystallization were subject to investigation. The first is initial, which corresponds to the genesis of individual structurally ordered subregions, and the second is the stage of crystallization in the volume of the nanocomposite.

Table 3 gives the results of calculation studies for the first stage of structure formation, obtained on the basis of the nucleation equation for two values of the shape parameter m (m=1, m=2). In Table 3, the following designations are adopted: a_1, a_2 – reduced nucleation parameter, K_1, K_2 – reduced transport barrier; R_1, R_2 – correlation coefficient of experimental and calculated data.

Fig. 3 illustrates the nature of change in the reduced nucleation parameters a_1 and a_2 depending on the mass fraction of the filler for the investigated nanocomposites.

Table 4 gives data from calculation studies for the stage of structure formation in the volume of the nanocomposite.

As already noted, the research was conducted based on the notion of the presence of two crystallization mechanisms. In Table 4 superscript indices «'» and «"» relate values to the first and second of these mechanisms. The value of f in Table 4 denotes the relative share of the mechanism of structure formation associated with the crystallization of the actual polymer matrix, the value χ^2 is the variance.

Table 3

Parameters of structure formation at the initial stage of crystallization of polymer composites based on polyamide 6, filled with carbon nanotubes and SiO_2 nanoparticles, at the cooling rate from the melt V_t=5 K/min and different contents of fillers ω

ω, %	a_1, K	K_1, 1/c	R_1	a_2, 10^{-6} K	K_2, 1/s	R_2
Polyamide 6						
0	0.168	0.425	0.9991	2.51	1.68	0.9996
Polyamide 6 filled with carbon nanotubes						
0.2	0.198	0.382	0.9923	2.95	1.67	0.991
0.3	0.204	0.362	0.9954	2.99	1.60	0.992
1.0	0.213	0.354	0.9942	3.07	1.49	0.996
4.0	0.234	0.341	0.9902	3.31	0.32	0.997
Polyamide 6 filled with SiO_2 nanoparticles						
0.2	0.202	0.380	0.9920	2.96	1.66	0.7791
0.3	0.256	0.349	0.9912	3.24	1.61	0.7825
1.0	0.284	0.327	0.9956	3.51	1.57	0.7821
4.0	0.312	0.305	0.9955	3.79	0.24	0.7832

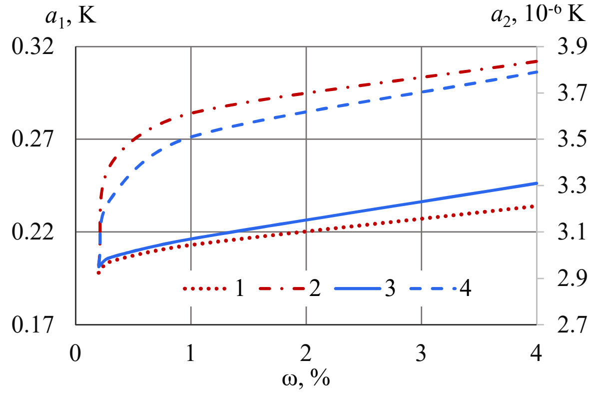


Fig. 3. Dependence on the mass fraction of the filler ω of the reduced nucleation parameters a_1 and a_2 for polymer composites based on polyamide 6 filled with carbon nanotubes and SiO_2 nanoparticles: 1, 2 – nucleation parameter a_1, filler carbon nanotubes and silicon dioxide nanoparticles; 3, 4 – nucleation parameter a_2, filler carbon nanotubes and silicon dioxide nanoparticles

Table 4

Parameters of structure formation at the stage of crystallization in the volume of polymer composites based on polyamide 6, filled with carbon nanotubes and SiO_2 nanoparticles, for different cooling rates from the melt V_t with a filler content ω=4 %

V_t, K/min	Kolmogorov-Avrami equation			Modified Kolmogorov-Avrami equation					
	n	K_n, 10^{-5} K^{-n}	$\chi^2 \cdot 10^{-5}$	f	n'	K'_n, 10^{-5} $K^{-n'}$	n''	K''_n, 10^{-5} $K^{-n''}$	$\chi^2 \cdot 10^5$
Polyamide 6 filled with carbon nanotubes									
0.5	3.85	915	23	0.76	3.85	164	4.96	745	3
2	3.84	70	27	0.75	3.84	50	5.01	20	4
5	3.82	20	57	0.74	3.82	14	5.02	35	4
20	3.80	15	61	0.73	3.80	42	5.05	2	3
Polyamide 6 filled with SiO_2 nanoparticles									
0.5	3.12	56	32	0.78	3.12	90	5.2	85	9
2	3.14	60	43	0.77	3.14	79	5.3	90	8
5	3.21	25	50	0.77	3.21	62	5.5	75	7
20	3.24	20	45	0.75	3.24	50	5.5	65	5

Fig. 4 shows, as an example, the value of the pseudo parameter χ^2 for the studied nanocomposites.

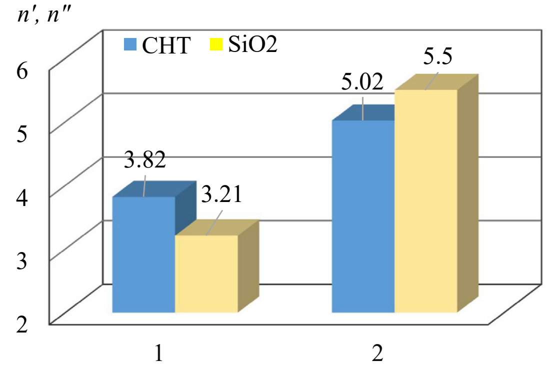


Fig. 4. Values of the form pseudo parameters n', n'' for polymer composites based on polyamide 6 filled with carbon nanotubes and SiO_2 nanoparticles, with a filler content ω=4 % and a cooling rate from the polymer melt V_t=5 K/min: 1 – n'; 2 – n''

The data shown in Fig. 4 correspond to the cooling rate from the melt V_t=5 K/min and the mass fraction of the filler ω=4 %.

6. Discussion of results of investigating features in the structure formation of polymer nanocomposites

The results of our research were obtained using the classical experimental and computational procedure used to analyze the mechanisms of structure formation in nanocomposites. The features of this procedure are described in detail, in particular, in [11].

As evidenced by the results of the performed experiments on the construction of crystallization exotherms, for the investigated nanocomposites and the polymer matrix, a decrease in the temperatures of the beginning T_N and the end T_K of crystallization, the temperature T_M and the heat flow Q^{max} with an increase in the cooling rate V_t is observed (Fig. 1, 2, Table 1). At the same time, the nature of dependence of these values on the cooling rate V_t has certain features. Namely, their sharpest decrease is observed in the region of relatively small values of V_t.

As for the decrease of the above-mentioned temperatures in the studied range of V_t change, this decrease is relatively insignificant. So, for the temperature T_N, it is about 20 K for all considered materials. A different pattern occurs for the value of the heat flow Q^{max}. As V_t increases, the value of Q^{max} undergoes significant changes. When the cooling rate increases from 0.5 K/min to 20 K/min, the value of Q^{max} decreases for polyamide 6 by 3.4 times, for the nanocomposite based on it filled with CNTs – by 3.2 times, and when polyamide 6 is filled with SiO_2 nanoparticles – 3.7 times.

The ratio of temperatures T_N, T_K, T_M and flow Q^{max} for the polymer matrix and the studied nanocomposites at fixed values of V_t are characterized by the following regularities. In the considered range of changes in V_t, the values of the indicated values are the largest for the polymer matrix, somewhat smaller for the nanocomposite based on it, filled with CNTs, and the smallest when it is filled with SiO_2 nanoparticles. At the same time, the differences between the above temperatures for the matrix and nanocomposites are insignificant. Thus, at V_t=0.5 K/min, the temperature T_K for polyamide 6 exceeds the corresponding temperature for the composite filled with SiO_2 nanoparticles by only 5.1 K. Significantly larger differences occur for the flow Q^{max}. For the specified conditions, the difference in Q^{max} values is 2.3 W/kg, which is 26 % of the Q^{max} value for the polymer matrix.

According to our data, the range of crystallization temperatures ΔT increases with an increase in the cooling rate V_t for all considered materials. This is explained by the fact that the temperature of the end of crystallization T_K decreases more intensively compared to the temperature of its beginning T_N with an increase in the cooling rate V_t.

The results of our studies indicate that the nature of influence of the mass fraction of the filler ω on the values of T_N, T_K, T_M, ΔT and Q^{max} are similar to the influence of the cooling rate V_t (Table 2). At the same time, an increase in ω from 0.2 **%** to 4.0 **%** causes significantly smaller changes in the values of the specified values than an increase in the rate V_t in the studied range.

The above experimental data on the kinetics of crystallization (Fig. 1, 2 and Tables 1, 2), as already noted, served as the basis for the theoretical determination of the relevant parameters for structure formation.

When studying the patterns in the structure formation of nanocomposites at the initial stage of crystallization (nucleation stage), it is necessary to determine such basic characteristics as the reduced nucleation parameter a_m and the reduced transport barrier K_m. In addition to this analysis, the dimensions of crystal formation related to the parameter m are subject to analysis.

The results given in Table 3 indicate that there is a quite satisfactory agreement between the experimental and calculated data. However, for the composite filled with SiO_2 nanoparticles, the correlation coefficient R_2 at m=2 is significantly smaller than the corresponding coefficient R_1 at m=1. So, according to these data, there are two mechanisms of structure formation at the initial stage of crystallization of the studied composites. Namely, two-dimensional, planar (m=1), and three-dimensional, volumetric (m=2). At the same time, for the composite filled with SiO_2 nanoparticles, the specified excess of R_1 over R_1 indicates a certain predominance of the planar mechanism.

Regarding the change with increasing filler content ω of the reduced nucleation parameter a_m and the reduced transport barrier K_m, the nature of this change is similar for m=1 and m=2 (Table 3). An increase in ω leads to an increase in the values of a_m and a decrease in the value of K_m. As is known, an increase in a_m is associated with an increase in the rate of crystallization at its initial stage, and a decrease in K_m is associated with a decrease in restrictions on the transport of matrix segments across the lamella-crystal surface.

According to the obtained data, the values of the given nucleation parameters a_1 and a_2 when the polymer is filled with SiO_2 nanoparticles exceed the corresponding values when it is filled with CNTs (Fig. 3). At the same time, the nucleation parameters a_1 and a_2 for polyamide 6 filled with SiO_2 change significantly in the region of relatively low values of ω from 0.2 % to 1 %. A further increase in the filler content causes a significantly smaller effect on these parameters.

When studying the patterns of structure formation at the second stage of crystallization – crystallization in the volume of the material as a whole, the obtained data are analyzed, as already noted, assuming the presence of two mechanisms of crystal formation. The first of these mechanisms is related to the crystallization of the actual polymer matrix and is realized by fluctuations in the density of the polymer. The second mechanism concerns crystallization, in which filler particles play the role of its centers.

As for the composite based on polyamide 6 filled with CNTs, as shown by our data (Table 3, Fig. 3), for polyamide 6 the form pseudo parameter is $n'\approx4$ in the entire considered range of rate V_t change. The indicated value of n' corresponds to the mechanism of the stressed matrix. Regarding the second of the above mechanisms, it is the same as for the polymer matrix. The form pseudo parameter n'' for all values of V_t is approximately 5.

Regarding the composite based on polyamide 6 when it is filled with SiO_2 nanoparticles, a slightly different pattern is observed. Namely, the form pseudo parameter $n'\approx3$, which indicates the presence of a volume mechanism of crystallization due to fluctuations in the density of the polymer. At the same time, the second mechanism of crystallization is the mechanism of a stressed matrix, as in the case of polyamide 6 CNT filling.

Our research expands the range of polymer nanocomposites, for which the regularities in their structure formation have been revealed. At the same time, in these studies, the dependence of characteristics in the structure formation process of nanocomposite materials on such factors as the mass fraction of the filler and the cooling rate of the composite was determined.

Among the areas of application of the proposed nanocomposite materials, energy equipment, electronic equipment, parts, and components of defense installations, etc. are promising. The importance of designing such materials is related, first of all, to increasing requirements for the operational characteristics of corresponding equipment. Designing polymer nanocomposite materials for the specified equipment is a competitive alternative to traditionally used materials in terms of their weight characteristics, resistance to aggressive environments, environmental friendliness, cost, etc.

Our studies concern only two types of polymer nanocomposites. In this case, one of the main shortcomings of the work is a too narrow range of changes in the mass fraction of fillers – carbon nanotubes and carbon dioxide nanoparticles (from 0.2 to 4.0 %). This range should be expanded to 10 % in order to cover high-temperature modifications of the studied nanocomposites that are important for practical use.

Further research may focus on determining the processes of structure formation in a wide range of polymer composite materials important for engineering practice. Difficulties in the process of such research are due to actual experiments involving composites based on thermosetting polymers and are associated with the increased temperature of their melts.

7. Conclusions

1. For nanocomposites based on polyamide 6 filled with carbon nanotubes or silicon dioxide nanoparticles, experimental studies on the construction of crystallization exotherms were performed. The dependence of various characteristics of the crystallization process on cooling rate V_t

of the polymer melt composite and on the mass fraction of the filler ω was established. In particular, it is shown that the nature of influence of the mass fraction of the filler ω on the temperatures of the onset T_N and the end T_K of crystallization and the value of the heat flow Q^{max} is similar to the influence of cooling rate V_t.

2. Based on the results of our experiments on the construction of crystallization exotherms for the studied nanocomposites, patterns of structure formation at two stages of crystallization were established – the initial (nucleation stage) and the stage of crystallization throughout the entire volume of the composite:

a) for the first stage of crystallization according to the nucleation equation, the presence of two crystallization mechanisms has been shown – planar and volumetric. In this case, for the composite based on polyamide 6 filled with SiO_2, there is some predominance of the planar mechanism;

b) for the second stage of crystallization, an analysis of the obtained experimental research data was performed within the limits of the standard and modified Kolmogorov-Avrami equations. It was established that at this stage crystallization occurs according to two mechanisms. The first of these mechanisms is related to the crystallization of the polymer matrix itself and is realized by fluctuations in the density of the polymer. The second mechanism concerns crystallization, the centers of which are filler particles. It is shown that the first of these mechanisms corresponds to the mechanism of the stressed matrix for polyamide 6 filled with CNTs and to the bulk mechanism when polyamide 6 is filled with SiO_2 nanoparticles. As for the second mechanism of crystallization, the mechanism of the stressed matrix operates for both investigated composites.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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Data availability

The data will be provided upon reasonable request.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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