

STRUCTURAL FORMATION OF HIGH-HEAT-CONDUCTING POLYMER MICRO- AND NANOCOMPOSITES IN THE PROCESSES OF THEIR CRYSTALLIZATION

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Abstract: The results of experimental and theoretical studies of the crystallization regularities of polymer micro- and nanocomposite materials based on polyethylene, polypropylene and polycarbonate filled with high-heat-conducting fillers - carbon nanotubes, microparticles of aluminum or copper are presented. The mechanisms of structure formation at the stage of the formation of individual ordered structures in the material and the formation of such subregions in the entire volume of the polymer composite were established based on the analysis of the crystallization exotherms obtained within the scope of the nucleation equation and Kolmogorov-Avrami.

Key words: POLYMER MICRO- AND NANOCOMPOSITES, MECHANISMS OF STRUCTURE FORMATION, HIGH-HEAT-CONDUCTING COMPOSITES.

1. Introduction

The effectiveness of the use of polymer micro- and nanocomposite materials in engineering practice is largely due to their characteristics, such as a wide range of heat-conducting properties, increased corrosion resistance, low specific weight, etc. [1-10]. Thus, the high heat-conducting properties of these materials determine the prospects of their use for the manufacture of heat exchange surfaces for various purposes, elements of electronic equipment, etc. Increased corrosion resistance of polymer composites allows their operation in various aggressive environments. A relatively small specific weight makes it possible to create from these materials details and nodes of different equipment with low mass size parameters, etc.

One of the important trends in expanding the fields of application of polymer micro- and nanocomposite materials is the use of their high-heat-conducting modifications. The tasks of developing such materials require in-depth investigations aimed at studying the features of their structure formation in the crystallization processes, which to a large extent determines the properties of the resulting materials.

This article is devoted to experimental and theoretical studies of the regularities of the structure formation of a wide class of high-heat-conducting polymer micro- and nanocomposite materials.

2. Prerequisites and means for solving the problem

The research task included the establishment of mechanisms of structure formation during cooling of polymer composites from the melt. These mechanisms were subject to consideration at the stage of nucleation of individual structurally ordered subregions (nucleation stage) and at the stage of formation of such subregions in the entire volume of the composite (the crystallization stage in the volume of the material as a whole). The studies were carried out for polymer composites based on polyethylene (PE), polypropylene (PP) and polycarbonate (PC) filled with carbon nanotubes (CNTs) or microparticles of aluminum or copper with a change in their mass fraction from 0.2 to 4% and varying the cooling velocity of the composite from 0.0083 K/s (0.5 K/min) to 0.333 K/s (20 K/min).

The experimental-theoretical technique used to establish the mechanisms of structure formation involved two stages, the first of which consisted in the experimental determination of the solidification exotherms of the composite when it was cooled from the melt at a given constant velocity. Here, the specific heat flux Q removed from the composite was determined in a dry nitrogen atmosphere by differential scanning calorimetry method on a Perkin Elmer DSC-2 unit with modified IFA GmbH, Ulm software. In this case, the sample placed in the cell was heated to a temperature exceeding the melting point of the matrix by approximately 50 K, held at this temperature for 180 s and then cooled to a temperature of 400 K at a fixed cooling velocity V_c . Samples were prepared by the method of hot pressing the composition obtained as a result of mixing in magnetic stirrer its components that are in a dry state.

The second stage of the applied technique consisted in the theoretical determination, based on the experimental data obtained, of the structure formation characteristics at the stage of formation of separate ordered structures (the nucleation stage) in the material and in determining the formation parameters of such structures at the stage of their formation in the entire volume of the composite. At the initial stage, the corresponding analysis was carried out using the nucleation equation.

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

where m - is the dimensionless parameter of the form; T_N - temperature of the beginning of crystallization; ΔT - temperature range of crystallization; T_M - is the melt temperature corresponding to the maximum value of the heat flux Q on the crystallization exotherm; K_m - reduced transport barrier; a_m is the reduced nucleation parameter.

At the stage of crystallization in the entire volume of the composite as a whole, the determination of the parameters of the structure formation was carried out on the basis of the standard and modified Kolmogorov-Avrami equation

$$(2) \alpha(\tau) = 1 - \exp(-K_n \tau^n)$$

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

Here $\alpha(\tau)$ - is the relative volume fraction of the crystalline phase; τ - is the reduced time, $\tau = V_c t$, where t - is time; f - is the relative fraction of the crystallization mechanism associated with crystallization on polymer density fluctuations; K_n - is the effective velocity constant; n - is the pseudo-parameter of the form; n' , n'' - are the values of n corresponding to the crystallization on density fluctuations of the polymer and the filler particles, respectively.

The fillers used in the polymer composite materials studied corresponded to the following geometric characteristics. For CNTs obtained by the chemical vapor deposition method, their outer diameter is 20 nm, the length is from 1 to 5 μm , the wall thickness is 5 nm, and the specific surface area is 190 m^2/g . Dimensions of microparticles of aluminum and copper were in the range 0.5 ... 1 μm . They were obtained from the corresponding sawdust by grinding in a ball mill.

Results and discussion

An analysis of the results of the experimental studies carried out to determine the exotherm of crystallization showed that for all the composites under consideration there is a generally similar pattern of change of these exotherms as a function of the cooling velocity V_c and the mass fraction ω of the filler. In Fig. 1 and in Table 1 as an example, the corresponding data for a polycarbonate filled with aluminum microparticles are given. Here, first of all, a very significant decrease in the maximum of the specific heat flux Q_{max} taken from the composite with an increase in the cooling velocity V_c

is noticeable, with a shift of this maximum position on the curve $Q=f(T)$ to lower temperatures. Thus, for a microcomposite containing 0.2% aluminum, the value $Q_{\max} = 1.84$ W/kg at $V_i = 0.0083$ K/s and decreases to 1.02 W/kg at $V_i = 0.333$ K/s. As for the temperature T_M corresponding to the heat flux Q_{\max} , for the indicated velocities V_i it is 463.5 K and 448.9 K, respectively.

An increase in the cooling velocity V_i of the composite also leads to a decrease in the temperatures of the beginning of the T_N and the end of the T_K crystallization. In this case, the temperature range of the crystallization ΔT ($\Delta T = T_N - T_K$) is markedly increased. For example, for a composite based on polycarbonate containing 4% aluminum microparticles, this ΔT interval is 7.7K at $V_i = 0.0083$ K/s and reaches 17.2 K at $V_i = 0.333$ K/s.

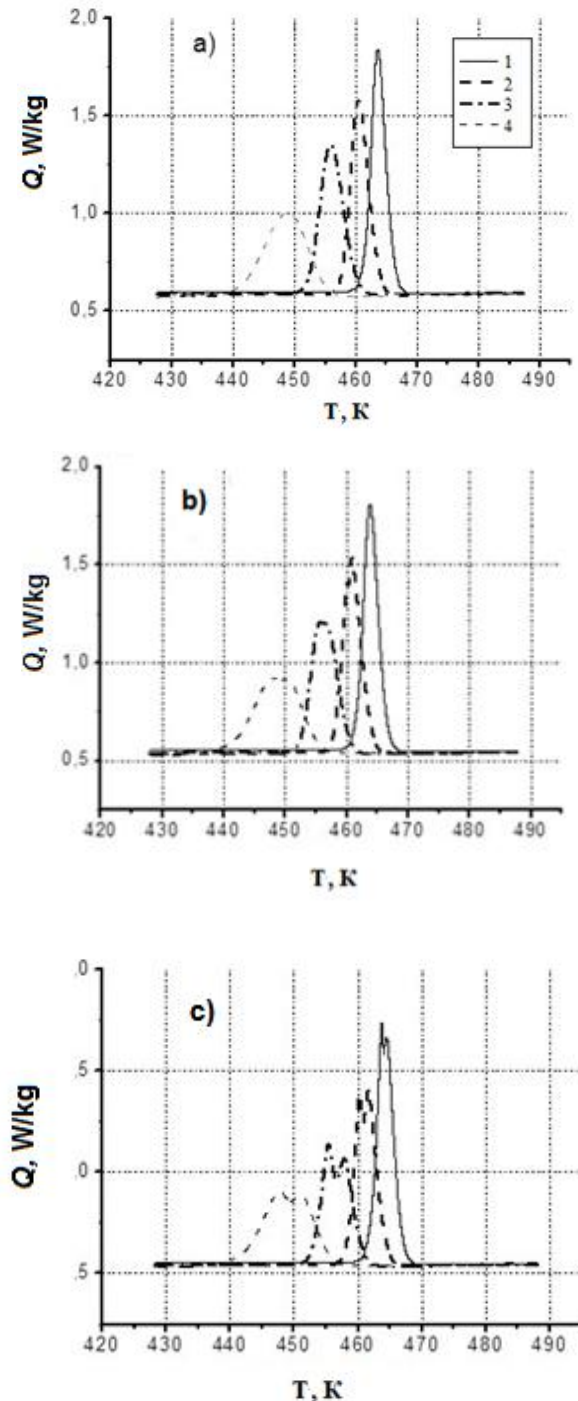


Fig. 1. Crystallization exotherms for polymer composite materials based on polycarbonate filled with aluminum microparticles with filler content $\omega = 0.2\%$ (a), 1.0 (b) and 4.0% (c) at different cooling velocity of the composite from melt: 1 - $V_i = 0.0083$ K/s; 2 - 0.0333 K/s; 3 - 0.0833 K/s; 4 - 0.333 K/s.

Table 1. Characteristics of the crystallization process of polymeric composites based on polycarbonate filled with aluminum microparticles with different filler contents ω and different cooling velocity V_i of the composite from melt

ω , %	T_N , K	T_M , K	T_K , K	ΔT , K	Q_{\max} , W/kg
$V_i = 0.0083$ K/s					
0	467.5	463.0	460.0	7.5	1.79
0.2	468.0	463.5	460.6	7.4	1.84
1	468.7	463.8	460.5	8.2	1.81
4	468.5	464.4; 463.7	460.8	7.7	1.75
$V_i = 0.0333$ K/s					
0	465.2	460.0	457.0	8.2	1.55
0.2	465.7	460.5	457.6	8.1	1.59
1	466.3	460.8; 460.0	457.5	8.8	1.57
4	466.2	461.7; 460.4	457.8	8.4	1.41
$V_i = 0.0833$ K/s					
0	461.2	455.4	451.9	9.3	1.32
0.2	461.7	455.9	452.3	9.4	1.38
1	462.4	456.9; 455.5	451.9	10.5	1.22
4	462.2	458.0; 455.5	452.1	10.1	1.14
$V_i = 0.333$ K/s					
0	456.5	448.4	441.5	15.0	0.97
0.2	457.0	448.9	440.6	16.4	1.02
1	457.7	450.9; 447.5	440.4	17.3	0.94
4	457.4	451.0; 447.8	440.2	17.2	0.90

As can be seen from the data presented in Fig. 1 and in Table 1, with an increase in the mass fraction of the filler from 0.2 to 4.0%, for all values of the cooling velocity V_i , a certain decrease in the value Q_{\max} occurs. In this case, there is a transformation of the monodalous type on the curve $Q=f(T)$ to the bimodal one.

On the basis of the experimental data on the crystallization kinetics of composite materials for the initial stage of crystallization - the nucleation stage, the crystal formation dimension m was determined from the results of solving the nucleation equation (1). The obtained data showed that for all the composites studied, there are two mechanisms of structure formation: two-dimensional, planar, ($m = 1$) and three-dimensional, volumetric ($m = 2$) in the investigated mass fraction of the filler. In this case, the three-dimensional mechanism predominates over the planar one.

As for the second stage of crystallization (crystallization throughout the volume of the composite), experimental crystallization exotherms were considered under the assumption of present of two mechanisms of crystal formation, the first of which is associated with the crystallization of the polymer matrix (which is realized on polymer density fluctuations) and the second of which with crystallization in which the filler particles play the role of its centers. Accordingly, the results of experiments on the kinetics of crystallization were analyzed according to the Kolmogorov-Avrami equations (2) and its modified version (3). The data obtained (Table 2) indicate that for composites based on the polyethylene, both mechanisms are volumetric ($n \approx 3$) for all fillers in the entire range of variation of ω . For composites based on PP and PC, crystallization on density fluctuations of a polymer occurs by the mechanism of a strained matrix. Regarding the mechanism of crystallization on the filler particles, for these polymers, when they are filled with copper microparticles, it is the same as for the polymer matrix. The same mechanism is also preserved for PP-based composites filled with aluminum microparticles.

According to the data obtained, the crystallization mechanism on the filler particles depends significantly on their mass fraction ω for PP-based composites filled with CNTs and for PC-based composites filled with CNTs or aluminum microparticles. Thus, for a PP filled with a CNTs, at $\omega = 0.2\%$, the mechanism of a strained matrix is realized, with $\omega = 1.0\%$, there is a three-dimensional (volumetric) mechanism, which is preserved with a further increase in ω . For a PC filled with CNTs, with increasing ω , this mechanism transforms from the mechanism of a strained matrix to a planar (two-dimensional) one, and when PC is filled with aluminum microparticles, from the same mechanism of a strained matrix to a rod matrix (one-dimensional).

Table 2. Parameters of the structure formation (n' , n'') in the crystallization stage in the volume of polymer composites based on polyethylene, polypropylene and polycarbonate for different filler content ω of fillers (CNT, microparticles of copper or aluminum) for different cooling velocity V_c

V_c , K/min.	Matrix PE																	
	Fillers																	
	CNTs						Copper						Aluminum					
	ω , %																	
	0.2		1.0		4.0		0.2		1.0		4.0		0.2		1.0		4.0	
	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''
0.5	3.2	3.1	3.2	2.9	3.1	2.8	3.1	3.1	3.2	3.0	3.1	3.2	3.2	3.0	3.2	3.0	3.1	3.1
2	3.3	3.0	3.2	2.8	3.1	2.9	3.0	3.2	3.0	2.9	3.0	3.1	3.1	3.0	3.0	2.9	3.1	3.0
5	3.2	3.1	3.1	2.7	3.0	2.9	3.1	3.0	3.2	3.0	3.1	3.1	3.2	3.2	3.2	3.0	3.0	3.0
20	3.2	3.0	3.2	2.8	3.1	2.7	3.1	3.0	3.0	2.9	3.2	3.2	3.3	3.1	3.1	2.9	3.1	3.1
	Matrix PP																	
	Fillers																	
	CNTs						Copper						Aluminum					
	ω , %																	
	0.2		1.0		4.0		0.2		1.0		4.0		0.2		1.0		4.0	
	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''
0.5	5.0	4.6	5.1	3.3	5.1	3.2	5.1	4.5	5.0	4.6	5.1	4.4	4.9	4.6	4.8	4.1	5.1	4.0
2	4.9	4.6	5.1	3.2	4.9	3.3	5.0	4.6	5.1	4.4	4.9	4.5	4.9	4.6	4.7	4.1	4.9	4.0
5	4.9	4.5	5.0	3.3	4.9	3.2	4.8	4.5	4.9	4.4	4.9	4.5	4.8	4.4	4.6	4.0	4.8	3.9
20	4.8	4.4	4.9	3.4	4.8	3.3	4.9	4.4	4.8	4.5	4.7	4.4	4.8	4.4	4.6	3.9	4.9	3.8
	Matrix PC																	
	Fillers																	
	CNTs						Copper						Aluminum					
	ω , %																	
	0.2		1.0		4.0		0.2		1.0		4.0		0.2		1.0		4.0	
	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''
0.5	4.8	4.0	4.5	2.3	4.3	2.2	4.6	4.6	4.7	4.0	4.5	4.0	4.8	4.6	4.6	1.2	4.7	1.2
2	4.6	3.8	4.4	2.1	4.2	2.2	4.7	4.4	4.5	4.0	4.4	4.0	4.6	4.3	4.6	1.3	4.5	1.2
5	4.5	3.9	4.3	2.2	4.2	2.1	4.6	4.2	4.5	4.1	4.3	3.9	4.5	4.2	4.5	1.1	4.4	1.2
20	4.4	3.8	4.2	2.2	4.1	2.0	4.5	4.3	4.4	4.1	4.4	4.1	4.4	4.2	4.4	1.2	4.7	1.3

Conclusions

For polymer micro- and nanocomposite materials based on polyethylene, polypropylene and polycarbonate filled with high-heat-conducting fillers (carbon nanotubes or aluminum or copper microparticles) using exotherm crystallization obtained crystallization mechanisms are established for two stages of structure formation in the range of changes in the mass fraction of the filler from 0.2 to 4% and the cooling velocity of composites from the melt in range from 0.5 to 20 K / min. Wherein:

1. At the initial stage of crystallization, based on the results of the solution of the nucleation equation, the presence of two mechanisms of structure formation, planar and volumetric, is shown, with a certain predominance of the latter for all investigated composites.

2. In the second stage of crystallization (the stage of crystallization in the entire volume of the composite), the investigations were performed assuming the presence of two crystal formation mechanisms, the first of which is associated with the crystallization of the polymer matrix proper, the second with crystallization, in which the microparticles of the filler play the role of its centers. According to the results of the analysis performed using the modified Kolmogorov-Avrami equation, it was shown that at this stage the crystallization mechanisms can depend substantially on the type of polymer matrix and filler, its mass fraction and the cooling velocity of the composite from the melt.

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