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NON-ISOTHERMAL CRYSTALLIZATION OF POLYMER NANOCOMPOSITES BASED ON POLYCARBONATE FILLED WITH CARBON NANOTUBES

The article is devoted to theoretical and experimental studies of the dependence of the heat of crystallization of polymer nanocomposites on such factors as the mass fraction of the filler and the cooling rate of composites from the melt. Enthalpy relaxation in the cooling runs was monitored with the temperature-modulated DSC instrument (Perkin Elmer DSC-2 upgraded and supplied with signal processing software by the IFA GmbH, Ulm). Each sample was initially "overheated" by ~ 25 K above the apparent melting temperature of PP ($T_m \approx 490$ K), stored for 3 min. and cooled in the standard DSC mode to ~ 360 K at one of the six available constant cooling rates $\bar{q}$ (from 20 K/min down to 1 K/min). Studies of non-isothermal crystallization of polycarbonate and nanocomposites containing from 0 to 5 wt.% of carbon nanotubes have been conducted. It was established that the value of the heat of crystallization of nanocomposites significantly decreases with an increase in their cooling rate and an increase in the mass fraction of the filler. It is shown that the crystallization for polymer nanocomposites has the assumption of a superposition of intravenous initial (unimpeded) and secondary (limited) mechanisms of crystal formation, respectively.

Keywords: *nanocomposite materials, carbon nanotubes, experimental studies, specific heat of crystallization.*

Wide use of polymer nanocomposite materials requires a large amount of knowledge about their thermophysical properties [1-15]. One of the important thermophysical characteristics of polymer nanocomposites is their specific heat of crystallization. This determines the urgency of researching the patterns of change in the heat of crystallization of such materials.

This article is devoted to establishing the dependence of the specific heat of crystallization of polycarbonate-based composites filled with carbon nanotubes (CNTs) on a number of factors (melt cooling rate, mass fraction of filler, etc.).

The determination of the specific heat of crystallization qc was based on the use of experimentally obtained exotherms of crystallization of the composite during its cooling from the melt at a given constant rate V_t (the method of construction of the indicated exotherms is given in [6, 8, 10]).

The value of qc was determined by dependence

$$q_c = \frac{\int_{T_N}^{T_K} (Q_p - Q_P^{min}) dT}{V_t}$$

where Q_P, Q_P^{min}, is the current and minimum value of the specific heat flow; T – is the current temperature; T_N, T_K – temperature of the beginning and end of crystallization; V_t is the cooling rate [10, 12].

The value of the specified integral F was determined graphically as a component of the area under the crystallization exotherm.

Samples of materials for research were prepared by the method of hot pressing of the composition obtained as a result of mixing its components in a powder state in a magnetic stirrer. The carbon nanotubes used in the research were produced by the CVD (chemical vapor deposition) method.

The content of mineral impurities in them was ~ 0.1%. The specific surface area of CNTs determined by N_2 adsorption was 190 m^2/g. The outer diameter of the CNT, found using the method of small-angle X-ray scattering, was 20 nm, the length - (1 ... 5) μm, the wall thickness ~ 5 nm. Manufacturer of carbon tubes - "Spetsmash" LLC.

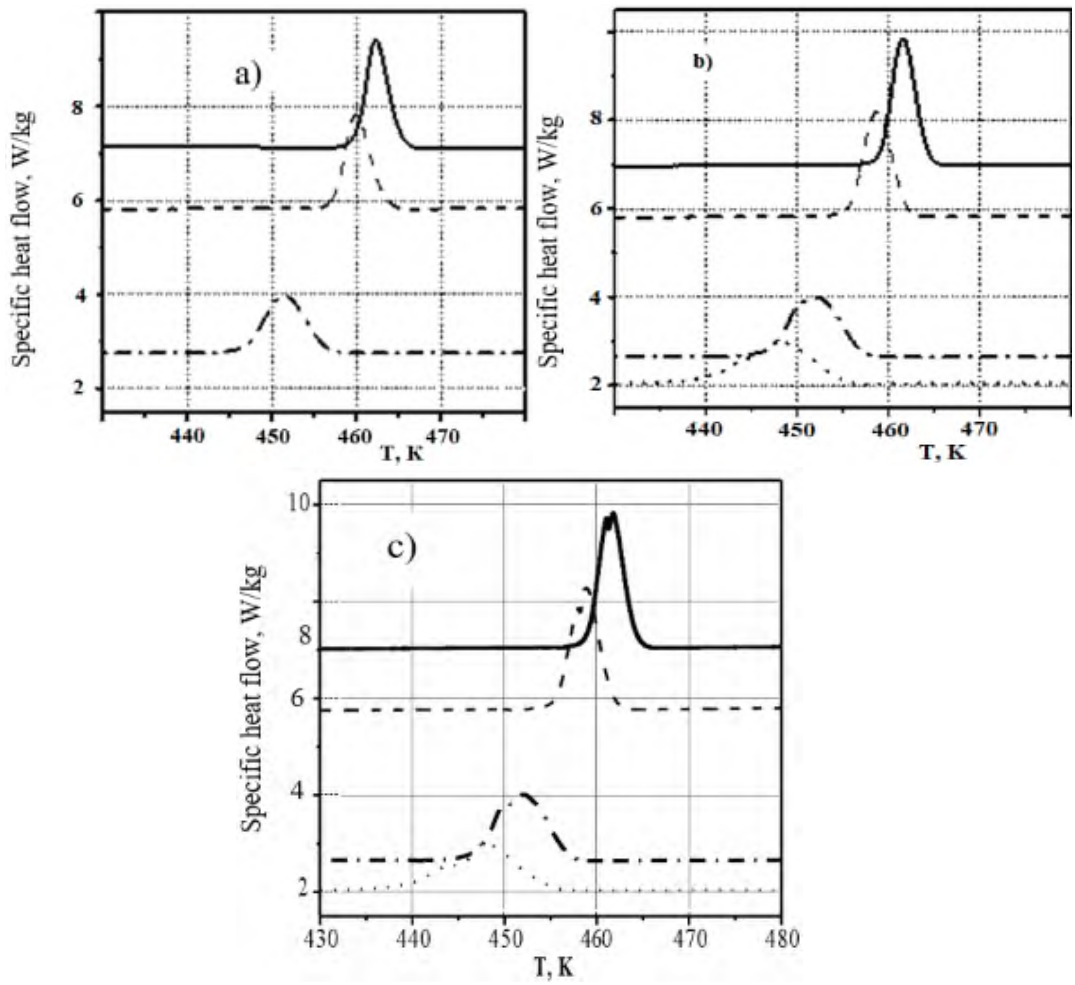

Fig. 1. Crystallization exotherms for polycarbonate-based composites with filler content ω = 0% (a), 0.4% (b), 5% (c) for different cooling rates of the composites: 1 – V_t = 0.0166 K/c; 2 – V_t = 0.0333 K/c; 3 – V_t = 0.1666 K/c; 4 – V_t = 0.3333 K/c.

Figure 1 and table 1 present data relating to the determination of the specific heat of crystallization q_c for the considered composite materials. Figure 1 illustrates the crystallization exotherms obtained as a result of experimental studies, which were used to find the q_c values. In the table 1 shows the values of q_c, found according to dependence (1).

Let's move on to the consideration of experimentally obtained crystallization exotherms. Let us dwell briefly on the highlighted features of the influence of the cooling rate V_t and the mass fraction of the filler ω on the characteristics of the crystallization process for the investigated polymer nanocomposites (Fig. 1).

As for the cooling rate V_t, with an increase in V_t, there is a decrease in the maximum heat flow Q_p and its shift on the curve Q_p = f (T) to the region of lower temperatures. In addition, with an increase in the cooling rate, there is a decrease in the temperatures of the beginning T_N and the end T_K of crystallization. For example, at ω = 4.0% for V_t = 0.0166 K/c the temperature of the beginning and end of crystallization is 465.6 K and 458.0 K, and for V_t = 0.3333 K/c – 455.6 K and 436.7 K, respectively.

According to the obtained data, the mass fraction of CNTs significantly affects the nature of crystallization exotherms for polycarbonate-based composites. Namely, as ω increases, the unimodal peak on the curve Q_p = f (T) transforms into a bimodal one.

Let us further analyze the dependence of the specific heat of crystallization qc on various factors (table 1).

Table 1.

The value of the heat of crystallization qc and the integral F for polymer nanocomposites based on polycarbonate filled with CNTs at different filler content ω and different cooling rates V_t of the composites

V_t, K/s	F, (W□K)/kg	q_c, J□kg
	ω = 0%	
0,0166	8,78	529

V_t, K/s	F, (W□K)/kg	q_c, J□kg
0,0333	8,72	262
0,0833	8,69	104
0,1666	8,65	52
0,3333	8,06	24
	ω = 0,4%	
0,0166	8,55	515
0,0333	8,49	256
0,0833	8,26	102
0,1666	8,08	51
0,3333	7,97	26
	ω = 5,0%	
0,0166	7,46	449
0,0333	7,23	219
0,0833	7,03	86
0,1666	6,90	42
0,3333	3,17	11

The conducted studies showed that the heat of crystallization of composites decreases with the growth of the mass fraction of the filler. For example, at a cooling rate of V_t = 0.0166 K/s and ω = 4.0%, the value of qc for a composite based on polycarbonate is less than q_c for pure polycarbonate by approximately 1.2 times.

It also follows from the obtained data that the value of qc for the considered composites significantly decreases with increasing speed of their cooling. As can be seen from the table 1, for ω = 4.0% with an increase in the speed of V_t from 0.0166 K/s (1 K/min) to 0.166 K/s (10 K/min), the value of qc decreases from 448 J/kg to 41 J/kg about 10.9 times.

Thus, based on the results of experimental studies, the value of the specific heat of crystallization of nanocomposites based on polycarbonate when used as a filler for carbon nanotubes was determined. It is shown that the heat of crystallization of these composite materials depends significantly on the mass fraction of the filler and the cooling rate of the composite.

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НЕІЗОТЕРМІЧНА КРИСТАЛІЗАЦІЯ ПОЛІМЕРНИХ НАНОКОМПОЗИТІВ НА ОСНОВІ ПОЛІКАРБОНАТУ, НАПОВНЕНОГО ВУГЛЕЦЕВИМИ НАНОТРУБКАМИ

Стаття присвячена теоретичним та експериментальним дослідженням залежності теплоти кристалізації полімерних нанокомпозитів від таких факторів, як масова частка наповнювача та швидкість охолодження композитів з розплаву. Релаксацію ентальпії в циклах охолодження відстежували за допомогою термомодульованого ДСК (Perkin Elmer DSC-2, модернізований і оснащений програмним забезпеченням для обробки сигналів фірми IFA GmbH, Ульм). Кожен зразок спочатку «перегрівали» на ~ 25 К вище видимої температури плавлення ПП (Tm ≈ 490 К), витримували протягом 3 хв. і охолоджували в стандартному режимі ДСК до ~ 360 К при одній з шести доступних постійних швидкостей охолодження q^- (від 20 К/хв до 1 К/хв). Проведено дослідження неізотермічної кристалізації полікарбонату та нанокомпозитів, що містять від 0 до 5 мас.ч. вуглецевих нанотрубок. Встановлено, що значення теплоти кристалізації нанокомпозитів суттєво зменшується зі збільшенням швидкості їх охолодження та збільшенням масової частки наповнювача. Показано, що кристалізація для полімерних нанокомпозитів має припущення про суперпозицію внутрішньовенного початкового (безперешкодного) і вторинного (обмеженого) механізмів кристалоутворення відповідно.

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