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THE CRYSTALLIZATION KINETICS OF NANOCOMPOSITES

POLYPROPYLENE/CARBON NANOTUBES: FRACTAL MODEL

Ключевые слова: нанокомпозит, углеродные нанотрубки, кристалличность, молекулярная подвижность, показатель Колмогорова-Аврами.

Показано влияние уровня молекулярной подвижности на значение степени кристалличности нанокомпозитов полимер / углеродные нанотрубки с полукристаллической матрицей была. Указанный уровень, характеризующийся фрактальной размерностью части цепи между точками фиксации, зависит от структуры поверхности нанонаполнителя.

Key words: nanocomposite, carbon nanotubes, crystallinity, molecular mobility, Kolmogorov-Avrami exponent.

Molecular mobility level influence on crystallinity degree value for nanocomposites polymer/carbon nanotubes with semi-crystalline matrix has been shown. The indicated level, characterized by fractal dimension of a chain part between its fixation points, depends on nanofiller surface structure.

Introduction

At present strong enough and diverse changes of polymers crystalline structure, occurring at the introduction in them of all sorts of fillers, are well-known [1]. As a rule, these changes are described within the frameworks of polymers crystalline morphology. However, lately the fractal model has been developed, which takes into consideration the whole complexity of polymers structure. It is assumed that changes occur not only on supramolecular level, but also on molecular and topological levels [2]. It is necessary to take into consideration simultaneously, that crystalline phase morphology variation causes noncrystalline regions structure changes [3]. The introduction in semicrystalline polymer inorganic nanofiller results, as a rule, to polymer matrix crystallinity degree increase, since nanofiller particles serve as nucleators. Such effect was observed in nanocomposites high density polyethylene/calcium carbonate (HDPE/CaCO$_3$) [4, 5]. Let us note an important feature of semicrystalline polymers filling: nanofiller introduction can result to both reduction and enhancement of polymer matrix crystallinity degree K. So, the authors [6] found K decrease from 0.72 up to 0.38 at carbon fibers introduction in HDPE at its volume content φ_n=0.303. Therefore the purpose of the present paper is quantitative description of polypropylene crystalline phase structural changes on the indicated above structural levels at the introduction in it carbon nanotubes.

Experimental

Polypropylene (PP) "Kaplen" of mark 01 030 was used as a matrix polymer. This PP mark has melt flow index of 2.3-3.6 g/10 min, molecular weight of ~ (2-3)×10^5 and polydispersity index of 4.5.

Carbon nanotubes (CNT) of mark "Taunite", having an external diameter of 20-70 nm, an internal diameter of 5-10 nm and length of 2 mcm and more, were used as nanofiller. They were prepared by chemical deposition (catalytic pyrolysis) of carbonhydrogens (C$_n$H$_m$) on catalysts (Ni/Mg) at atmospheric pressure and temperature of 853-923 K. CNT preparation process

duration made up 10-80 min. In the studied nanocomposites CNT contents was changed within limits of 0.25-3.0 mass %.

Nanocomposites PP/CNT were prepared by components mixing in melt on twin screw extruder Thermo Haake, model Reomex RTW 25/42, production of German Federal Republic. Mixing was performed at temperature 463-503 K and screw speed of 50 rpm during 5 min. Testing samples were obtained by casting under pressure method on a casting machine Test Samples Molding Apparate RR/TS MP of firm Ray-Ran (Taiwan) at temperature 503 K and pressure 8 MPa.

Uniaxial tension mechanical tests have been performed on the samples in the shape of two-sided spade with sizes according to GOST 112 62-80. The tests have been conducted on universal testing apparatus Gotech Testing Machine CT-TCS 2000, production of German Federal Republic, at temperature 293 K and strain rate ~ 2×10^{-3} s^{-1}.

The nanocomposites PP/CNT crystallization kinetics was studied by differential scanning calorimetry (DSC) method on apparatus DSC 204 F1 Phoenix of the firm NETZSCH at scanning rate 10 K/min. During the entire scanning time the samples were in helium atmosphere with cleaning rate 25 ml/min. The melting temperature was determined by DSC peaks the greatest intensity position and crystallinity degree – by area under these peaks.

Results and Discussion

A polymeric materials crystallinity degree K change is closely connected with kinetics of thir crystallization, which can be described quantitatively according to the sell-known Kolmogorov-Avrami equation [7]:

$$K = 1 - e^{-zt^n},\qquad (1)$$

where z is crystallization rate constant, t is crystallization process duration, n is Kolmogorov-Avrami exponent, characterizing nucleation and growing crystalline structures type for the given polymer material.

As it has been shown in paper [8], the exponent n is connected with fractal dimension D_{ch} of the chain part between local order domains (nanoclusters) as follows:

$$n = 3(D_{ch} - 1) + 1 \cdot \tag{2}$$

The value D_{ch}, which characterizes molecular mobility level of polymeric material, can be calculated with the aid of the following equation [9]:

$$\frac{2}{\varphi_{cl}} = C_\infty^{D_{ch}}, \tag{3}$$

where φ_{cl} is nanoclusters relative fraction, C_∞ is characteristic ratio, which is polymer chain statistical flexibility indicator [10], and its value estimation method will be given below.

The value φ_{cl} can be calculated as follows. At first the nanocomposite structure fractal dimension d_f is determined according to the equation [11]:

$$d_f = (d - 1)(1 + \nu), \tag{4}$$

where d is dimension of Euclidean space, in which a fractal is considered (it is obvious, that in our case $d=3$), ν is Poisson ratio, which is estimated according to the mechanical tests results with the aid of the relationship [12]:

$$\frac{\sigma_Y}{E_n} = \frac{1 - 2\nu}{6(1 + \nu)}, \tag{5}$$

where σ_Y is yield stress, E_n is nanocomposite elasticity modulus.

Further the value C_∞ can be determined according to the formula [9]:

$$C_\infty = \frac{2d_f}{d(d - 1)(d - d_f)} + \frac{4}{3} \cdot \tag{6}$$

In Fig. 1 the dependence $K(n)$ for nanocomposites PP/CNT is adduced. As it was expected, K growth at n increasing is observed. This dependence is described according to the following empirical approximation:

$$K = 0.83(n - 1). \tag{7}$$

As it follows from the equation (7), the value $K=0$ is reached at $n=1.0$, or, according to the equation (2), at $D_{ch}=1.0$, i.e. at fully suppressed molecular mobility. The value $K=1.0$ is reached at $n=2.20$ or $D_{ch}=1.40$.
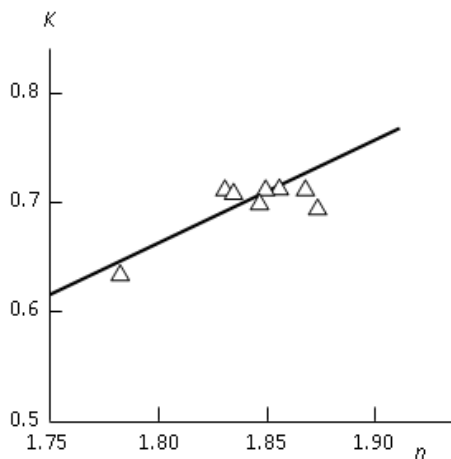

Fig. 1 - The dependence of crystallinity degree K on Kolmogorov-Avrami exponent n for nanocomposites PP/CNT

Since a carbon nanotubes are simultaneously nucleator in nanocomposite matrix crystallization process, then it the exponent n increase at CNT contents φ_n growth should be expected.

The nanofiller volume contents φ_n was calculated according to the known relationship [13]:

$$\varphi_n = \frac{W_n}{\rho_n}, \tag{8}$$

where W_n is nanofiller mass contents, ρ_n is its density, which is estimated as follows [13]:

$$\rho_n = 188(D_n)^{1/3}, \qquad \text{kg/m}^3, \tag{9}$$

where D_n is CNT diameter, which is given in nanometers.

In Fig. 2 the dependence $n(\varphi_n^{2/3})$, where the value $\varphi^{2/3}$ characterizes CNT surface total area, which shows linear growth of n at $\varphi_n^{2/3}$ (or φ_n) increase.
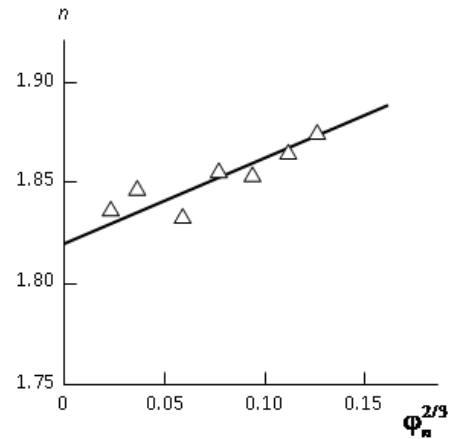

Fig. 2 - The dependence of Kolmogorov-Avrami exponent n on nanofiller contents φ_n for nanocomposites PP/CNT

At $\varphi_n=0$ the dependence $n(\varphi_n^{2/3})$ is extrapolated to $n \approx 1.82$, that is approximately equal to Kolmogorov-Avrami exponent for the initial PP and at $\varphi_n=1.0$ is the greatest for the studied nanocomposites value $n \approx 2.23$ is reached. Let us note, that for carbon fibers (CF) in paper [6] the opposite effect was obtained, namely, n decrease at φ_n growth. Such discrepancy is explained by different surface structure of the used filler – CF and CNT. If in the first case fibers have smooth surface with dimension $d_{surf} \approx 2.15$, then in the second one carbon nanotubes possess very rough surface with dimension $d_{surf} \approx 2.73$ [13]. As Pfeifer has been shown [14], such filler surface structure difference defines the difference of conformations of adjoining to surface macromolecular coils – they are stretched (straightened) on smooth surface and maintain the initial conformation of a statistical coil on a rough one. In its turn, this defines D_{ch} decrease in the first case and constant value or this dimension enhancement – in the second one. For CNT the dependence of n on their contents φ_n can be described by the following empirical equation:

$$n = n_{PP} + 2.90\varphi_n, \tag{10}$$

where n_{PP} is n value for the initial PP, which is equal to 1.78.

As it is known [7], the exponent n defines the forming crystalline phase morphology of polymeric

materials. In the athermic nucleation case at $n\leq2$ a ribbons are formed by two-dimensional growth mechanism, at $n\leq3$ – circles and at $n>3$ – spheres. Fractional values n mean the combined mechanism of thermal/athermic nucleation, moreover fractional part decrease indicates athermic mechanism role enhancement, i.e. intensification of all crystallites growth simultaneous start [7]. As it follows from Fig. 2 data, the exponent n fractional part increasing at φ_n growth is observed. This means nucleation thermal mechanism role enhancement, i.e. crystalline regions on carbon nanotubes growth intensification, Besides, for the studied nanocomposites the limiting value $n\approx2.25$ assumes, that in them spherical crystalline structures (spherolites) formation is impossible [7].

The theoretical value of crystallinity degree K^T can be determined according to the equation [2]:

$$K^T = 0.32C_\infty^{1/3}. \tag{11}$$

In Fig. 3 the comparison of experimental K and calculated according to the equation (11) crystallinity degree values for nanocomposites PP/CNT is adduced. As one can see, the obtained by the indicated method K^T values are systematically lower than K. It is supposed, that this effect is due to interfacial regions crystallization in the studied nanocomposites. The interfacial regions relative fraction φ_{if} can be estimated with the aid of the following equation [13]:

$$\frac{E_n}{E_m} = 1 + 11\left(\varphi_n + \varphi_{if}\right)^{1.7}, \tag{12}$$

where E_n and E_m are elasticity moduli of nanocomposite and matrix polymer, accordingly.

In Fig. 3 the comparison of the parameters K and $(K^T+\varphi_{if})$ for nanocomposites PP/CNT is adduced, which has shown their good enough correspondence (the average discrepancy of the indicated parameters makes up 6.2 %). Hence, this observation assumes interfacial regions crystallization in the studied nanocomposites.
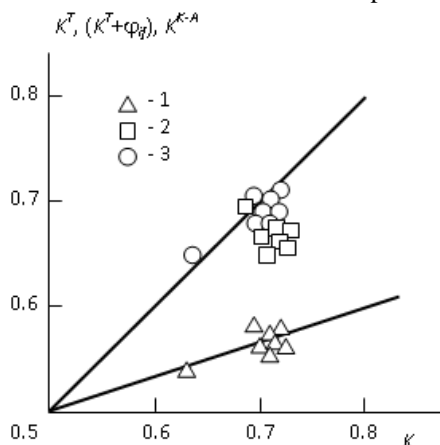

Fig. 3 - The comparison of experimental K and calculated according to the equations (11) K^T (1), (11) and (12) (K^T+φ$_{if}$) (2) and (1) K^{K-A} (3) crystallinity degree values for nanocomposites PP/CNT

Besides, the theoretical calculation of crystallinity degree K^{K-A} according to the equation (1) was performed at the following values with including in it parameters: $z=0.06$ and $t=5$. As it follows from Fig. 3 data, in this case theory and experiment excellent correspondence was obtained (the average discrepancy of K and K^{K-A} makes up 2.5 % only).

Conclusions

Therefore, the present paper results have demonstrated molecular mobility decisive influence on crystallinity degree value for nanocomposites with semicrystalline polymer matrix. In its turn, fractal dimension of a chain part between nanoclusters, characterizing the indicated mobility, is defined by nanofiller surface structure. The offered fractal model of crystallization process is a universal one for polymer composites with semicrystalline matrix irrespective of filler type [15].

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