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EFFECT OF A NANOFILLER STRUCTURE ON THE DEGREE OF REINFORCEMENT OF POLYMER–CARBON NANOTUBE NANOCOMPOSITES WITH THE USE OF A PERCOLATION MODEL

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Abstract: Fractal analysis methods are used to construct a model describing the effect of a nanofiller structure (carbon nanotubes) on the structure of a nanocomposite as a whole and its mechanical properties. It is shown that an increase in the fractal dimension of carbon nanotubes, which are ring-like formations in a polymer matrix, or their compaction can increase the elasticity modulus of the nanocomposites. It is determined that a significant effect on the mentioned properties of nanocomposites is produced by the spatial structure of carbon nanotubes.

Keywords: nanocomposite structure, carbon nanotubes, fractal analysis, percolation, elasticity modulus.

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It is assumed in [1] that the properties of polymer nanocomposites depend on a nanofiller structure in a polymer matrix. In [2, 3], modern experimental techniques (ultra-small-angle x-ray scattering, small-angle neutron scattering, etc.) are used for polymer–carbon nanotube nanocomposites to show that, due to a high degree of anisotropy and a small transversal elasticity modulus, carbon nanotubes in any state (solution, suspension, and polymer matrix) are annular formations similar to macromolecular coils of branched polymer chains. This makes it possible to use the methods of fractal physical chemistry to analyze the structure of carbon nanotubes [4]. Note that anisotropic fillers have this structure too [5, 6].

It should be noted that the macroscopic properties of polymer nanocomposites are determined both by a nanofiller structure and a nanocomposite as a whole. It is shown in [7] that the degree of reinforcement of polymer nanocomposites is a function of molecular characteristics of the polymer matrix. As polymer nanocomposites are thermodynamically nonequilibrium solids, their properties could only be described using at least two order parameters [8].

No analytical models allowing one to estimate the degree of reinforcement of nanocomposites were given in [1]. In [9], the degree of reinforcement of polymethylmethacrylate–functionalized carbon nanotube nanocomposites is described by means of a percolation model, whose main equation has the form

$$E_n/E_m = 1 + 11(\varphi_n)^a, \qquad (1)$$

where E_n and E_m are the elastic moduli of the nanocomposite and the matrix polymer, respectively (the ratio E_n/E_m is called the degree of reinforcement of the nanocomposite), φ_n is the volume fraction of the nanofiller, and a is the percolation index, whose value is close to the values of the standard percolation indices β, ν, and t [10] and determined as follows [9]:

$$a = n/d_f^n \qquad (2)$$

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(n is the order of the structural subset of the nanocomposite and d_f^n is the fractal dimension of the nanocomposite structure).

In [9], the above-mentioned subsets for the structure of the nanocomposites are determined: the first subset ($n = 1$) is interphase regions, the second subset ($n = 2$) is a set of interphase regions and nanofiller, and the third subset is the network of the nanofiller particles ($n = 4$).

The percolation model proposed in this paper uses the dimension of the nanocomposite structure as a whole d_f^n, and the degree of reinforcement of the nanocomposite is determined by two order parameters (n and d_f^n) even with a fixed value of φ_n. This model allows one to determine analytically the degree of reinforcement of the nanocomposite using a structural approach [11].

In this paper, the effect of the structure of the nanocomposite components on the nanocomposite structure is studied and the degree of reinforcement of the polymethylmethacrylate–functionalized carbon nanotube nanocomposites is determined within the framework of a percolation model. The results obtained in [12] for multilayer carbon nanotubes (MCNTs) with a diameter of (16.6 ± 3.9) nm and a length of (1.2 ± 0.6) μm are analyzed. The above-mentioned MCNTs are functionalized by $-$OH groups in order to obtain a mixture with polymethylmethacrylate (PMMA). The mass fraction of MCNTs in the nanocomposites under consideration vary in the range 0.065–1.300% [12].

The PMMA–MCNT is synthesized by radical polymerization in situ. The nanocomposite films with a thickness of 75 μm are obtained by covering the Teflon surface with a solution of nanocomposite in toluene. Tests are carried out with samples in the form of 10×25 -mm bands [12].

Mechanical tests on uniaxial tension of film samples of the PMMA–MCNT nanocomposite are carried out at a temperature equal to 293 K and with a strain rate of about 10^{-3} s^{-1} by using a Zwick/Roell Z100 universal testing machine [12].

As noted above, the carbon nanotubes in the polymer matrix of the nanocomposite are annular formations, whose fractal dimension varies in a wide range: $D_f = 1.57$–2.85 [2]. The dimension D_f of the indicated annular formations of carbon nanotubes can be determined with the help of the equation [13]

$$R_{\rm CNT} = 3.40\varphi_n^{-1/(d-D_f)},$$

where $R_{\rm CNT}$ is the radius of the annular formation and d is the dimension of the Euclidean space in which the fractal is considered (in this case, $d = 3$).

The value of $R_{\rm CNT}$ is determined using the equation [14]

$$b_\alpha = 5.8(R_{\rm CNT}^2 - 0.022),$$

where b_α is the dimensionless parameter characterizing the level of interphase adhesion at the polymer matrix–nanofiller interface and calculated using the equation [7]

$$E_n/E_m = 1 + 11(2.85 b_\alpha \varphi_n)^{1.7},$$

and the value φ_n is determined using the well-known expression

$$\varphi_n = W_n/\rho_n,$$

where W_n is the mass fraction of the nanofiller, and ρ_n [kg/m^3] is the nanofiller density:

$$\rho_n = 188(D_{\rm CNT})^{1/3}$$

($D_{\rm CNT}$ [nm] is the outer diameter of the carbon nanotube).

It is assumed that the structure of the polymer nanocomposite as a whole is determined by the interaction of its components (matrix polymer and nanofiller, which are fractal objects [9]). In this case, in the simulation of an annular formation as a macromolecular coil of branched polymer chains with dimension D_f, the dimension of a similar coil of polymer chains of the matrix D_f^n can be determined by the expression [15]

$$D_f^n = \frac{d(2D_f^m - D_f)}{d + 2(D_f^m - D_f)}, \qquad (3)$$

where D_f^m is the fractal dimension of the macromolecular coil of the original matrix polymer.

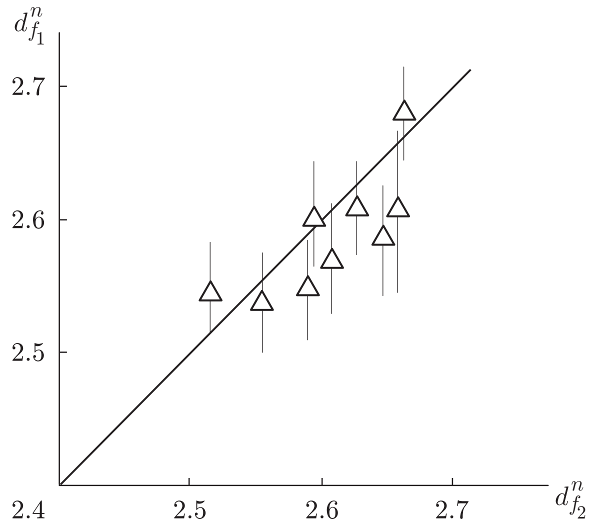

Fig. 1.

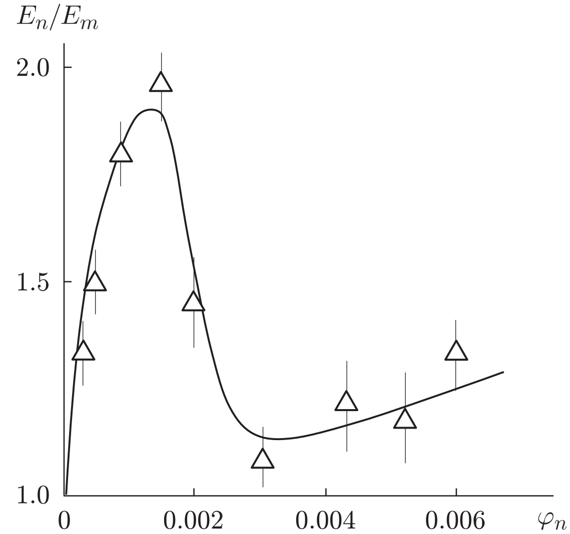

Fig. 2.

Fig. 1. Fractal dimension of the structure $d^n_{f_1}$, calculated from Eqs. (3) and (4), versus the fractal dimension of $d^n_{f_2}$ calculated by Eq. (5) for the PMMA–MCNT nanocomposite; the curve refers to $d^n_{f_2} = d^n_{f_1}$.

Fig. 2. Degree of reinforcement E_n/E_m versus the volume fraction of the nanofiller φ_n for the PMMA–MCNT nanocomposite: the points refer to the experimental data and the curve refers to the calculation results from Eq. (1).

The values of D^m_f for the linear polymers can be calculated according to the rule [16]

$$D^m_f = 2d^m_f/3, \tag{4}$$

where $d^m_f = (d-1)(1+\nu^m)$ is the fractal dimension of the structure of the matrix polymer and ν^m is Poisson's ratio for the matrix polymer, determined by the results of the mechanical tests with the help of the equation [8]

$$\frac{\sigma^m_Y}{E_m} = \frac{1-2\nu^m}{6(1+\nu^m)}$$

(σ^m_Y is the yield stress of the matrix polymer).

Moreover, the dimension of the nanocomposite structure d^n_f can be calculate by the expression [17]

$$d^n_f = 1.86 + 0.38D_{\text{net}}, \tag{5}$$

where D_{net} is the dimension of the network of the nanofiller particles in the polymer matrix of the nanocomposite, determined from using the equation [7]

$$\varphi_{if} = 0.506(D_{\text{net}} - 2),$$

φ_{if} is the fraction of the interphase regions in the nanocomposite, calculated using the percolation equation

$$E_n/E_m = 1 + 11(\varphi_n + \varphi_{if})^{1.7}.$$

Figure 1 shows the dependence of the fractal dimension $d^n_{f_1}$ of the PMMA–MCNT nanocomposite structure, calculated from Eqs. (3) and (4), in which D^m_f and d^m_f are replaced by D^n_f and d^n_f, respectively, on the fractal dimension $d^n_{f_2}$ calculated from Eq. (5). It is seen that the values of $d^n_{f_1}$ and $d^n_{f_2}$ calculated by the two methods are in good agreement: their average discrepancy in the fractional part of the dimension, which contains the main information on the structure [16, 17], does not exceed 5%. This means that, with a fixed value of D^m_f [or d^m_f in Eq. (4)], the properties of the nanocomposite structure is characterized by the dimension d^n_f depend on the properties of the structure of the carbon nanotubes in the polymer matrix, characterized by the dimension D_f.

It was shown in [9] that, for the PMMA–MCNT nanocomposites under consideration, the percolation threshold of carbon nanotubes φ_c is reached for $\varphi_n \approx 0.0025$, which results in the fact that the critical value of a is determined from Eq. (2) with $n = 1$ in the case $\varphi_n < \varphi_c$ and from the same equation with $n = 2$ in the case $\varphi_n > \varphi_c$. Figure 2 illustrates the dependence of the degree of reinforcement E_n/E_m on the volume fraction of the nanofiller φ_n for the PMMA–MCNT nanocomposite for the critical value of a. It can be seen that the calculation results and experimental results are in good agreement (their average difference is 6%). This confirms the correctness of the proposed percolation model.

According to the model for reinforcing the polymer–carbon nanotube nanocomposites, considered in this paper, the degree of reinforcement of these nanomaterials depends on a rather large number of factors, including the nanofiller structure in the polymer matrix. It follows from Eq. (3) that an increase in the dimensions D_f^m and D_f leads to an increase in the dimension D_f^n and, accordingly, d_f^n. This, in its turn, causes a decrease in the coefficient a and an increase in the degree of reinforcement E_n/E_m in accordance with Eq. (1) as φ_n is always smaller than unity. The value of E_n/E_m is significantly affected by the spatial structure of the carbon nanotubes, i.e., the achievement of the percolation threshold, which corresponds to the aggregate threshold and the formation of annular carbon nanotubes [9]. As the value of φ_c is reached, the structure of the reinforcing element of the nanocomposite changes: there is a transition from interphase regions (true nanocomposites) to the set of the nanofiller and interphase regions (intermediate nanocomposites), i.e., a transition from $n = 1$ and $n = 2$ in Eq. (2), which leads to a sharp decrease in the valueE_n/E_m (see Fig. 2) [11].

The effect of molecular characteristics on the degree of reinforcement of the nanocomposite is studied below. The dimension of the nanocomposite structure d_f^n and rigidity of the polymer matrix chain are bound by the expression [16]

$$C_\infty = \frac{2d_f^n}{d(d-1)(d-d_f^n)} + \frac{4}{3}$$

from which it follows that an increase in the value of C_∞ leads to an increase in d_f^n and, accordingly, to an increase in E_n/E_m. Therefore, the largest values of E_n/E_m have nanocomposites based on elastomers and rigid-chain polymers with high rigidity [7].

In conclusion, here is a study of the effect of chemical cross-linking of the polymer matrix on the degree of the nanocomposite reinforcement. For the linear polymers, Eq. (4) is valid. For the "cross-linked" polymers, the following equation is valid [16]:

$$D_f^m = d_f^m/1.667. \tag{6}$$

It follows from Eqs. (3) and (6) that the values of D_f^m with $d_f^m = \text{const}$ are greater for the linear polymers than for the "cross-linked" polymers, so the values of d_f^n and, accordingly, E_n/E_m are also greater for the linear polymers [18].

Thus, it is shown in this paper that the structure of carbon nanotubes in the polymer matrix affects the properties of the nanocomposites, particularly an increase in the fractal dimension of the annular formations, or their compactification leads to an increase in the dimension of the nanocomposite structure and its degree of reinforcement. A similar effect on the properties of the nanocomposites is produced by the structure of the matrix polymer and the spatial structure of carbon nanotubes. The percolation model proposed takes into account the effect of all these factors on the degree of reinforcement of the polymer–carbon nanotubes nanocomposites.

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