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NANOSCALE AND NANOSTRUCTURED MATERIALS AND COATINGS

The Effect of the Affinity of Components of Polymer/Carbon Nanotube Nanocomposites on Their Properties

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Abstract—We introduce the concept of structural affinity of the components of polymer/carbon nanotube nanocomposites quantitatively estimated in the framework of fractal analysis. The affinity of the components significantly affects the characteristics that are essential for nanocomposites, that is, the level of interfacial adhesion and the degree of aggregation of the nanofiller. This means that the degree of affinity completely determines the elastic modulus of the nanocomposite at a fixed concentration of the nanofiller. In turn, this indicator is determined by the structure of carbon nanotubes in the polymer matrix. The creation of high-modulus nanocomposites requires achieving full (or close to it) affinity of the components of these nanomaterials.

Keywords: nanocomposite, carbon nanotubes, affinity, structure, aggregation, interfacial adhesion, fractal dimension

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INTRODUCTION

Affinity is a thermodynamic characteristic that quantitatively describes the degree of interaction between substances [1]. This term refers to the affinity of one substance for another during a reaction. The terms "chemical affinity," "electron affinity," "proton affinity," etc. are commonly used. In the case of nanocomposites, affinity is usually understood as the thermodynamic affinity between a nanofiller and a polymer matrix [2, 3]. Regarding polymer nanocomposites, in addition to chemical aspects, there is also structural affinity defined as the closeness of the structural characteristics of the nanocomposite components, which can be characterized by the difference in the fractal dimensions of the surface of the nanofiller and the polymer matrix.

The goal of this work is a quantitative description of this structural affinity and its effect on the final properties of nanocomposites.

EXPERIMENTAL

Industry-produced (PP) Kaplen grade 01030 was used as the matrix polymer. Polypropylene of this grade has a melt flow index of 2.3–3.6 g/10 min, a weight-average molecular weight of ~$(2–3) \times 10^5$, and a polydispersity index of 4.5.

We used Taunit carbon nanotubes (CNTs) with an outer diameter of 20–70 nm, an inner diameter of 5–10 nm, and a length of 2 μm or more as a nanofiller. In the studied PP/CNT nanocomposites, the CNT concentration varied within 0.25–3.0 wt %.

PP/CNT nanocomposites were obtained by mixing the components in a melt in a Thermo Haake Reomex RTW 25/42 twin-screw extruder (Germany). Mixing was performed at a temperature of 463–503 K and a screw rotation speed of 50 rpm for 5 min. Test samples were obtained by injection molding using a Test Sample Molding Apparate RR/TS (Ray-Ran, United Kingdom) at a temperature of 503 K and a pressure of 43 MPa.

Mechanical tests for uniaxial tension were performed using samples in the form of a double-sided blade with dimensions according to GOST (State Standard) 11262-80. The tests were carried out with a universal Gotech Testing Machine CT-TCS 2000 (Germany) at a temperature of 293 K and a strain rate of ~2×10^{-3} s^{-1}.

RESULTS AND DISCUSSION

Affinity, as applied to the description of interfacial effects in polymer nanocomposites, can be interpreted as difference Δd_f between fractal dimensions of the polymer matrix structure d_f and nanofiller surface d_{surf}:

$$\Delta d_f = d_f - d_{surf}. \quad (1)$$

Dimensions d_f and d_{surf} can be determined as follows. Carbon nanotubes in the polymer matrix of the

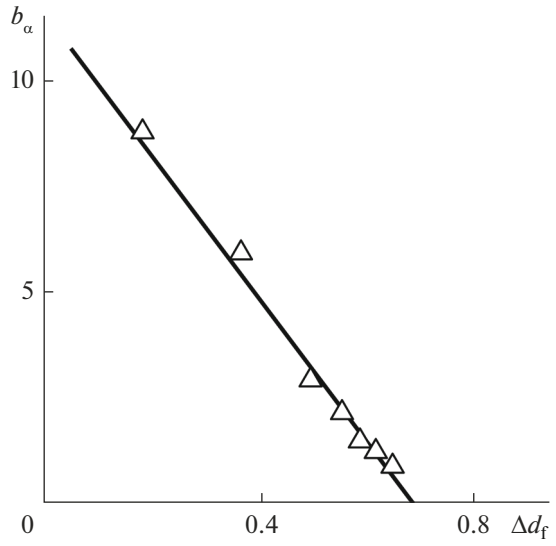

Fig. 1. Dependence of parameter b_α characterizing the level of interfacial adhesion on difference in dimensions Δd_f for PP/CNT nanocomposites.

nanocomposite form ring-shaped formations of radius R_{CNT} [4], the value of d_{surf} of which is [5]

$$d_{surf} = 2 + 1.75(R_{CNT} - 0.14), \quad (2)$$

where radius R_{CNT}, specified in micrometers, for the nanocomposites under consideration is taken according to the data of [6].

The dimension of the nanocomposite structure d_f, which is assumed to be the dimension of the polymer matrix structure, is determined by the equation [6]

$$d_f = (d-1)(1+\nu), \quad (3)$$

where d is the dimension of the Euclidean space in which the fractal is considered (in our case, $d = 3$) and ν is the Poisson's ratio determined from the results of mechanical tests using the relation [7]

$$\frac{\sigma_Y}{E_n} = \frac{1-2\nu}{6(1+\nu)}, \quad (4)$$

where σ_Y and E_n are the yield stress and elastic modulus of the nanocomposite, respectively.

It should be expected that degree of affinity (structural affinity) of the nanocomposite components Δd_f primarily affects the level of the polymer matrix–nanofiller interfacial adhesion, which can be characterized by dimensionless parameter b_α [8]. The value of b_α can be determined using the following percolation relation [8]:

$$\frac{E_n}{E_m} = 1 + 11(cb_\alpha\varphi_n)^{1.7}, \quad (5)$$

where E_n and E_m are the elastic moduli of the nanocomposite and matrix polymer, respectively (the ratio E_n/E_m is usually called the "degree of reinforcement" of the nanocomposite), c is a coefficient (c ~2.8 for carbon nanotubes [8]), and φ_n is the volume concentration of the nanofiller, which can be estimated according to the well-known equation [8]

$$\varphi_n = \frac{W_n}{\rho_n} \quad (6)$$

Here, W_n is the weight concentration of the nanofiller and ρ_n is its density determined for carbon nanotubes as [8]

$$\rho_n = 188(D_{CNT})^{1/3}, \ \mathrm{kg/m^3}, \quad (7)$$

where D_{CNT} is the outer diameter of a carbon nanotube given in nanometers.

Figure 1 shows the dependence of the level of interfacial adhesion characterized by parameter b_α on the affinity of the nanocomposite components characterized by the difference in the dimensions Δd_f for PP/CNT nanocomposites. As expected, there is a strong decrease in b_α as Δd_f increases, which is described by a linear relationship, analytically expressed by the following equation:

$$b_\alpha = 11.8 - 17.5\Delta d_f. \quad (8)$$

It follows from Eq. (8) that the maximum value $b_\alpha = 11.8$ for the nanocomposites under consideration takes place in the case of complete affinity of the nanocomposite components, i.e., at $\Delta d_f = 0$. At $\Delta d_f = 0.68$, $b_\alpha = 0$; that is, interfacial adhesion is completely absent.

Next, let us consider the effect of the affinity of the components of PP/CNT nanocomposites on the degree of nanofiller aggregation; this process is the most significant of those adversely affecting the properties of these nanomaterials. The degree of such aggregation can be estimated by parameter χ determined by the equation [9]

$$\chi = \frac{\varphi_n}{\varphi_n + \varphi_{if}}, \quad (9)$$

where φ_{if} is the relative proportion of interfacial regions.

The sum of $(\varphi_n + \varphi_{if})$ can be determined using the following percolation relation [8]:

$$\frac{E_n}{E_m} = 1 + 11(\varphi_n + \varphi_{if})^{1.7}. \quad (10)$$

Figure 2 shows dependence $\chi[(\Delta d_f)^3]$ for the nanocomposites under consideration; we selected such a form of this dependence to linearize it. The data in Fig. 2 are analytically described by the following equation:

$$\chi = 0.02 + 1.07(\Delta d_f)^3, \quad (11)$$

which indicates two specific features of the relationship between parameters χ and Δd_f. First, the degree of

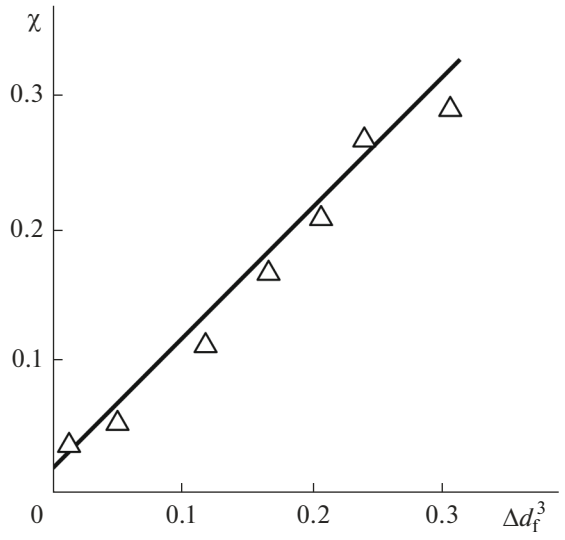

Fig. 2. Dependence of the degree of nanofiller aggregation, characterized by parameter χ on difference in dimensions Δd_f for PP/CNT nanocomposites.

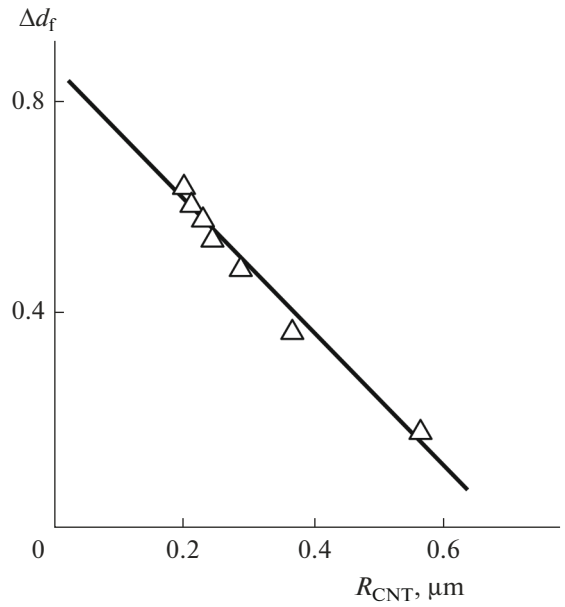

Fig. 3. Dependence of difference in dimensions Δd_f on radius R_{CNT} of ring-shaped formations of carbon nanotubes for PP/CNT nanocomposites.

nanofiller aggregation cannot be zero, and the minimum value of χ for PP/CNT nanocomposites is 0.02. Second, there is a strong (cubic) dependence of the degree of aggregation of carbon nanotubes on the affinity of the nanocomposite components. This dependence is explained by comparing the graphs in Figs. 1 and 2. An increase in the degree of affinity, characterized by the difference Δd_f, weakens the level of interfacial bonds, characterized by the parameter b_α, which prevents the "sticking" (combining) of individual nanoparticles into their aggregates. Consequently, a decrease in b_α due to an increase in Δd_f intensifies the aggregation process.

An increase in Δd_f with an increase in the concentration of carbon nanotubes in PP/CNT nanocomposites is due to structural factors. An increase in φ_n determines a decrease in radius R_{CNT} of ring-shaped formations in CNTs and decreases surface dimension d_{surf} of these formations according to Eq. (2) at a practically constant dimension of the structure of PP/CNT nanocomposites $d_f = 2.74$ [6]. This conclusion is confirmed by the dependence $\Delta d_f(R_{CNT})$ for PP/CNT nanocomposites (Fig. 3). As expected, there is a decrease in Δd_f as R_{CNT} increases, which can be analytically expressed by the following empirical equation:

$$\Delta d_f = 0.89 - 1.28 R_{CNT}, \quad (12)$$

where R_{CNT} is again given in micrometers.

The value of R_{CNT} cannot be zero or less than D_{CNT}, and its theoretical minimum value can be estimated from a combination of Eqs. (8) and (12). At the maximum value of $\Delta d_f = 0.68$, the minimum value of R_{CNT} is 0.164 μm, which is close to the similar value of this radius of 0.208 μm, obtained within the percolation theory [6]. In turn, the value $\Delta d_f = 0$ is realized at $R_{CNT} = 0.72$ μm. This confirms the structural origin of the affinity of the polymer nanocomposite components.

In [9], the following percolation relation was proposed to determine degree of reinforcement E_n/E_m of polymer nanocomposites:

$$\frac{E_n}{E_m} = 1 + 11\left(\frac{\varphi_n}{\chi}\right)^{1.7}. \quad (13)$$

The combination of Eqs. (11) and (13) yield the following relationship for estimating degree of reinforcement E_n/E_m of nanocomposites:

$$\frac{E_n}{E_m} = 1 + 11\left(\frac{\varphi_n}{0.02 + 1.07(\Delta d_f)^3}\right)^{1.7}. \quad (14)$$

Equation (14) is significant in two aspects. First, it demonstrates that one of the essential indicators of polymer nanocomposites, namely, the degree of reinforcement, is determined only by the affinity of the nanocomposite components at a fixed concentration of nanofiller. Second, this ratio indicates a way to increase the elastic modulus of nanocomposites with high-modulus nanofillers (carbon nanotubes, graphene) by decreasing Δd_f. The potential of these nanofillers is underused; the current level of their utilization is approximately 8% [4]. The maximum achievable elastic modulus of a nanocomposite can be estimated using a simple mixture rule [10]:

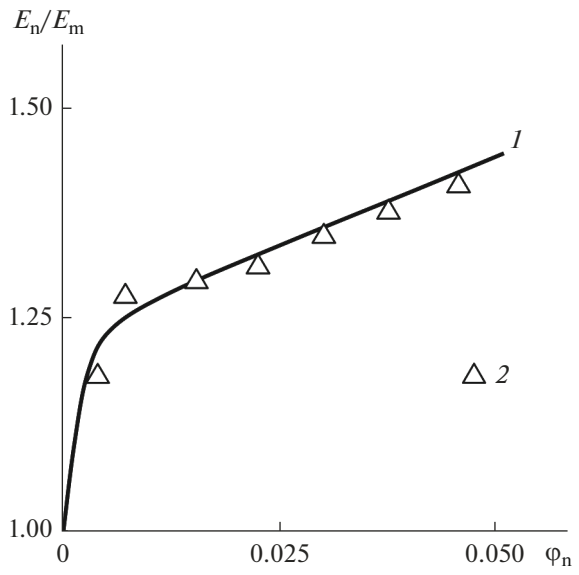

Fig. 4. The comparison of degree of reinforcement E_n/E_m, (*1*) calculated by Eq. (14) and (*2*) experimental, on volume concentration of the nanofiller φ_n for PP/CNT nanocomposites.

$$E_n^{max} = E_{CNT}\varphi_n + E_m(1-\varphi_n), \quad (15)$$

where E_{CNT} is the nominal modulus of elasticity of carbon nanotubes, which is ~1000 GPa [4].

The estimates by Eq. (15) at $\varphi_n = 0.05$ yield E_n^{max} or, for the case of the nanocomposites under consideration with the value $E_m \approx 1$ GPa, $E_n/E_m \approx 51$. The estimate of E_n/E_m by Eq. (14) at $\varphi_n = 0.05$ and $\Delta d_f = 0$ gives the same E_n/E_m value. This means that, for the full implementation of high values of the elastic modulus of CNTs and graphene, it is necessary to achieve the full affinity of the nanocomposite components or the condition $\Delta d_f = 0$.

Figure 4 compares the dependences of degrees of reinforcement E_n/E_m on volume concentration of the nanofiller φ_n for PP/CNT nanocomposites calculated by Eq. (14) and experimentally obtained. We observed a good agreement between theory and experiment: their average discrepancy is 3%, which does not exceed the experimental error in determining this parameter, confirming the correctness of the model proposed in this work.

In conclusion, the following circumstance should be noted. In the Euclidean approximation, quantities d_f and d_{surf} are constant; $d_f = 3$ and $d_{surf} = 2$; that is, $\Delta d_f = 1$. According to Eq. (9), this means negative values of φ_{if} and, according to Eq. (12), negative values of R_{CNT}, which has no physical meaning. Therefore, the analysis of the structure and properties of polymer nanocomposites requires the use of fractal analysis methods.

CONCLUSIONS

Therefore, in this work, we introduced the postulate of physical or structural affinity of the nanocomposite components as the difference between the fractal dimensions of the polymer matrix structure and the nanofiller surface. An increase in this difference (decrease in affinity) significantly decreases the level of interfacial adhesion and dramatically (as the cubic dependence) enhances the process of nanofiller aggregation. Affinity is controlled by a structural factor, namely, the formation of ring-shaped formations of carbon nanotubes, i.e., their bend. The level of affinity expressed by the above difference in dimensions completely controls the degree of reinforcement or modulus of elasticity of the nanocomposite at a fixed concentration of the nanofiller. The creation of high-modulus polymer/carbon nanotube nanocomposites requires achieving full (or close to it) affinity of the components of these nanomaterials.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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