ISSN 0021-8944, Journal of Applied Mechanics and Technical Physics, 2018, Vol. 59, No. 3, pp. 508–510. © *Pleiades Publishing, Ltd., 2018.*
Original Russian Text © *G.V. Kozlov, I.V. Dolbin.*

FRACTAL MODEL OF THE NANOFILLER STRUCTURE AFFECTING THE DEGREE OF REINFORCEMENT OF POLYURETHANE–CARBON NANOTUBE NANOCOMPOSITES

G. V. Kozlov and I. V. Dolbin

UDC 541.64: 546.26

Abstract: A percolation model of nanocomposite reinforcement is under study. It is shown that the degree of reinforcement of polyurethane–carbon nanotube nanocomposites depends on the structure of nanofillers, which are annular formations. This structure is most accurately characterized by its fractal dimension. It is established that the creation of a structure with negative percolation indices allows for a significant increase in the degree of reinforcement of considered nanocomposites at low nanofiller concentrations.

Keywords: nanocomposite, polyurethane, carbon nanotubes, fractal structure, degree of reinforcement, percolation.

DOI: 10.1134/S002189441803015X

INTRODUCTION

As is known, the degree of reinfocement of elastomers by carbon nanotubes is much larger than the degree of reinfocement of glassy polymers [1, 2]. In [1, 2], this phenomenon is explained by clustering of carbon nanotubes into annular formations similar to branched macromolecular coils. It is assumed in [2] that this clustering causes a new reinforcement mechanism based on elastic deformation of clusters. Such a mechanism occurs only in the case of matrices made of elastomers, which explains the larger degree of reinforcement of nanocomposites on their basis. Nevertheless, the authors of [2] failed to determine the degree of reinforcement of polyurethane–carbon nanotube nanocomposites, caused by the mechanism described above. This paper describes the percolation model of reinforcement of nanocomposites [3]. A fractal analysis [4] is used to study the structure of clusters (annular formations) of carbon nanotubes.

Inorgan PS455-203 (Morthane) thermoplastic polyurethane based on aromatic polyester, manufactured by Huntsman Polyurethanes (USA), serves as a matrix polymer, and PR-19-HT carbon nanotubes, manufactured by Applied Science Inc. (USA), play the role of nanofillers. The outer diameter of carbon nanotubes is 50–120 nm, the wall thickness is 20 nm, and the initial aspect ratio is 50–200 [2].

The thickness of the samples of polyurethane–carbon nanotube nanocomposites obtained by watering from solutions of polyurethane with carbon nanotubes in tetrachloroethane is approximately 0.3 mm, and the mass fraction of carbon nanotubes in them ranges within 2–22% [2].

Tension tests are carried out on (60×5)-mm rectangular samples. Uniaxial tension tests are performed at a temperature of 293 K and a slider velocity of 40 mm/min with the use of an Instron (UTM, Model 4465) universal device [2].

Kabardino-Balkarian State University, Nalchik, 360004 Russia; kgv_1945@mail.ru; i_dolbin@mail.ru. Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, Vol. 59, No. 3, pp. 141–144, May–June, 2018. Original article submitted June 21, 2017.

As noted above, carbon nanotubes in the polymer matrix of the nanocomposite form annular formations with radius R_{CNT}, which can be determined with the help of the equation [3]

$$(2R_{\text{CNT}})^3 = \pi L_{\text{CNT}}\, r_{\text{CNT}}^2/\varphi_n,$$

where L_{CNT} and r_{CNT} are the length and radius of the carbon nanotube, respectively, and φ_n is the volume fraction of the nanofiller. In [5] and in this paper, the value of φ_n is determined by the use of the equation [6]

$$\varphi_n = W_n/\rho_n, \tag{1}$$

where W_n and ρ_n are the mass fraction and density of the nanofiller.

In [5], the value $\rho_n = 1560$ kg/m^3 is used in Eq. (1), but here the density of carbon nanotubes is estimated using the equation [6]

$$\rho_n = 188(D_{\text{CNT}} - d_{\text{CNT}})^{1/3}, \tag{2}$$

where D_{CNT} and d_{CNT} [nm] are the outer and inner diameters of the carbon nanotubes, respectively.

In [2], a rather complicated equation was proposed for determining φ_n. The calculations carried out using this equation result in the values of φ_n close to the values determined from Eqs. (1) and (2), but approximately twice as large as the values determined in [5]. The structure of the annular formations of carbon nanotubes is characterized by their fractal dimension D_f, which is determined with the help of the equation [4]

$$R_{\text{CNT}} = 3.4\varphi_n^{-1/(d-D_f)},$$

where d is the dimension of the Euclidean space in which the fractal (in this case, $d = 3$) is considered.

In the percolation model of reinforcement of nanocomposites, the base ratio has the form [3]

$$E_n/E_m = 1 + 11(\varphi_n)^a, \tag{3}$$

where E_n and E_m are the elastic moduli of the nanocomposite and matrix polymer, respectively (the ratio E_n/E_m is called the degree of reinforcement of the nanocomposite), and a is the percolation index, whose values vary in the same interval as the values of the standard percolation indexes β, ν, and t.

The proximity of the value of a to a particular standard percolation index determines the type of reinforcing component of the nanocomposite. Thus, the nanocomposite is reinforced by interphase regions (true nanocomposites) for $a \approx \beta \approx 0.40$, by the set of nanofillers and interphase regions for $a \approx \nu \approx 0.80$, and only by nanofillers or fillers (microcomposites) for $a \approx t \approx 1.60$. Thus, the introduction of nanometer-sized initial particles into the matrix polymer does not guarantee that a nanocomposite is obtained [1, 3].

Figure 1 shows the dependence of a on the square of the value of the fractal dimension D_f of the annular formations of carbon nanotubes for the polyurethane–carbon nanotube nanocomposites. It is seen that, as D_f increases, the index a decreases linearly:

$$a = 1.60 - 0.29D_f^2. \tag{4}$$

Taking into account that the largest standard percolation index is $t = 1.60$, Eq. (4) can be written as follows:

$$a = t - 0.29D_f^2.$$

We consider some critical points on the curve of the dependence $a(D_f^2)$ shown in Fig. 1. For $D_f = 1.0$, for straight-line carbon nanotubes $a = 1.31$, i.e., in this case, the nanostructured composites obtained are close to microcomposites. To obtain true nanocomposites ($a \leqslant \beta \approx 0.40$), the fractal dimension should be equal to $D_f = 2.0$. At the same time, there should be no interaction between the annular formations [7]. In order to obtain the negative values of a, the condition $D_f > 2.34$ should be satisfied. This dimension corresponds to a compensated state of a branched fractal [8].

Within the framework of the percolation model of two-component materials with random distribution of components, the transition from the positive to negative values of a means a transition from a random resistor network ("ant" limit) to a random superconducting network ("termite" limit) [9], which corresponds to a sharp increase in the degree of reinforcement of the polyurethane–carbon nanotube nanocomposites. It should be noted that this transition is implemented with the value $\varphi_n \approx 0.16$, which corresponds to the threshold value of φ_c for spheres [1]. This means that, at least for the nanocomposites under consideration, carbon nanotubes are an analog of spheres that are annular formations in the first approximation. Also note that the condition $\varphi_n = \varphi_c \approx 0.16$ is obtained only when φ_n is estimated by the methods proposed in [2, 6].

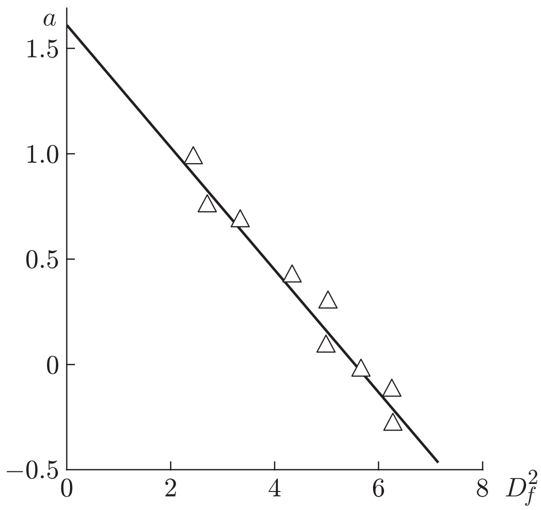

Fig. 1.

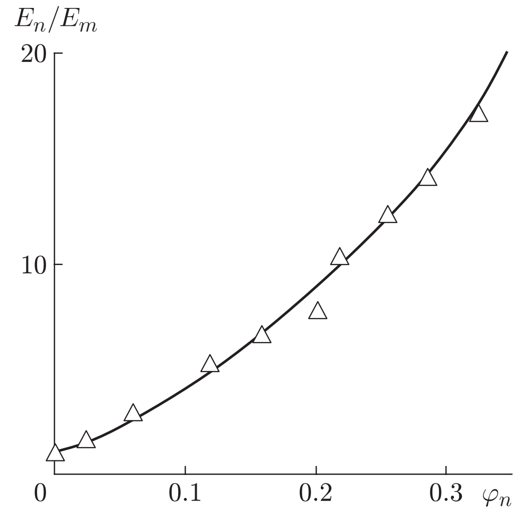

Fig. 2.

Fig. 1. Percolation index a in Eq. (3) versus the fractal dimension D_f of annular formations of the nanofiller for the polyurethane–carbon nanotube nanocomposites: the curve refers to the relationship (4), and the points show the experimental results experiment.

Fig. 2. Relationships between the degree of reinforcement E_n/E_m and the volume fraction of the nanofiller φ_n for the polyurethane–carbon nanotube nanocomposites, one of which is determined by Eqs. (3) and (4) (curve) and the other one experimental (points).

Figure 2 shows the relationship calculated from Eqs. (3) and (4) and the experimental relationship $E_n/E_m(\varphi_n)$ for the nanocomposites under consideration. It can be seen that the calculation results and experimental results are in good agreement (the difference does not exceed 10%).

In this paper, it is shown that the degree of reinforcement of the polyurethane–carbon nanotube nanocomposites depend on the structure of annular formations of nanofillers. The specified structure is most accurately described on the basis of a fractal analysis. In the case of negative values of the percolation index a in Eq. (3), the degree of reinforcement of nanocomposites substantially increases.

REFERENCES

1. D. W. Schaefer and R. S. Justice, “How Nano Are Nanocomposites?,” Macromolecules **40**, 8501–8517 (2007).
2. D. W. Schaefer, J. Zhao, H. Dowty, et al., “Carbon Nanofibre Reinforcement of Soft Materials,” Soft Mater. **4**, 2071–2079 (2008).
3. A. K. Mikitaev and G. V. Kozlov, “Description of the Degree of Reinforcement of Nanocomposites of Polymer/Carbon Nanotubes in the Framework of Percolation Models,” Fiz. Tverd. Tela **57** (5), 961–964 (2015).
4. A. K. Mikitaev and G. V. Kozlov, “Dependence of the Degree of Reinforcement of Nanocomposites of Polymer/Carbon Nanotubes on the Dimension of Nanofillers,” Dokl. Akad. Nauk **462** (1), 41–44 (2015).
5. H. Koerner, W. Liu, M. Alexander, et al., “Deformation—Morphology Correlations in Electrically Conductive Carbon Nanotube—Thermoplastic Polyurethane Nanocomposites,” Polymer **46**, 4405–4420 (2005).
6. A. K. Mikitaev, G. V. Kozlov, and G. E. Zaikov, *Polymer Nanocomposites: A Variety of Structural Forms and Applications* (Nauka, Moscow, 2009) [in Russian].
7. A. K. Mikitaev and G. V. Kozlov, “Effect of Interaction of Carbon Nanotubes (Nanofibers) on the Level of Interfacial Adhesion in Polymer Nanocomposites,” Vse Materialy, No. 6, 13–18 (2015).
8. F. Family, “Fractal Dimension and Grand Universality of Critical Phenomena,” J. Stat. Phys. **36**, 881–896 (1984).
9. H. Stanley, “Fractal Surfaces and “Termite” Model for Two-Component Random Materials,” in *Fractals in Physics*, Ed. by L. Pietronero and E. Tosatti (Amsterdam–Oxford–ew York–Tokyo– North-Holland, 1986).