

## THE SIMULATION OF CARBON NANOTUBES AS MACROMOLECULAR COILS: INTERFACIAL ADHESION

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**Abstract.** Simulation of carbon nanotubes ring-like formations as macromolecular coils was performed within the frameworks of fractal physical chemistry of polymer solutions. The dependence of interfacial adhesion level has been shown in nanocomposites polymer/carbon nanotubes on the indicated formations structure, characterized by its fractal dimension. This treatment correctness was confirmed by nanocomposites reinforcement degree description within the framework of reinforcement molecular theory.

**Keywords:** nanocomposite; epoxy polymer; ring-like formation; interfacial adhesion; fractal dimension.

### 1. Introduction

As it is well-known [1, 2], carbon nanotubes in polymer nanocomposites form ring-like structure, outwardly resembling macromolecular coils. This circumstance allows to use for the carbon nanotubes indicated structures methods of both classical [3] and fractal [4] physical chemistry of polymer solutions. The authors [2] found interfacial adhesion level reduction in nanocomposites polymer/carbon nanotubes at this specific nanofiller ring-like formations radius, that restricted essentially its possibilities of the indicated nanocomposites properties improvement.

At present a number of extreme experimental dependences of nanocomposites elasticity modulus on carbon nanotubes contents at very small values of the latter (of the order of 0.1 mass % and less) was obtained [5-7], which up to now do not obtain proper explanation. Therefore the present work purpose is intercommunication clarification of ring-like formations structure and interfacial adhesion level in polymer nanocomposites, where the indicated structures are simulated as macromolecular coils, and the explanation of the obtained extreme dependences of elasticity modulus on this basis.

### 2. Experimental

Epoxy polymers (EP) based on diglycidyl ether of bisphenol A (ED-20) and diglycidyl ether of diphenylolpropane (DED) were used as matrix polymer. The eutectic mixture of  $\mu$ -phenylenediamine (40 mass %) and 4,4'-diaminodiphenylmethane (60 mass %) at equifunctional ratio was applied as curing agent. The eutectic mixture was prepared in vacuum at heating up to 373 K during 1 hour, cooled and preserved in argon atmosphere. Epoxy polymers were cured by the stepped regime (353 K – 2 hours, 393 K – 2 hours and 443 K – 5 hours) [6].

The single-walled carbon nanotubes (CNT) with diameter of 1.2-1.6 nm and length of  $\leq 2$   $\mu$ m were prepared by voltaic arc method with purification (up to 95 %) by gas-phase oxidation

and washing in hydrochloric acid. After this procedure CNTs are in strongly agglomerated state in the form of bundles with a diameter of  $\sim 30$  nm [6].

The tensile tests are performed in accordance with ASTM D638-96, D882-95a on a tensile tester Zwick at temperature 293 K and deformation rate 1 mm/min [6].

### 3. Results and Discussion

CNT ring-like structures radius  $R_{CNT}$  can be determined within the framework of percolation model [8] with the aid of the following equation:

$$\varphi_n = \frac{\pi L_{CNT} r_{CNT}^2}{(2R_{CNT})^3}, \quad (1)$$

where  $\varphi_n$  is nanofiller volume contents,  $L_{CNT}$  and  $r_{CNT}$  are length and radius of carbon nanotube, accordingly.

The value  $\varphi_n$  was determined according to the well-known formula [9]:

$$\varphi_n = \frac{W_n}{\rho_n}, \quad (2)$$

where  $W_n$  is nanofiller mass contents,  $\rho_n$  is its density, which for nanoparticles is determined as follows [9]:

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

where  $D_{CNT}$  is carbon nanotubes bundle diameter, which is given in nm.

And at last, the fractal dimension  $D_f^{CNT}$  of CNT ring-like formations was calculated within the framework of an irreversible aggregation model with the aid of the equation [2]:

$$R_{CNT} = 3.40\varphi_n^{-1/(d-D_f^{CNT})}, \quad (4)$$

where  $d$  is dimension of Euclidean space, in which a fractal is considered (it is obvious, that in our case  $d = 3$ ) and  $R_{CNT}$  is given in nm.

The interfacial adhesion level in polymer nanocomposites can be characterized with the aid of the dimensionless parameter  $b_\alpha$ , which is determined with the equation usage [9]:

$$\frac{E_n}{E_m} = 1 - 11(c\varphi_n b_\alpha)^{1.7}, \quad (5)$$

where  $E_n$  and  $E_m$  are elasticity moduli of nanocomposite and matrix polymer, respectively (the ratio  $E_n/E_m$  is accepted to call nanocomposite reinforcement degree),  $c$  is constant coefficient, which is equal to  $\sim 2.8$  for carbon nanotubes [9].

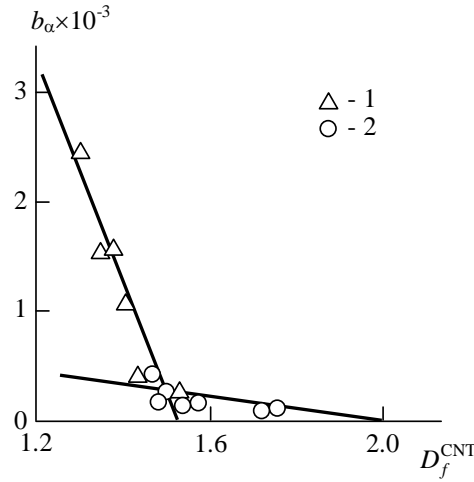
In Figure 1 the dependence  $b_\alpha(D_f^{CNT})$  is adduced for the considered nanocomposites, breaks down into two linear parts with a very differing slope. This dependence can be described analytically by the following empirical equations:

$$b_\alpha = 5.5 \times 10^3 - 10^4(D_f^{CNT} - 1) \text{ for } D_f^{CNT} < 1.50, \quad (6)$$

and

$$b_\alpha = 5.5 \times 10^2(2 - D_f^{CNT}) \text{ for } D_f^{CNT} < 1.50 \quad (7)$$

Let us note two specific features of the dependence  $b_\alpha(D_f^{CNT})$ , adduced in Fig. 1 and described by the equations (6) and (7). As it is known [9], parameter  $b_\alpha$  allows not only quantitative, but qualitative gradation of interfacial adhesion level in polymer nanocomposites as well. So, the condition  $b_\alpha = 0$  defines interfacial adhesion absence,  $b_\alpha = 1.0$  means perfect (by Kerner) adhesion and the condition  $b_\alpha > 1.0$  gives criterion of nanoadhesion effect realization in the considered nanomaterials. The data of Fig. 1 demonstrated the possibility of nanoadhesion very high level realization at carbon nanotubes small contents. So, according to the equation (6) the value  $b_\alpha = 5500$  for  $D_f^{CNT} = 1.0$ , i.e. for completely straight-line nanotubes. In case of nanocomposites polymer/carbon nanotubes with large enough nanofiller contents ( $\geq 1$  mass %) the value  $b_\alpha$  does not exceed 10.5 (even in case of functionalized CNT) [9].



**Fig. 1.** The dependence of parameter  $b_\alpha$ , characterizing interfacial adhesion level, on fractal dimension  $D_f^{CNT}$  CNT ring-like formations for nanocomposites EP/CNT based on DED (1) and ED-20 (2).

The value  $D_f^{CNT}$  at the transition point, which is equal to 1.50 (Fig. 1), is the second very important feature of the adduced above data. The indicated dimension corresponds to leaking (transparent) macromolecular coil or corresponding CNT ring-like formation. This means, that at  $D_f^{CNT} \leq 1.50$  polymer can go freely inside CNT ring-like structure and this, in its turn, assumes, that the greater part of polymer matrix-nanofiller contacts is formed in CNT ring-like formations inner regions. Polymer access (diffusion) restriction inside the indicated structures at  $D_f^{CNT} > 1.50$  results in such contacts number sharp decrease and in corresponding interfacial adhesion level reduction, characterized by parameter  $b_\alpha$  (Fig. 1).

Let us consider another important structural aspect. The percolation threshold  $\varphi_c$  value for CNT can be determined by several methods and in the present work the method, proposed in paper [1], will be used, where the value  $\varphi_c$  is determined according to the equation:

$$\varphi_c = \frac{0.48}{4\alpha_{ef}^2 N_{cl}^{(3-D_f^{CNT})/D_f^{CNT}}}, \quad (8)$$

where  $\alpha_{ef}$  is effective aspect ratio of carbon nanotube,  $N_{cl}$  is stiffness sections number per CNT ring-like formation.

The value  $\alpha_{ef}$  can be determined with the aid of the following equation [1]:

$$\frac{E_n}{E_m} = 1 + 2\alpha_{ef} C_{or} \varphi_n, \quad (9)$$

where  $C_{or}$  is the orientation factor, which is accepted equal to 0.2 for the case of CNT statistically oriented stiffness sections [1].

The parameter  $N_{cl}$  was calculated with the following formula usage [1]:

$$R_{CNT} = L_{ef} N_{cl}^{1/D_f^{CNT}}, \quad (10)$$

where  $L_{ef}$  is CNT stiffness section effective length, determined as the product  $\alpha_{ef} D_{CNT}$ .

Calculation according to the indicated methodics, namely, according to the equations (8)-(10), gives the value  $\varphi_c = 0.62 \times 10^{-4}$ . In its turn,  $R_{CNT}$  calculation according to the equation (1) at  $\varphi_n = \varphi_c$  gives the value  $D_f^{CNT} \approx 1.44$ . The adduced estimations show that realization of CNT leaking (transparent) ring-like structures, allowing matrix polymer free diffusion in their inner region, is possible at the condition  $\varphi_n < \varphi_c$  only.

The estimated by such method values  $b_\alpha$  correctness checking can be performed within the framework of nanocomposites reinforcement molecular conception, the basic equation of which has the look [9]:

$$\frac{E_n}{E_m} = 1 + \frac{0.19W_n l_{st} b_\alpha}{D_{CNT}^{1/2}}, \quad (11)$$

where  $l_{st}$  is polymer matrix chain statistical segment length and  $D_{CNT}$  value is accepted for a separate carbon nanotube, i.e. equal to  $\sim 1.5$  nm [6].

The value  $l_{st}$  was determined as follows [10]:

$$l_{st} = l_0 C_\infty, \quad (12)$$

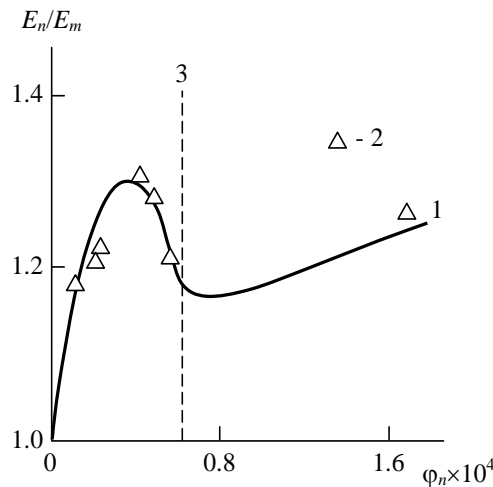
where  $l_0$  is the main chain skeletal bond length, which is equal to 0.154 nm for the considered EP [10],  $C_\infty$  is characteristic ratio, the value of which is connected with structure fractal dimension  $d_f$  by the equation [11]:

$$C_\infty = \frac{2d_f}{d(d-1)(d-d_f)} + \frac{4}{3}, \quad (13)$$

where  $d$  is, as earlier, the dimension of Euclidean space, in which a fractal is considered (it is obvious, that in our case  $d = 3$  again).

For epoxy polymers the value  $d_f \approx 2.7$  [12] and then  $C_\infty = 4.33$  and  $l_{st} = 0.667$  nm.

In Fig. 2 the comparison of calculated according to the equation (11) and the obtained experimentally dependences  $E_n/E_m(\varphi_n)$  is adduced for nanocomposites EP/CNT based on DED. As one can see, the proposed model gives a good both qualitative (the dependence extreme character description) and quantitative (the average discrepancy of theory and experiment makes up 2.5 %) correspondence to the experiment. The similar results were obtained for nanocomposites EP/CNT based on ED-20, but with somewhat larger theory and experiment discrepancy (4.5 %).



**Fig. 2.** The comparison of calculated according to the equation (11) (1) and obtained experimentally (2) dependences of reinforcement degree  $E_n/E_m$  on nanofiller volume contents  $\varphi_n$  for nanocomposites EP/CNT based on DED. The vertical dashed line 3 indicates percolation threshold  $\varphi_c$ .

#### 4. Conclusions

Hence, the obtained in the present work results have shown that carbon nanotubes ring-like formations in polymer nanocomposites can be simulated successfully as macromolecular coils. The indicated structures fractal dimension reduction results in interfacial adhesion level enhancement and this effect is expressed especially strongly for CNT leaking (transparent) ring-like formations. This supposes that contacts polymer matrix-nanofiller main part is formed in ring-like formations interior part.

## References

- [1] D.W. Schaefer, R.S. Justice // *Macromolecules* **40** (2007) 8501.
- [2] Yu.G. Yanovsky, G.V. Kozlov, Y.N. Karnet, Z.M. Zhirikova, V.Z. Aloeov // *Nanoscience and Technology: An International Journal* **3** (2012) 99.
- [3] V.P. Budtov, *Physical Chemistry of Polymer Solutions* (Chemistry, Saint Petersburg, 1992). (In Russian).
- [4] G.V. Kozlov, I.V. Dolbin, G.E. Zaikov, *The Fractal Physical Chemistry of Polymer Solutions and Melts* (Apple Academic Press, Toronto, New Jersey, 2014).
- [5] D. Blond, V. Barron, M. Ruether, K.P. Ryan, V. Nicolosi, W.J. Blau, J.N. Coleman // *Advanced Functional Materials* **16** (2006) 1608.
- [6] B.A. Komarov, E.A. Dzhavadyan, V.I. Irzhak, A.G. Ryabenko, V.A. Lesnichnaya, G.I. Zvereva, A.V. Krestinin // *Polymer Science, Series A* **53(6)** (2011) 502.
- [7] Ya.I. Estrin, E.R. Badamshina, A.A. Grishchuk, G.S. Kulagina, V.A. Lesnichnaya, Yu.A. Ol'khov, A.G. Ryabenko, S.N. Sul'yanov // *Polymer Science, Series A* **54(4)** (2012) 290.
- [8] B. Bridge // *Journal of Materials Science Letters* **8** (1989) 102.
- [9] A.K. Mikitaev, G.V. Kozlov, G.E. Zaikov, *Polymer Nanocomposites: Variety of Structural Forms and Applications* (Nova Science Publishers, Inc., New York, 2008).
- [10] S. Wu // *Journal of Polymer Science Part B: Polymer Physics* **27** (1989) 723.
- [11] G.V. Kozlov, G.E. Zaikov, *Structure of the Polymer Amorphous State* (Brill Academic Publishers, Utrecht, Boston, 2004).
- [12] G.M. Magomedov, G.V. Kozlov, G.E. Zaikov, *Structure and Properties of Cross-Linked Polymers* (A Smithers Group Company, Shawbury, 2011).