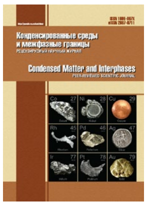

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The influence of the structure of carbon nanotubes in the polymer matrix on interfacial effects in nanocomposites

G. V. Kozlov, I. V. Dolbin✉

Kh.M. Berbekov Kabardino-Balkarian State University,
173 Chernyshevsky str., Nalchik 360004, Russian Federation

Abstract

It is now a well-known fact that interfacial effects play a decisive role in the formation of the properties of polymer composites on the whole and nanocomposites in particular. Therefore, this article investigates the relations between the structure of carbon nanotubes in the polymer matrix of a nanocomposite and the level of interfacial adhesion which is characterised by dimensionless parameter b_α.

It was shown that carbon nanotubes form ring-like structures, which are analogous to macromolecular coils of branched polymer chains and represent a specific type of aggregates for nanofillers of this type. Such ring-like structures can be geometrically described either by a full circle (“closed” structures) or by a part of it (arc) (“open” structures). The amplification of the aggregation process of carbon nanotubes characterised by a decrease in the radius of the ring-like structures is accompanied by a decrease in the fractal dimension of their surface compared to the nominal maximum value. When the ring-like structures reach the smallest possible (about 130 nm) radius, their surface is perceived by the polymer matrix as absolutely smooth, i.e. with a dimension of d=2. This determines the transition of the level of interfacial adhesion from nanoadhesion to perfect adhesion by Kerner. The nanoadhesion effect allows significantly improving the properties of polymer/carbon nanotube nanocomposites. The nanoadhesion effect only takes place if the surface of the ring-like structures of nanotubes is fractal.

Parameter b_α, which characterises the level of interfacial adhesion in polymer nanocomposites, linearly increases with an increase in the fractal dimension of the surface of carbon nanotube aggregates. In this case, the highest attainable nominal dimension of the nanotubes surface, equal to ~ 2.85, is only achieved for “open” ring-like structures. The proposed analytical methods make it possible to predict both interfacial characteristics and the properties of polymer/carbon nanotube nanocomposites.

Keywords: nanocomposite, carbon nanotubes, ring-like structures, aggregation, interfacial adhesion, surface, fractal dimension

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✉ Igor V. Dolbin, e-mail: i_dolbin@mail.ru

1. Introduction

Currently, carbon nanotubes, which have a number of unique properties (in particular, an elastic modulus of up to 1 TPa), are considered one of the most promising nanofillers for polymer nanocomposites [1]. However, a significant number of experimental studies have shown that an increase in the elastic modulus of the matrix polymer resulting from the introduction of the nanofiller is much smaller than expected [2, 3]. As a rule, this has been explained by a low degree of dispersion of carbon nanotubes or, which is just the same, a high degree of aggregation of the nanofiller [4, 5]. It should be noted that generally nanoparticles have a high tendency to aggregate due to very high values of specific surface [6, 7]. However, this effect has not been generalised to a proper theory.

As is known [8, 9], the structure of initially one-dimensional carbon nanotubes in any environment (melt, solution, solid phase) has its own specific features such as the formation of ring-like structures, which structurally are similar to macromolecular coils of branched polymer chains [8]. This ability is common to all one-dimensional (1D-dimensional) fillers [10]. Since it is currently believed that the properties of polymer nanocomposites are determined by the structure of the nanofiller (or more precisely, its aggregates) in the polymer matrix [11, 12], it seems necessary to take into account the formation of these ring-like formations. Thus, the purpose of this work is to quantitatively analyse the change in the characteristics of interfacial effects (fractal dimension of the nanotube surface and the level of interfacial adhesion) as a function of the structure of carbon nanotube aggregates modelled as ring-like formations, using epoxy polymer/multi-walled carbon nanotube (EP/MCNT) nanocomposites as an example [13].

2. Experimental

Multi-walled carbon nanotubes (MCNTs) obtained by deposition of chemical vapours in the Research Institute of Petroleum Industry (Iran) were used as nanofillers. They had an outer diameter of 10–50 nm, a length of 1–3 µm and their mass content in the studied nanocomposites varied in the range of 0.25–10.0 wt% [13].

A LY-5052 low-viscosity epoxy resin and a HY-5052 hardener were used to form the polymer matrix of EP/MCNT nanocomposites. First, MCNTs were dispersed in the hardener by sonication for 30 min. The sonication was carried by the pulse method at 60% amplitude to avoid overheating the material. The epoxy resin and hardener were mixed at a mass ratio of 100:30, after that the mixture was stirred at 900 rpm for 15 min. Then it was poured into metal molds and cured at 333 K for 15 hours [13].

Mechanical tests for uniaxial tension were performed using a Zwick/Roel machine at a temperature of 293 K and a slider speed of 1 mm/min. The used samples were 168 mm long, 13 mm wide, and 5 mm thick. The average value for 5 samples was taken as the test result [13].

3. Results and Discussion

Since the authors [13] did not use any methods of nanofiller processing (for example, functionalisation, *in situ* polymerisation, etc.) when preparing EP/MCNTs, the radius of ring-like MCNT formations R_{CNT} could be determined using the ratio [10, 14]:

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

where r_{CNT} and L_{CNT} are the radius and the length of the carbon nanotube, respectively, φ_n is the volume content of the nanofiller estimated by the following simple formula [6]:

$$\varphi_n = \frac{W_n}{\rho_n}, \tag{2}$$

where W_n and ρ_n are the weight content and density of carbon nanofiller, respectively. For MCNT, the value of ρ_n = 1500 kg/m³ [15].

Further, it is possible to determine the effective (real) fractal dimension of the surface of ring-like MCNT formations d_{sur} using the following equation [16]:

$$\frac{E_n}{E_m} = 1 + 130\varphi_n\left[1 - \left(d - d_{sur}\right)^{1/1,7}\right], \tag{3}$$

where E_n and E_m are the elastic moduli of the nanocomposite and matrix polymer, respectively (the ratio E_n/E_m is commonly referred to as reinforcement degree of the nanocomposite) and d is the dimensionality of the Euclidean space in which the fractal is considered (obviously, in our study, $d = 3$).

Fig. 1 shows the dependence of fractal dimension d_{sur} of the surface of nanotube aggregates (ring-like formations) on the radius of these formations R_{CNT} for EP/MCNT nanocomposites. As can be seen from the graph in Fig. 1, there was a linear decrease in d_{sur} as R_{CNT} decreased, i.e. as MCNT aggregation increased [9]. The value of $d_{sur} = 2.0$ determining the smooth Euclidean surface of MCNT aggregates was achieved at a certain finite value of $R_{CNT} \approx 0.13$ μm. The latter result was expected since the condition $R_{CNT} = 0$ is physically unrealistic and the minimum value of R_{CNT} cannot be less than two outer diameters of the nanotube, i.e. 0.10 μm in the studied case. The dependence $d_{sur}(R_{CNT})$ presented in Fig. 1 can be described analytically by the following empirical equation:

$$d_{sur} = 2 + 1,6\left(R_{CNT} - 0,13\right), \quad (4)$$

where the value of R_{CNT} was given in μm.

It should be noted that the value of d_{sur} for separate straight carbon nanotubes was ~ 2.85. From equation (4), it follows that such maximum value of d_{sur} is achieved for nanotubes with $R_{CNT} > 0.66$ μm. The authors [17] revealed a significant change in the properties of epoxy polymer/single-walled carbon nanotube nanocomposites during the transition of ring-like formations of these nanotubes from "closed" to "open" structures. The latter structure type referred to a nanotube in the shape of an arc, and the former could be approximated by a ring. It is obvious that boundary R^{cr}_{CNT} between these types of structures of ring-like formations can be determined purely geometrically by equation [17]:

$$R^{cr}_{CNT} = \frac{L_{CNT}}{2\pi}. \quad (5)$$

For the maximum length of the MCNT in the studied nanocomposites, $L_{CNT} = 3$ μm, the value of $R^{cr}_{CNT} \approx 0.48$ μm, which is quite close to the above value of $R_{CNT} \approx 0.66$ μm at which the condition of $d_{sur} = 2.85$ is fulfilled. This means that the maximum possible value of $d_{sur} = 2.85$ for carbon nanotubes is only achieved for fully "open" ring-like MCNT formations, i.e. under the condition of $R_{CNT} > R^{cr}_{CNT}$ [17].

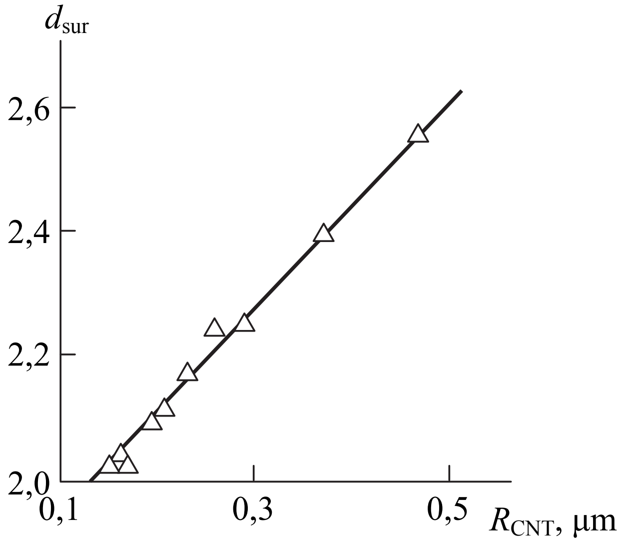

Fig. 1. Dependence of the dimension of the surface of ring-like formations of carbon nanotubes d_{sur} on their radius R_{CNT} for EP/MNCT nanocomposites

The level of interfacial adhesion between the polymer matrix and the nanofiller can be estimated quantitatively using dimensionless parameter b_α, which also allows the qualitative gradation of this level. Thus, when $b_\alpha = 0$, no interfacial adhesion is present; $b_\alpha = 1.0$ corresponds to perfect adhesion by Kerner; and $b_\alpha > 1.0$ defines the nanoadhesion effect [1]. The value of b_α can be determined according to the following percolation relation [6]:

$$\frac{E_n}{E_m} = 1 + 11\left(2,85 b_\alpha \varphi_n\right)^{1,7}. \quad (6)$$

Fig. 2 shows the dependence of the level of interfacial adhesion characterised by parameter b_α on fractal dimension d_{sur} of the surface of the MNCT aggregates for the studied nanocomposites. As can be seen, there is a linear increase in b_α with an increase in d_{sur}, which can be described analytically by the following equation:

$$b_\alpha = 1 + 11,2\left(d_{sur} - 2\right). \quad (7)$$

Equation (7) allows us to draw two important conclusions. First, the nanoadhesion effect ($b_\alpha > 1.0$) is only observed for the aggregates of a nanofiller with a fractal surface, i.e. for $d_{sur} > 2$. At $d_{sur} = 2.0$, i.e. a smooth Euclidean surface of the nanofiller, $b_\alpha = 1.0$, which corresponds to perfect interfacial adhesion by Kerner. Secondly, the

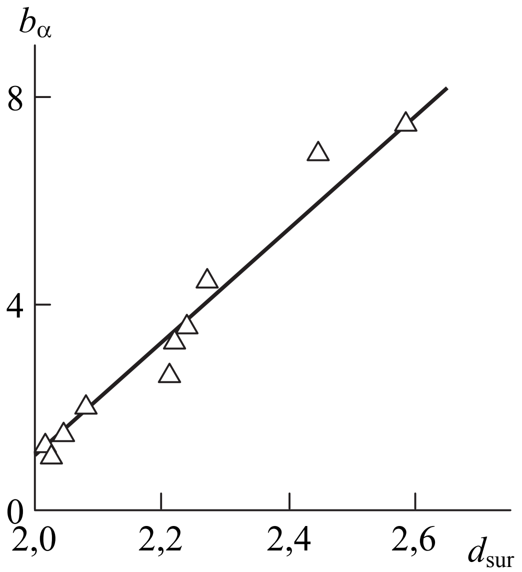

Fig. 2. Dependence of the level of interfacial adhesion characterised by parameter b_α on the dimension of the surface of ring-like formations of carbon nanotubes d_{sur} for EP/MNCT nanocomposites

combination of equations (6) and (7) indicates a very strong influence of the level of interfacial adhesion, or more precisely nanoadhesion, on the properties of nanocomposites. Thus, under the condition of $b_\alpha = 1.0$ (perfect adhesion) and the maximum value of $\varphi_n = 0.0667$ for the studied nanocomposites, the value of $E_n/E_m = 1.65$, which is close to the experimental value of 1.74, and the value of E_n in this case with $E_m = 3.11$ GPa, is 5.2 GPa. If at the specified value of j_n the maximum value of $d_{sur} = 2.85$ is observed, then according to equation (7) $b_a = 10.5$. It follows from equation (6) that in the latter case $E_n/E_m = 36.6$ or $E_n = 113.9$ GPa. Thus, the transition from perfect adhesion to the maximum possible level of nanoadhesion for the studied nanocomposites ($b_\alpha = 10.5$) allows increasing the elastic modulus of nanocomposites by approximately 22 times.

4. Conclusions

Therefore, the results of this work have demonstrated that the dimension of the surface of aggregates (ring-like formations) of carbon nanotubes is controlled by their radius, i.e. the degree of aggregation. Nominal dimension of this surface can only be achieved for "open" ring-like formations. The nanoadhesion effect, which strongly affects the properties of nanocomposites, can only be observed in the case of fractal surfaces, while the smooth Euclidean surface of the nanofiller corresponds to perfect interfacial adhesion by Kerner. The nanoadhesion effect in polymer nanocomposites opens up many opportunities for improving their properties.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Information about the authors

Georgii V. Kozlov, Research Fellow, Kabardino-Balkarian State University named after H. M. Berbekov (Nalchik, Russian Federation).

https://orcid.org/0000-0002-9503-9113

i_dolbin@mail.ru

Igor V. Dolbin, Cand. Sci. (Chem.), Associate Professor at the Department of Organic Chemistry and High-Molecular Compounds, Kabardino-Balkarian State University named after H. M. Berbekov (Nalchik, Russian Federation).

https://orcid.org/0000-0001-9148-2831

i_dolbin@mail.ru

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