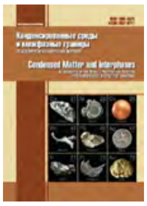

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The structure of carbon nanotubes in a polymer matrix

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Abstract

We carried out an analytical structural analysis of interfacial effects and differences in the reinforcing ability of carbon nanotubes for polydicyclopentadiene/carbon nanotube nanocomposites with elastomeric and glassy matrices. In general, it showed that the reinforcing (strengthening) element of the structure of polymer nanocomposites is a combination of the nanofiller and interfacial regions. In the polymer matrix of the nanocomposite, carbon nanotubes form ring-like structures. Their radius depends heavily on the volume content of the nanofiller. Therefore, the structural reinforcing element of polymer/carbon nanotube nanocomposites can be considered as ring-like formations of carbon nanotubes coated with an interfacial layer. Their structure and properties differ from the characteristics of the bulk polymer matrix. According to this definition, the effective radius of the ring-like formations increases by the thickness of the interfacial layer. In turn, the level of interfacial adhesion between the polymer matrix and the nanofiller is uniquely determined by the radius of the specified carbon nanotube formations. For the considered nanocomposites, the elastomeric matrix has a higher degree of reinforcement compared to the glassy matrix, due to the thicker interfacial layer. It was shown that the ring-like nanotube formations could be successfully modelled as a structural analogue of macromolecular coils of branched polymers. This makes it possible to assess the effective (true) level of anisotropy of this nanofiller in the polymer matrix of the nanocomposite. When the nanofiller content is constant, this level, characterised by the aspect ratio of the nanotubes, uniquely determines the degree of reinforcement of the nanocomposites.

Keywords: Nanocomposite, Carbon nanotubes, Structure, Interfacial layer, Ring-like formations, Reinforcement degree

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1. Introduction

The authors of [1] showed that carbon nanotubes (CNTs), both in solution and in the polymer matrix of the nanocomposite, form ring-like structures that look like macromolecular coils of branched polymers [1, 2]. In [2], the formation of these structures was analytically studied, a number of methods were proposed to calculate their radius, this study also reveals the dependence of the properties of polymer/carbon nanotube (nanofiber) nanocomposites on the structure of CNTs. With regard to this issue, one well-known effect is of interest: the degree of reinforcement of the same nanocomposite, regardless of the type of its filler, is always significantly higher for a nanocomposite with an elastomeric matrix as compared to a glassy matrix [3–5]. The same effect was observed for polymer/carbon nanotube nanocomposites [6-9]. Obviously, the radius of the ring-like formations of CNTs cannot change abruptly during the indicated transition, since the elastomeric matrix (especially the cross-linked one) has sufficiently high parameters of viscosity and strength to prevent any significant change in the structure of the ring-like formations of CNTs, i.e., their radius. Therefore, the aim of this study is to study the aforementioned effect and to develop a structural model to describe it quantitatively.

2. Experimental

The nanofillers were multi-walled carbon nanotubes (MWCNTs) with 15–20 nm outer diameter, 5-10 nm inner diameter, and 0.5–20 μm length. These MWCNTs were functionalized with norbornene to increase the level of interfacial adhesion between the polymer matrix and the nanofiller. Polydicyclopentadiene (PDCPD) was used as the polymer matrix [10].

To obtain nanocomposites, functionalized MWCNTs were dispersed in an aqueous solution of PDCPD and were sonicated to improve the dispersion of the nanofiller. Then this mixture was stirred with a catalyst (dichloro-(3-methyl-2-butenylidine) bis-(tricyclofentyl) ruthenium phosphine) until a homogeneous solution was obtained. Then it was cross-linked for 2 h at 343 K and 1.5 h at 443 K [10].

Mechanical uniaxial tension tests were performed using an Instron 5569 universal testing machine according to ASTM D638 (type V samples) at a temperature of 293 K and a crosshead speed of 1 mm/min. Each result was obtained as an average of the data from four tests [10].

Dynamic mechanical analysis (DMA) was performed using a TA Instruments Q800 DMA. The tension tests of the samples were carried out at a frequency of 1 Hz in the temperature range of 303–583 K at a heating rate of 3 K/min. The samples were 35×5×1 mm in size [10].

3. Results and discussion

The authors of [2] used several methods for calculating the radius of ring-like formations of CNTs, R_{CNT}. One of them, proposed in [11], takes into account only the geometric parameters of carbon nanotubes and their volume content φ_{n}:

$$\left(2R'_{\mathrm{CNT}}\right)^3 = \frac{\pi L_{\mathrm{CNT}} r_{\mathrm{CNT}}^2}{\varphi_{\mathrm{n}}}, \qquad (1)$$

where L_{CNT} and r_{CNT} are the length and radius of carbon nanotubes, respectively.

The value of φ_{n} can be determined using a well-known formula [12]:

$$\varphi_{\mathrm{n}} = \frac{W_{\mathrm{n}}}{\rho_{\mathrm{CNT}}}, \qquad (2)$$

where W_{n} and ρ_{CNT} are the weight content and density of carbon nanotubes, respectively. For PDCPD/MWCNT nanocomposites, the value of W_{n} ranged from 0.05 to 0.40 wt.%.

For carbon nanotubes, the value of ρ_{CNT} can be calculated as follows [12]:

$$\rho_{\mathrm{CNT}} = 188\left(D_{\mathrm{CNT}} - d_{\mathrm{CNT}}\right)^{1/3}, \text{ kg/m}^3, \qquad (3)$$

where D_{CNT} and d_{CNT} are the outer and inner diameters of a nanotube, respectively.

Another method for calculating R_{CNT} (R''_{CNT}) takes into account the actual conditions for the formation of a CNT structure in the polymer matrix of the nanocomposite (for example, sonication [13], functionalisation [14, 15], etc.) and uses the following empirical formula [2]:

$$b_\alpha = 57\left[\left(R''_{\mathrm{CNT}}\right)^2 - 0.022\right], \qquad (4)$$

where b_α is a dimensionless parameter characterising the level of interfacial adhesion in the polymer nanocomposites, and the value of R''_{CNT} is given in μm.

The value of b_α can be determined according to the following percolation relation [12]:

$$\frac{E_n}{E_m} = 1 + 11\left(cb_\alpha\varphi_n\right)^{1,7}, \quad (5)$$

where E_n and E_m are the elastic moduli of the nanocomposite and the original matrix polymer, respectively (the E_n/E_m ratio is usually called the reinforcement degree of a nanocomposite), and c is a constant coefficient, which is ~ 2.86 for CNTs [12].

Fig. 1 shows a comparison of the dependences R'_{CNT} and R''_{CNT} on the weight content of nanofiller W_n for PDCPD/MWCNT nanocomposites with a glassy and elastomeric matrix. We can see that the values of R'_{CNT} and R''_{CNT} are similar in the absolute value for the first of the specified series of nanocomposites (their average discrepancy is less than 9 %). However, in the case of an elastomeric matrix, the value of R''_{CNT} is double the value of R'_{CNT}. As noted above, the two-fold "swelling" of the ring-like formations of CNTs in the cross-linked elastomer matrix is unlikely. Therefore, the physical basis of the observed effect should be considered.

So far, two facts have been well established. First, it was shown experimentally [10] and theoretically [16] that the elastic modulus of interfacial regions in polymer nanocomposites significantly exceeds the corresponding parameter for a bulk polymer matrix. It is close in absolute value to the elastic modulus of nanofiller aggregates. Second, in polymer/carbon nanotube nanocomposites with low nanofiller content, very extended interfacial regions are formed. Their thickness l_{if} can exceed the radius of the nanotube by an order of magnitude or more [10]. Thus, for the considered nanocomposites with an elastomeric matrix with an average radius of MWCNTs r_{CNT} = 8.75 nm, l_{if} ranges from 125 to 226 nm [10], i.e., exceeds the value of r_{CNT} 14.3–25.8 times. From the above observations, it follows that the reinforcing element of polymer/carbon nanotube nanocomposites is ring-like CNT formations surrounded by an interfacial layer. Then the effective radius of such reinforcing element R'''_{CNT} can be described as follows:

$$R'''_{CNT} = R'_{CNT} + l_{if}. \quad (5)$$

The values of l_{if} for PDCPD/MWCNT nanocomposites with an elastomeric matrix are

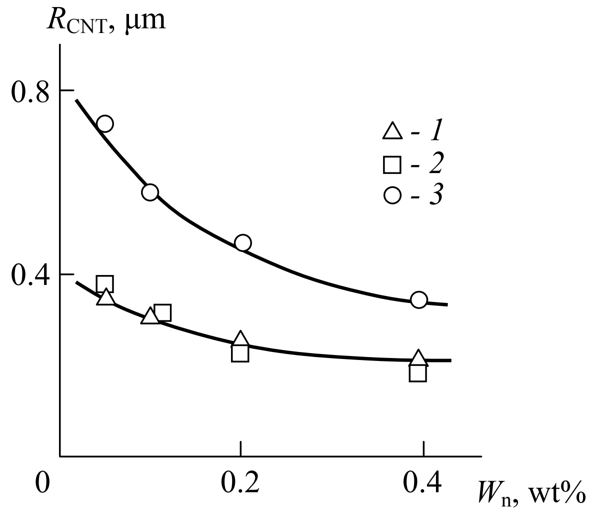

Fig. 1. Dependences of the radius of ring-like formations of MWCNTs R_{CNT} on the weight content of nanofiller W_n for PDCPD/MWCNT nanocomposites with a glassy (*1*, *2*) and elastomeric (*3*) matrix. R_{CNT} was calculated using equations (4) (for *1*, *3*) and (1) (for *2*)

provided in [10]. For the same nanocomposites with a glassy matrix, the l_{if} values were determined as described below. First, the relative fraction of interfacial regions φ_{if} was estimated using the following relation [12]:

$$\frac{E_n}{E_m} = 1 + 11\left(\varphi_n + \varphi_{if}\right)^{1.7}. \quad (6)$$

Then we calculated the value of l_{if}, using the following equation [16]:

$$\varphi_{if} = \left(\frac{l_{if}^2 + 2r_{CNT}l_{if}}{r_{CN^{\prime\prime}}^2}\right)\varphi_n. \quad (7)$$

Fig. 2 shows a comparison of the values of the radii of ring-like formations R''_{CNT} and R'''_{CNT}, calculated according to equations (4) and (5), respectively, for PDCPD/MWCNT nanocomposites with elastomeric and glassy matrices. We can see that the R_{CNT} values calculated by these two methods are in good agreement. This correspondence confirms the above assumption about the nature of the reinforcing element in polymer/carbon nanotube nanocomposites. It should be noted that in the case of PDCPD/MWCNT nanocomposites with a glassy matrix, the use of the radius of ring-like formations R'''_{CNT} instead of R'_{CNT} (Fig. 1) gives even a slightly better agreement of this parameter. The average discrepancy between R''_{CNT} and R'''_{CNT} is less than 7 %.

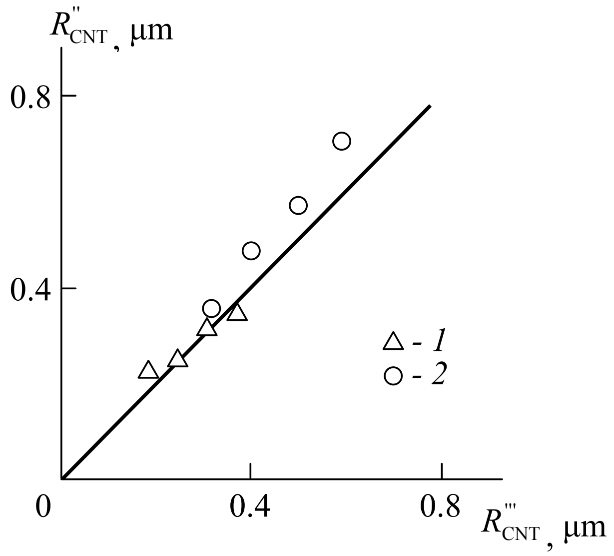

Fig. 2. Comparison of the radii of the ring-like formations of MWCNTs R''_{CNT} and R'''_{CNT}, calculated using equations (4) and (5), respectively, for PDCPD/MWCNT nanocomposites. A straight line means a ratio of 1:1

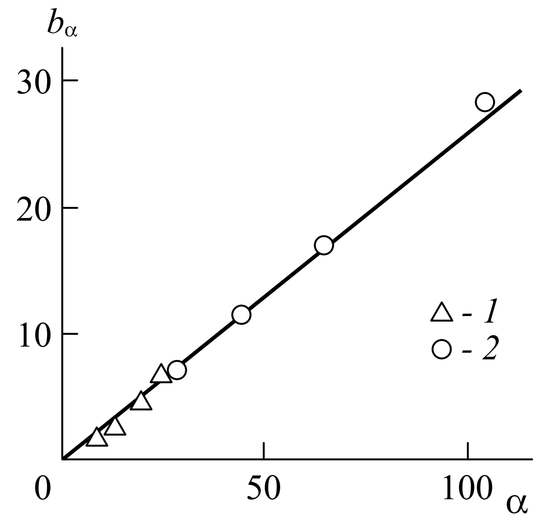

Fig. 3. Dependence of the parameter b_α, characterising the level of interfacial adhesion, on the MWCNTs' true aspect ratio α for PDCPD/MWCNT nanocomposites

It is known [17] that carbon nanotubes are considered the most promising nanofiller for polymer nanocomposites due to two factors: a high longitudinal elastic modulus of the nanofiller, which can reach 1000–2000 GPa, and a high nominal degree of anisotropy. However, in practice, these expectations are usually not met. The reason for this is well-known: generally, nanocomposites are reinforced not by nanoparticles, but by their aggregates. In the case of carbon nanotubes, the aggregates are their ring-like formations [1, 2]. The true level of anisotropy of CNTs in such aggregates can be determined by modelling the ring-like formations of CNTs as macromolecular coils of branched polymers [1, 18]. In this case, the persistent length of a ring-like formation L_p is determined using the following equation [19]:

$$\left(R'''_{CNT}\right)^2 = \frac{L_{CNT}L_p}{6}, \qquad (8)$$

and the true aspect ratio is calculated as the ratio [20]:

$$\alpha = \frac{L_p}{D_{CNT}}. \qquad (9)$$

It is known [12] that the level of interfacial adhesion, characterised by the parameter b_α, largely determines the properties of nanocomposites. Fig. 3 shows the dependence of the parameter b_α on the actual degree of anisotropy of carbon nanotubes, characterised by the aspect ratio α. As we can see, a linear correlation was obtained between these parameters, which can be described analytically by the following empirical equation:

$$b_\alpha = 0.257\alpha. \qquad (10)$$

If we substitute formula (10) into relation (5), we obtain the following equation, which can be used to determine the degree of reinforcement of polymer/carbon nanotube nanocomposites:

$$\frac{E_n}{E_m} = 1 + 11\left(0.72\alpha\varphi_n\right)^{1,7}. \qquad (11)$$

Fig. 4 shows a comparison of the experimentally obtained and equation-based (11) dependences of the reinforcement degree E_n/E_m on the volume content of the nanofiller φ_n for PDCPD/MWCNT nanocomposites with glassy and elastomeric matrices. As can be seen, both cases show a good agreement between theory and experiment (their average discrepancy is ~ 2 %, which corresponds to the experimental error for this parameter [10]). Note that the difference in the E_n/E_m values at the same values of φ_n is determined by only one parameter, the true aspect ratio of MWCNTs α. In turn, according to equations (5), (8), and (9), the difference in values of α for nanocomposites with

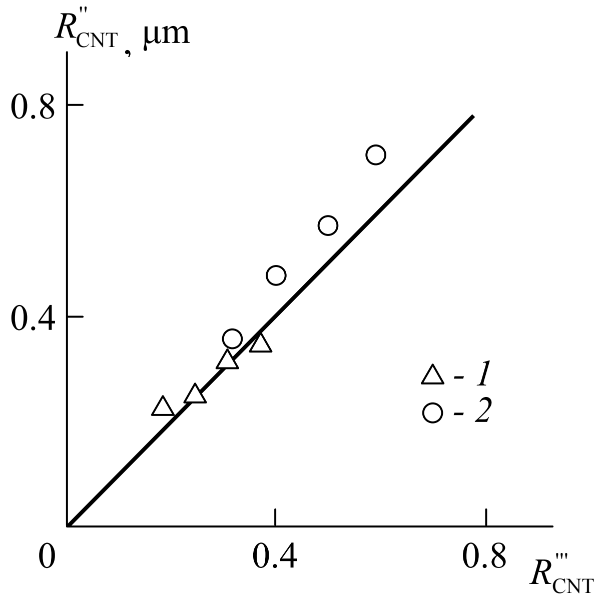

Fig. 4. Comparison of the dependences of the reinforcement degree E_n/E_m on the nanofiller volume content φ_n for PDCPD/MWCNT nanocomposites with elastomeric (*1*, *3*) and glassy (*2, 4*) matrices, calculated according to equation (11) (*1*, *2*) and obtained experimentally (*3*, *4*)

elastomeric and glassy matrices is determined only by the thickness of the interfacial layer l_{if}.

4. Conclusions

Thus, the results of this study showed that the reinforcing element in polymer/carbon nanotube nanocomposites is a ring-like formation (aggregate) of carbon nanotubes surrounded by an interfacial layer. This predetermines the fact that the effective radius of the specified formation increases by the thickness of the interfacial layer. Modelling the ring-like formation of nanotubes as a macromolecular coil of a branched polymer showed that the actual level of anisotropy of carbon nanotubes is determined by the effective radius of this structural reinforcing element of the nanocomposite. This level is characterised by the true aspect ratio of the nanotubes. When the volume content of the nanofiller is constant, it is the only factor that determines the degree of reinforcement of the nanocomposite.

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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