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The influence of transverse $\pi-\pi$-bridging on formation properties of high-modulus fibers of carbon nanotubes

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The theoretical model, treating increasing of elastic modulus of fibers from carbon nanotubes at introduction of transverse $\pi-\pi$-bridging between separate nanotubes in fiber. It has been shown that on elastic modulus of fiber three factors influenced, namely, elastic modulus of starting nanotubes, level of interactions between separate nanotubes in fiber and its aspect ratio, i.e. the ratio of fiber length to its diameter. In transition point of the indicated interactions from repulsion to attraction the elastic modulus of fiber achieves the value of corresponding parameter individual carbon nanotube and in region of attractive interactions exceeds it. The structure of fibers, characterized by their fractal dimension, is basic factor for stiffness of fibers of carbon nanotubes.

Keywords: fiber, carbon nanotubes, $\pi-\pi$-bridging, nanotubes interactions, structure, elastic modulus, fractal dimension.

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1. Introduction

Carbon nanotubes (CNT) in virtue of their outstanding mechanical, thermal and electrical properties are one of the most promising nanofillers to create high-modulus and high strength polymer nanocomposites for use in innovative industries [1]. For this purpose, fibers of a large number of unidirectionally aligned CNTs [2] are widely used. However, CNT fibers obtained in this way demonstrated much lower mechanical characteristics compared to individual CNTs, which is due to weak interactions between the CNTs in the fiber and the heterogeneity of stress [3,4]. Therefore, quite a few technological methods have been developed to enhance these interactions [5]. For example, authors [6] used the reaction of infiltrated 1.5-hexadiene under ultraviolet light irradiation for this purpose. In paper [7], hydrogen bonds between individual CNTs in the fiber were introduced by infiltration of polyvinyl alcohol with a relatively high content of it (up to 19 mass%). This list of various methods of enhancing interactions between individual CNTs in their fiber can be continued [8,9]. However, all these methods, although they improve the mechanical properties of the CNT fibers, but require sufficiently stringent conditions for their production, such as high temperatures. This deficiency may be eliminated by the method proposed by authors [5], which uses the formation of transverse $\pi-\pi$-bridging between individual CNTs in their fiber using the reaction of ester N-hydrosuccinimide 1-pyrenebutyric acid (PBA) and 1-amino-pyrene (AP) at room temperature. Application of this method makes it possible to increase both the elastic modulus and the strength of CNT fibers [5].

Despite obvious technological achievements in development of high-modulus CNT fibers and polymer nanocomposites based on them, the theoretical basis in these papers is clearly underrepresented. So, at present, there is no quantitative model of interactions between individual nanotubes in a fiber, evaluation of the ultimate achievable values of mechanical characteristics of such fibers, their structural analysis, etc. Therefore, the aim of the present paper is theoretical analysis of CNT fibers mechanical parameters improvement at introduction of transverse $\pi-\pi-$bridging between individual nanotubes in a fiber by infiltration of PBA-AP mixture in them and prediction of potential realization of limiting values of elastic modulus there in (comparable with this parameter for individual CNTs). As experimental data to confirm the correctness of the proposed theoretical model, results of paper [5] were used for fibers of aligned CNTs obtained by chemical vapor deposition (CVD) of acetylene gas with their subsequent drawing and impregnation with dimethylformamide, PBA and AP with intermediate drying between the stages of impregnation (infiltration). Elastic modulus E_{fl} of the specified CNT fibers was determined using a Shimadzu AGS-X Tester with uniaxial tension mode at 293 K and a creep speed of 0.4 mm/min. Diameter of the investigated fibers was determined by scanning electron microscopy [5].

2. Results and discussion

First of all, it should be noted that the effect of processing (drawing and infiltration) of CNT fibers in paper [5] was assessed by value of the achieved final characteristics of these fibers (elastic modulus, viscosity, electrical conductiv-

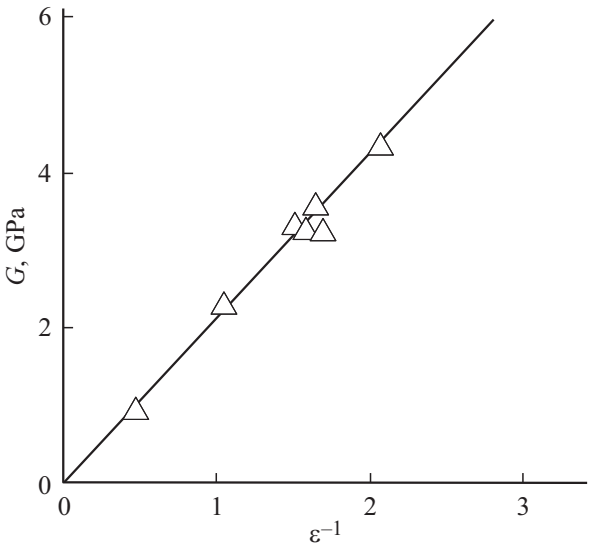

Figure 1. Dependence of shear modulus of CNT fibers G on the interaction parameter ε for CNT/PBA fibers-AP. Dots correspond to the experimental data. Straight line shows linear correlation of parameters G and ε^{-1}.

ity, strength). This method is purely practical and provides no opportunity to estimate the factors influencing these characteristics and their ultimate achievable values. It is obvious that for the theoretical analysis of the obtained final results, it is necessary to use quantitative values of the factors determining them. This is especially true for the level of nanotube interactions in a fiber, as noted above. The following equation [1] can be used for this purpose:

$$\frac{1}{E_{fl}} = \frac{1}{E_{\text{CNT}}} + \frac{10}{3G}\left(\frac{D_{fl}}{L_{fl}}\right)^2 \qquad (1)$$

where E_{fl} and E_{CNT} — elastic moduli of fiber and individual nanotube, respectively, G — shear modulus, D_{fl} and L_{fl} — diameter and length of fiber, respectively.

Shear modulus G takes into account displacement (shear) of CNTs in a fiber relative to each other and can therefore serve as an indicator of the level of interactions between these CNTs — the greater the value G, the higher the level of interactions.

The structure of a CNT fiber can be characterized by its fractal dimension D_f, which is defined using the following equation [10]:

$$E_{fl} = 17D_f^2 E_m, \qquad (2)$$

where E_m — elastic modulus of the matrix (in the case in question — infiltrated) polymer, which is ~ 3.5 GPa [5] for PBA.

Estimates according to equation (2) demonstrated that for CNT fiber without treatment, $D_f = 0.64$; for dimethylformamide-treated fiber, $D_f = 1.04$ and for CNT fiber with infiltrated mixture of PBA-AP at different concentration of this mixture, D_f varies between 1.20–1.35. Knowing the fiber structure characterized by dimension D_f allows using another way to estimate the interactions between CNTs in a fiber using the parameter ε, which is defined as follows [11]:

$$\varepsilon = \frac{2 - D_f}{D_f}. \qquad (3)$$

Value $\varepsilon = 0$ achieved at $D_f = 2.0$ indicates no interactions between CNTs in a fiber, $\varepsilon > 0$, i.e., at $D_f < 2$, defines repulsion interactions between CNTs and $\varepsilon < 0$ at $D_f > 2$ gives a criterion for attraction interactions between individual CNTs in a fiber. Note that for the considered fibers D_f is always lower than 2 and it means that for them only repulsion interactions between CNTs are implemented.

Fig. 1 shows dependence of shear modulus G on inverse value ε for the considered CNT fibers. As one would expect for parameters characterizing the same interaction process between individual CNTs in a fiber, they are related by a correlation, which can be expressed analytically as follows:

$$G = 2\varepsilon^{-1}, \text{ GPa}. \qquad (4)$$

Equation (4) suggests an increase G as the ε decreases, i.e., as the repulsion interactions between the individual CNTs in their fiber weaken. In paper [1] it was stated that the typical value of G is 1 GPa and according to equation (3) this value of G corresponds to the value of $\varepsilon = 2$, i.e., quite strong repulsive interactions between the CNTs in a fiber. In other words, value $G = 1$ GPa corresponds to unmodified fibers of CNTs.

By combining equations (1) and (4), the following relationship between elastic modulus of CNT fibers E_{fl} and interaction parameter of CNTs in their fiber ε is produced:

$$\frac{1}{E_{fl}} = \frac{1}{E_{\text{CNT}}} + 0.0167\varepsilon\alpha^{-2}, \qquad (5)$$

where α — degree of anisotropy of the CNT fiber, equal to the ratio L_{fl}/D_{fl}, the value E_{CNT} for the CNT obtained by CVD can be taken as 600 GPa [12], and value $\alpha \approx 10$ [5].

Equation (5) allows determining three factors that control magnitude of CNT fiber elastic modulus. First, the higher the elastic modulus of starting individual CNTs E_{CNT}, the higher the value of E_{fl}. Second, the weaker the repulsive interactions between the individual nanotubes in a fiber, the higher its elastic modulus E_{fl}. And, third, an increase in the degree of fiber anisotropy leads to the same effect, and influence α on value E_{fl} is quite strong due to quadratic dependence of E_{fl} on α (equations (1) and (5)).

Equation (5) demonstrates that condition $E_{fl} = E_{\text{CNT}}$ is implemented at $\varepsilon = 0$ or $D_f = 2$. In addition, condition $E_{fl} > E_{\text{CNT}}$ can be obtained at the maximum possible value $D_f = 3$ for the three-dimensional volumetric Euclidean space. For CNT fibers in question, transition from positive values ε to negative values, i.e., transition of interactions of individual CNTs in a fiber from repulsion to attraction, leads to an increase of E_{fl} by approximately 30 GPa or approximately 5%.

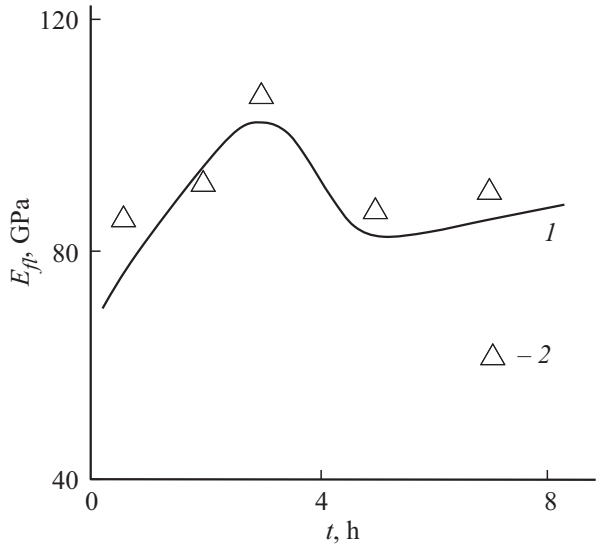

Figure 2. Comparison of CNT fiber elastic modulus E_{fl} dependences on duration t of their soaking in PBA-AP solution theoretically calculated according to equation (5), (1) and experimentally produced (2).

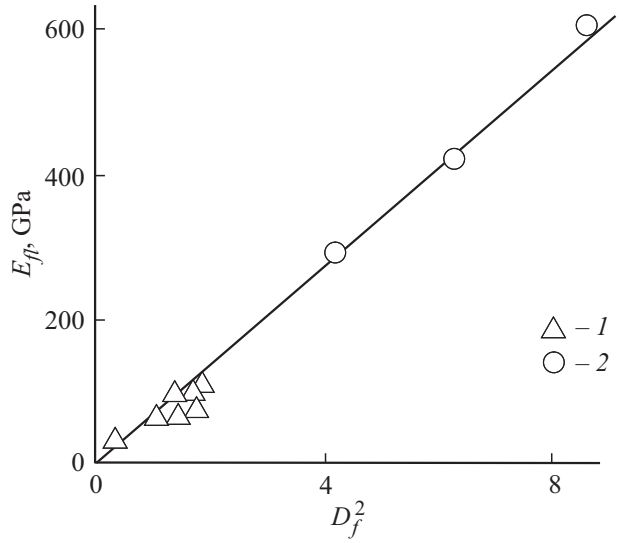

Figure 3. Dependence of elastic modulus E_{fl} of CNT/PBA-AP (1) and CNT/BMI (2) on fractal dimension D_f of the structure of these fibers.

Fig. 2 provides comparison of CNT fiber elastic modulus E_{fl} dependences on duration t of their soaking in PBA solution-AP experimentally produced and theoretically calculated according to equation (5). As follows from this comparison, a good both quantitative (average discrepancy between theory and experiment is 7.8%) and qualitative (the trends of theoretical and experimental dependences $E_{fl}(t)$ are in complete agreement) correspondence between the theoretical model and experiment.

Finally, it is worth recalling an important fact for predicting the properties of CNT fibers. As is known [13], in the case of polymer nanocomposites, their elastic modulus at a fixed nanofiller content is determined only by the structure of nanofiller in the polymer matrix, characterized by the fractal dimension of nanofiller aggregates. In this case, increase of D_f determines the growth of elastic modulus. The same pattern is also true for high-modulus polymer/carbon nanotube nanocomposites, where CNTs are represented as fibers of aligned CNTs [14]. Dependence $E_{fl}(D_f^2)$ (this form of the specified dependence is chosen for the purpose of its linearization) for the considered fibers and nanofiller fibers in carbon nanotubes/bismaleimide nanocomposites (CNT/BMI) [14], which appeared to be linear and common for two specified nanomaterials, is shown in Fig. 3. Note that as dimension D_f approaches its maximum value 3, value of E_{fl} approaches $E_{textCNT}$, i.e., limiting value E_{fl} for carbon nanotubes obtained by CVD ($E_{\mathrm{CNT}} \approx 600$ GPa [12]) is achieved.

3. Conclusion

Thus, this paper proposes a quantitative model that interprets growth of carbon nanotube fibers elastic modulus due to enhanced transverse $\pi-\pi$-bridging between individual nanotubes in the fiber. This model captures three factors affecting the fiber elastic modulus E_{fl}: elastic modulus of starting nanotubes, level of interaction between individual nanotubes in a fiber and fiber aspect ratio, expressed for it by length/diameter ratio. When the interactions of the carbon nanotubes in a fiber transition from repulsion to attraction, elastic modulus of a fiber reaches the corresponding value for the individual nanotube, and in the case of attraction interactions exceeds it. The main and strong influence on elastic modulus of carbon nanotubes fibers is their structure characterized by its fractal dimension.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A.V. Eletskii. Uspekhi fiz. nauk, **177**, 233 (2007). (in Russian).
[2] A. Mikhalchan, J.J. Vilatela. Carbon **150**, 191 (2019).
[3] X. Zhang, K. Jiang, C. Feng, P. Liu, L. Zhang, J. Kong. Adv. Mater. **18**, 1505 (2006).
[4] W. Ma, L. Liu, R. Yang, T. Zhang, L. Song. Adv. Mater. **21**, 603 (2009).
[5] X. Liang, Y. Gao, J. Duan, Z. Liu, S. Fang, R.H. Baughman, L. Liang, Q. Cheng. Carbon **150**, 268 (2019).
[6] S. Boncel, R.M. Sundaram, A.H. Windle, K.K.K. Koziol. ACS Nano **5**, 9339 (2011).
[7] K. Liu, Y.H. Sun, X.Y. Lin, R.F. Zhou, J.P. Wang, S.S. Fang. ACS Nano **4**, 5827 (2010).
[8] Y.O. Im, S.H. Lee, T. Kim, J. Park, J. Lee, K.H. Lee. Appl. Surf. Sci. **392**, 342 (2017).
[9] X. Lu, N. Hiremathi, K. Hong, M.C. Evora, V.H. Ranson, A.K. Naskar. Nanotechnology **28**, 145603 (2017).

[10] G.V. Kozlov, P.G. Rizvanova, I.V. Dolbin, G.M. Magomedov. Izv. vuzov. Fizika **62**, 112 (2019). (in Russian).
[11] L.B. Atlukhanova, G.V. Kozlov. Fizikokhimiya nanokompozitov polimer-uglerodnye nanotrubki. Izd-vo „Sputnik +“, M. (2020). 292 p. (in Russian).
[12] D. Blond, V. Barron, M. Ruether, K.P. Ryan, V. Nicolosi, W.J. Blau, J.N. Coleman. Adv. Funct. Mater. **16**, 1608 (2006).
[13] A.K. Mikitaev, G.V. Kozlov. FTT **57**, 961 (2015). (in Russian).
[14] G.V. Kozlov, I.V. Dolbin, Yu.N. Karnet, A.N. Vlasov. Nanosci. Technology: An Int. J. **11**, 275 (2020).