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THE ULTRASOUND PROCESSING INFLUENCE ON CARBON NANOTUBES STRUCTURE IN POLYMER NANOCOMPOSITES

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Abstract. It has been shown that two types of nanofiller aggregation processes are realized during polymer/carbon nanotubes nanocomposites production: formation of nanotubes ropes and their bending. The first one from the indicated processes is realized at carbon nanotubes contents larger than the percolation threshold. The ultrasound affects only carbon nanotubes aggregation of the second type.

Keywords: nanocomposite, carbon nanotubes, aggregation, ring-like structure, ultrasound.

1. Introduction

At it is known [1], carbon nanotubes (CNT) being in their production process form aggregates, consisting of tangled separate nanotubes. For this effect of weaking the number of methods is used: CNT functionalization [2], processing by ultrasound [3] and so on. Besides, it is well-known [2, 4], that possessing high anisotropy degree and small transversal stiffness CNT form ring-like structures. It is naturally to expect, that the indicated effects will influence CNT structure in polymer nanocomposites and these nanomaterials properties. The present communication purpose is the study of the processing by ultrasound influence of nanocomposites epoxy polymer/carbon nanotubes and CNT ring-like structure formation.

2. Experimental

The data of the paper [3] for nanocomposites epoxy polymer/carbon nanotubes with nanofiller supersmall contents (≤ 0.1 mas %) have been used. The epoxy diane resin ED-20 (ED) and diphenylolpropane diglycidyl ether (DDE) have been used as a matrix polymer. Carbon nanotubes with the diameter of ~ 50 nm and length of ~ 2 μm and contents of 0.0009–0.10 mas % were dispersed by ultrasonic (US) vibrations with the frequency of 22 Mc/s. The details of nanocomposites ED/CNT and DDE/CNT and their testing methods are adduced in the paper [3].

3. Results and Discussion

As it has been shown in the paper [5], CNT ring-like structures with radius R_n formation in the polymer nanocomposite influence nanomaterials properties, particularly, interfacial adhesion level, characterized by the parameter b_α. The intercommunication of b_α and R_n (μm) is given by the following relationship [5]:

$$b_a = 4.8\left(R_n^2 - 0.28\right) \qquad (1)$$

In its turn, the parameter b_α is determined with the help of the percolation relationship [6]:

$$\frac{E_n}{E_m} = 1 + 11\left(cb_a j_n\right) \qquad (2)$$

where E_n and E_m are elasticity modules of nanocomposite and matrix polymer, respectively; E_n/E_m represents a reinforcement degree, c is a proportionality coefficient between interfacial regions relative fraction j_{if} and nanofiller volume content j_n.

For nanocomposites polymer/CNT c = 2.41 [6] and the value j_n is determined according to the well-known formula [7]:

$$j_n = \frac{W_n}{r_n} \qquad (3)$$

where W_n is nanofiller mass contents, r_n (kg/m^3) is its density, determined as follows [6]:

$$r_n = 188\left(D_n\right)^{1/3} \qquad (4)$$

where D_n is CNT diameter, nm.

Since the value R_n determined according to the Eq. (1), was obtained according to the nanocomposites ED/CNT and DDE/CNT samples tests results, then it reflected CNT geometry, formed under US action (R_n^{US}). In its turn, the value R_n of CNT ring-like structures, which does not take into account US-processing, can be estimated with the help of the percolation relationship [8]:

$$j_n = \frac{p L_n r_n^2}{(2R_n)^3} \quad (5)$$

where L_n and r_n are CNT length and radius, respectively.

In Fig. 1 the dependences of R_n^{US} and R_n on j_n for nanocomposites ED/CNT and DDE/CNT are adduced. As it was expected US-processing application results in R_n essential growth and this effect is expressed particularly strongly in the case of CNT very small concentrations, namely, for $j_n \le 10^{-4}$. The estimations according to Eq. (5) showed that US-processing application was equivalent to j_n reduction in 540 times at the smallest j_n values and in 115 times – at the greatest ones.

Since the US-processing efficiency is reduced at CNT contents growth, then in Fig. 2 the dependence of R_n values with US application and without application of US ($\Delta R = R_n^{\text{US}} - R_n$) difference, characterizing the indicated efficiency, on the $j_n^{1/3}$ value is adduced. Such form of the $\Delta R_n(j_n)$ dependence was chosen with its linearization purpose. As it follows from the data of Fig. 2, the value ΔR_n reduces with j_n growth, that can be expressed analytically by the following equation:

$$\Delta R_n = 36 - 600 j_n^{1/3} \quad (6)$$

According to Eq. (6) the value $\Delta R_n = 0$, *i.e.* when US-processing ceases to influence CNT geometry, is equal to ~ $21.6 \cdot 10^5$. Let us consider the physical aspect of this effect. The value of percolation threshold j_c in the case of CNT continuous network formation can be determined according to the equation [8]:

$$j_c = \frac{p}{12}\left(\frac{D_n}{2R_n}\right) \quad (7)$$

The calculation according to Eq. (7) shows, that the value j_c varies within the limits of $(29–94) \cdot 10^5$ at R_n change within the range of 7–28 μm. This value j_c is approximately by an order of magnitude smaller than the similar parameter, determined by the authors [3] with the help of other methods.

It is assumed [3], that CNT aggregation process in ropes (bundles) begins at $\varphi_n > \varphi_c$. The above stated results allow to assume, that US-processing does not influence CNT aggregation process (CNT bundles formation), but influences strongly nanotubes geometry, characterized by ring-like structures radius R_n, at j_n, which is smaller than the percolation threshold j_c.

In Fig. 3 the dependence of elasticity modulus E_n on CNT volume contents j_n for the considered nanocomposites is adduced. As one can see, the systematic E_n change at j_n variation more than by one order of magnitude is not observed. This observation is explained by b_α reduction in 16 times at j_n growth within the range of $(1.2–16) \cdot 10^{-5}$ according to Eq. (2) and corresponding R_n decreases in 4 times according to Eq. (1). In other words, CNT contents increase is compensated by their geometry change, which is expressed by CNT ring-like structures radius R_n reduction.

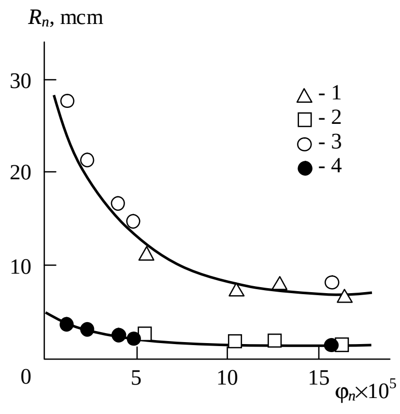

Fig. 1. The dependences of CNT ring-like structures radius R_n using US-processing (1, 3) and without it (2, 4) on nanofiller volume contents j_n for nanocomposites ED/CNT (1, 2) and DDE/CNT (3, 4).

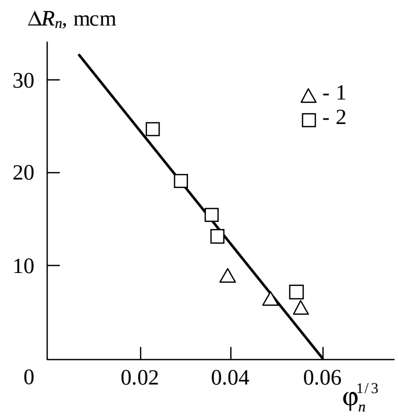

Fig. 2. The dependence of CNT ring-like structures radius difference ΔR_n at US-processing using and without it on $j_n^{1/3}$ parameter for nanocomposites ED/CNT (1) and DDE/CNT (2)

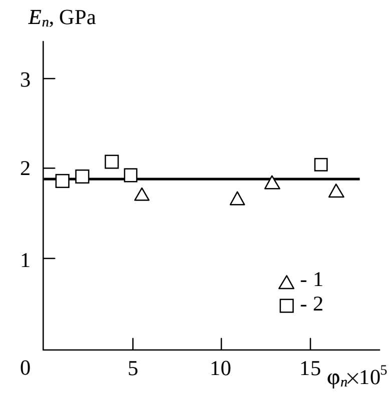

Fig. 3. The dependence of elasticity modulus E_n on nanofiller volume contents j_n for nanocomposites ED/CNT (1) and DDE/CNT (2)

4. Conclusions

Thus, the above adduced results showed that in nanocomposites polymer CNT production process two mechanisms were realized: CNT aggregation (nanotubes bundles formation) and CNT ring-like structures formation. The first one from the indicated processes is realized at CNT contents, which are higher than the percolation threshold. The ultrasound action extends only to CNT geometry and consists of strong (almost by an order of magnitude) increase of CNT ring-like structures radius enhancement. At CNT content lower than the percolation threshold its increase is compensated by the indicated radius reduction that results in practically constant value of nanocomposites elasticity modulus.

References

[1] Eletsky A.: Uspekhi Fizich. Nauk, 2007, **177**, 223.
[2] Sow C.-H., Lim K.-Y., Cheong F.-C. and Saurakhiya N.: Current Res. Nanotechn., 2007, **1**, 125.
[3] Komarov B., Dzhavadyan E., Irzhak V. *et al*.: Vysokomol. Soed. A, 2011, **53**, 897.
[4] Zhirikova Z., Aloev V., Kozlov G. and Zaikov G.: [in:] Lipanov A., Kodolov V., Kubica S. and Zaikov G. (Eds.), The Problems of Nanochemistry for the Creation of New Materials. REKPOL, Torun 2012, 37.
[5] Kozlov G., Yanovsky Ty., Zhirikova Z. *et al*.: Mekhanika Kompoz. Mat. i Konstruktsii, 2012, **18**, 131.
[6] Mikitaev A., Kozlov G. and Zaikov G.: Polymer Nanocomposites: Variety of Structural Forms and Applications. Sci. Publ. Inc., New York 2008.
[7] Sheng N., Boyce M., Parks D. *et al*.: Polymer, 2004, **45**, 487.
[8] Bridge B.: Mater. Sci. Lett., 1989, **8**, 102.

ВПЛИВ УЛЬТРАЗВУКОВОЇ ОБРОБКИ НА СТРУКТУРУ ВУГЛЕЦЕВИХ НАНОТРУБОК В ПОЛІМЕРНИХ НАНОКОМПОЗИТАХ

Анотація. *Показано, що при виробництві нанокомпозитів полімер/вуглецеві нанотрубки реалізовані два типи процесів агрегації нанонаповнювачів, зокрема формування нанотрубних пучків та їх вигин. Перший із зазначених процесів реалізується при вмісті вуглецевих нанотрубок більшому ніж поріг перколяції. Ультразвукова дія поширюється лише на агрегацію вуглецевих нанотрубок другого типу.*

Ключові слова: *нанокомпозит, вуглецеві нанотрубки, агрегація, кільцеподібна структура, ультразвук.*