

The Interconnection of Carbon Nanotubes (Nanofibers) Stiffness and their Structure in Polymer Nanocomposites

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Abstract: The possibility of carbon nanotubes (nanofibers) ring-like structures simulation as macromolecular coils was considered. These anisotropic nanofillers contents increasing results in corresponding reduction of their real anisotropy degree. This effect influences essentially on polymer nanocomposites properties.

Keywords: Nanocomposite, carbon nanotubes (nanofibers), macromolecular coil, anisotropy, reinforcement degree.

1. INTRODUCTION

As it is well-known [1], carbon nanotubes (nanofibers) possess very high longitudinal elasticity modulus (1000-2000 GPa) and low transversal stiffness. These factors together with a large ratio length/diameter (high anisotropy degree), typical for the indicated nanofillers, result in formation by them ring-like structures, resembling outwardly macromolecular coils [2, 3]. This circumstance has already been noted in literature. So, the authors [2] supposed, that carbon nanotubes ring-like structures could be considered as macromolecular coils in semidiluted solutions. The authors [4] used Flory formula for rod-like molecules in case of determination of carbon nanotubes percolation threshold in polymer nanocomposite. Nevertheless, such examples are rare enough and do not have systematic character. The present work purpose is the study of carbon nanotubes (nanofibers) real stiffness and their ring-like formations structure interconnection within the frameworks of the last analogy with macromolecular coils.

2. EXPERIMENTAL

Polypropylene (PP) of industrial production “Kaplen” of mark 01 030 was used as matrix polymer. This PP mark has a melt flow index of 2.3-3.6 g/10 min, average weight molecular weight of $\sim (2-3) \times 10^5$ and polydispersity index of 4.5.

Carbon nanotubes (CNT) of mark “Taunite”, having an external diameter of 20-70 nm, an internal diameter of 5-10 nm and length of 2 μm and more, were used as a nanofiller. In the studied nanocomposites PP/CNT taunite contents was varied within the limits of 0.25-3.0 mass %. Besides, the multiwalled nanofibers (CNF) were used, having a layers number of 20-30, a diameter of 20-30 nm and length of the order of 2 μm . In the nanocomposites PP/CNF CNF contents was varied within the limits of 0.15-3.0 mass %.

Nanocomposites PP/CNT and PP/CNF were prepared by the components mixing in melt on a twin screw extruder Thermo Haake, model Reomex RTW 25/42, production of German Federal Republic. Mixing was performed at temperature 463-503 K and screw speed of 50 rpm during 5 min. Testing samples were prepared by casting under pressure method on a casting machine Test Samples Molding Apparate RR/TS MP of firm Ray-Ran (Taiwan) at temperature 503 K and pressure of 43 MPa.

Uniaxial tension mechanical tests have been performed on the samples in the shape of two-sided spade with sizes according to GOST 112 62-80. The tests have been conducted on a universal testing apparatus Gotech Testing Machine CT-TCS 2000, production of German Federal Republic, at temperature 293 K and strain rate of $\sim 2 \times 10^{-3} \text{ s}^{-1}$.

3. RESULTS AND DISCUSSION

The model of freely-conjugated chain, introduced by Kuhn and Mark [5], has an important significance for the description of polymers conformational properties. In this model the polymer chain is replaced by the equivalent one, consisting of stiff rectilinear segments, spatial orientation of which is mutually independent. The possibility of the application of freely-conjugated chain statistic to real macromolecules is based on the fact, that any real chain at a sufficient length acquires freely-conjugated chain properties. The authors [2] proposed the similar model for carbon nanotubes, which considers them as a branched worm-like cluster with finite persistent length L_p . The supposition, that from the mechanical point of view the indicated cluster behaves itself as a group of disconnected stiff rods with the length of L_p . By its physical significance persistent length L_p corresponds to Kuhn segment length A in the model of freely-conjugated chain.

The value A can be determined with the aid of the following equation [5]:

$$R_g^2 = \frac{LA}{6}, \quad (1)$$

Where R_g is macromolecular coil gyration radius, L is polymer chain length.

The value A (A_{CNT}) for CNT (CNF) can be estimated according to the equation (1) at the condition: $R_g=R_{CNT}$, $L=L_{CNT}$, where R_{CNT} is CNT (CNF) ring-like formations radius, L_{CNT} is carbon nanotube (nanofiber) length. In its turn, the radius R_{CNT} can be determined within the framework of the percolation model [6] with the aid of the following equation:

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

Where φ_n is nanofiller volume content, r_{CNT} is carbon nanotube (nanofiber) radius.

The value φ_n was calculated according to the well-known formula [7]:

$$\varphi_n = \frac{W_n}{\rho_n}, \quad (3)$$

Where W_n is nanofiller mass content, ρ_n is its density, which is estimated for nanoparticles as follows [7]:

$$\rho_n = 188(D_{CNT})^{1/3}, \text{ kg/m}^3, \quad (4)$$

Where D_{CNT} is a carbon nanotube (nanofiber) diameter, which is given in nm.

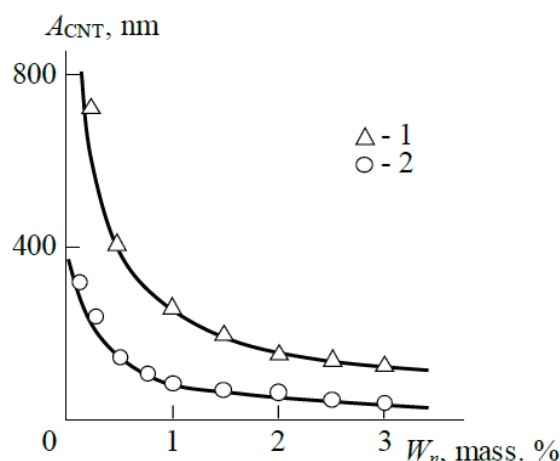


Fig1. The dependences of carbon nanotubes (nanofibers) Kuhn segment length A_{CNT} on nanofiller mass contents W_n for nanocomposites PP/CNT (1) and PP/CNF (2).

In Fig. 1 the dependence of carbon nanotubes (nanofibers) stiffness, characterized by the value A_{CNT} , on nanofiller mass contents W_n for the considered nanocomposites was adduced. As it follows from the adduced plots, the nanofiller stiffness strong reduction (in about 5-8 times) is observed at its contents growth. The data of Fig. 1 correspond well to the values L_p , obtained in work [2], where $L_p=61-500$ nm. CNT (CNF) ring-like formations structure can be characterized most precisely by their fractal dimension D_f^{CNT} , which is the strict structural characteristic, describing the indicated structures elements distribution in space [3]. The value D_f^{CNT} was estimated according to the following methodics [4]. The value R_{CNT} calculation according to the equation (2) showed its reduction at φ_n growth. At the greatest from the used values φ_n , corresponding to $W_n=3.0$ mass %, the indicated dependences have the tendency of asymptotic branch achievement, that supposes the achievement by ring-like CNT (CNF) formations of their R_{CNT} minimum values. By analogy with the macromolecular coils this means the achievement of the densest ring-like structure with the greatest limiting value of its fractal dimension $D_f^{CNT} (D_f^{lim})$, which is determined according to the equation [8]:

$$D_f^{lim} = \frac{4(d+1)}{7}, \quad (5)$$

Where d is dimension of Euclidean space, in which a fractal is considered (it is obvious, that in our case $d=3$). For $d=3$ the value $D_f^{lim}=2.286$.

Further for value D_f^{CNT} estimation the irreversible aggregation model, which describes polymerization processes (macromolecular coil formation), can be used, that gives the following relationship for particles aggregate radius R_{ag} determination [14]:

$$R_{ag} \sim c_0^{-1/(d-D_f)}, \quad (6)$$

Where c_0 is aggregating particles initial concentration, D_f is aggregate fractal dimension.

The coefficient in the relationship (6) can be determined at the following conditions: $R_{ag}=R_{CNT}$, $c_0=\varphi_n$ and $D_f=D_f^{lim}$. The values R_{CNT} and φ_n are accepted at $W_n=3.0$ mass %. As the estimations according to the indicated relationship showed, the value D_f^{CNT} grew at φ_n increasing (and R_{CNT} reduction) from 1.91 up to 2.29 for nanocomposites PP/CNT and from 1.76 up to 2.21 for nanocomposites PP/CNF.

In Fig. 2 the dependences $D_f^{CNT} (A_{CNT})$ for the considered CNT (CNF) are adduced, which showed D_f^{CNT} reduction at A_{CNT} growth, i.e. CNT (CNF) stiffness increasing results in ring-like structures compactness reduction of these nanofillers in polymer nanocomposite. The adduced in Fig. 2 correlations are described analytically by the following empirical equations:

$$D_f^{CNT} = 2.29 - 0.55 \times 10^{-3} A_{CNT} \quad (7)$$

for carbon nanotubes and

$$D_f^{CNT} = 2.29 - 1.75 \times 10^{-3} A_{CNT} \quad (8)$$

for carbon nanofibers, where the value A_{CNT} is given in nm.

The data of Fig. 2 demonstrated full analogy of CNT (CNF) ring-like structures in nanocomposite polymer matrix and macromolecular coils in polymer solutions behavior [10].

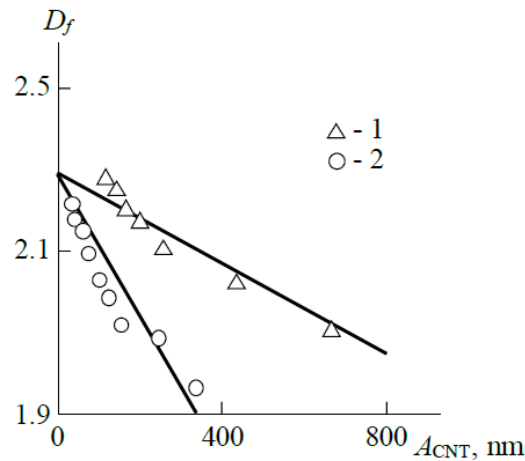


Fig2. The dependences of CNT (CNF) ring-like structures fractal dimension D_f^{CNT} on Kuhn segment length A_{CNT} for nanocomposites PP/CNT (1) and PP/CNF (2).

The parameter A_{CNT} has a large practical significance. As it has been shown in work [2], for nanocomposites polymer/carbon nanotubes the following relationship is true:

$$\frac{E_n}{E_m} = 1 + 2\alpha c_{or} \varphi_n, \quad (9)$$

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 as nanocomposite reinforcement degree), α is the aspect ratio of analog of stiff short fiber with persistent length of L_p , c_{or} is an orientation factor, which is accepted equal to 0.2 for carbon nanotubes [2].

From the equation (9) it follows, that nanocomposite reinforcement degree, besides nanofiller contents φ_n , in essence is defined by the parameter α only, characterizing CNT (CNF) real anisotropy degree. In Fig. 3 the dependence $\alpha(A_{\text{CNT}})$ is adduced, which proves to be linear and shows α increasing at A_{CNT} growth, that is described analytically by the following simple empiric equation:

$$\alpha = 0.212A_{\text{CNT}}, \quad (10)$$

where A_{CNT} is given again in nm.

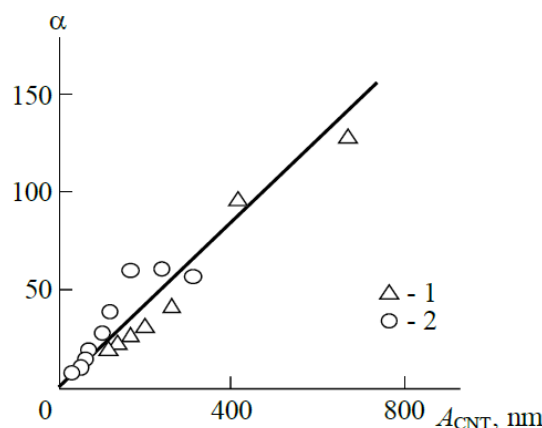


Fig3. The dependence of real nanofiller anisotropy degree α on CNT (CNF) Kuhn segment length A_{CNT} for nanocomposites PP/CNT (1) and PP/CNF (2).

The values $\alpha=9.2-128$, obtained for the considered nanocomposites, correspond well to the adduced ones in work [2], where $\alpha=4.4-75$. The equations (9) and (10) demonstrate, that besides φ_n value, A_{CNT} is the only parameter, controlling nanocomposites PP/CNT and PP/CNF reinforcement degree magnitude.

4. CONCLUSION

Thus, the present work results have been shown that carbon nanotubes (nanofibers) contents increasing in polymer nanocomposite reduces nanofiller stiffness, characterized by Kuhn segment according to the analogy with macromolecular coil. Carbon nanotubes (nanofibers) stiffness reduction results in nanofiller ring-like structures fractal dimension increasing, i.e. in their compactness enhancement. In its turn, Kuhn segment length decreasing means real nanofiller anisotropy degree reduction, that results in polymer nanocomposites reinforcement degree decreasing.

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