Original articles

The interconnection of efficiency and the degree of aggregation of nanofiller in polymer nanocomposites

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Abstract

The rule of mixtures was the first theoretical model, used for a description of the elastic modulus of multicomponent systems, including those of polymer nanocomposites. However, the use of nominal magnitudes of the characteristics of system components in such an approach led to overestimated values of their elastic modulus. Therefore, various modified versions of the rule of mixtures are currently used for this purpose, which significantly complicate its application and do not indicate the physical factors leading to overestimated theoretical results.

In this study, a modified rule of mixtures was proposed, taking into account the decrease in the effective (actual) elastic modulus of the nanofiller in a polymer matrix of the nanocomposite compared to the nominal value determined only by the aggregation of the nanofiller. It is known that the aggregation process is the main negative factor reducing the final properties of nanomaterials, while other factors (for example, the interfacial adhesion level, nanofiller orientation, etc.) depend on the degree of aggregation. The physical sence of the aggregation process is a decrease in the relative proportion of nanofiller-polymer matrix interfacial regions, i.e., the effectiveness of a nanofiller as a reinforcing element of a nanocomposite is determined by its ability to generate high-modulus interfacial regions.

The rule of mixtures modified in this way correctly describes the dependence of the elastic modulus of the nanocomposite on the content of the nanofiller, regardless of the type of the latter (carbon nanotubes, graphene, etc.). Therefore, the nanofiller efficiency indicator can serve as a complex parameter that is characteristic of the nanocomposite quality.

Keywords: The rule of mixtures, Nanocomposite, Carbon nanotubes, Graphene, Aggregation, Elastic modulus, Interfacial regions

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1. Introduction

It is known [1], that the rule of mixtures was the first mathematical apparatus used for the description of the properties of polymer composites. Since the simplest initial version of this rule rarely provides a correct description of the properties of composites, in particular, their elastic modulus, a large number of modified versions of the rule of mixtures, taking into account the orientation and anisotropy of the nanofiller, its efficiency, etc., have been developed [2]. The most commonly used modification of the rule of mixtures for anisotropic fillers is as follows [2]:

$$E_c = \left(\eta_0 E_{ef} - E_m \right) \varphi_n + E_m, \quad (1)$$

where E_c, E_{ef}, and E_m are the elastic modulus of the composite, the effective modulus of the filler, and the elastic modulus of the matrix polymer, respectively, η_0 is the fibre orientation factor, φ_n is the volume content of the filler.

It should be noted that value of E_{ef} refers to the actual elastic modulus of the filler in the polymer matrix of the composite, which decreases compared to the nominal value of this parameter due to the aggregation of the filler and other factors. Obviously, the complex parameter $\eta_0 E_{ef}$ is the actual elastic modulus of the filler in the polymer matrix. Therefore, the purpose of this study was the determination of the effectiveness of a nanofiller in the reinforcing process of polymer nanocomposites based on the example of two types of these nanomaterials, filled with anisotropic 1D (carbon nanotubes) and 2D (graphene oxide) nanofillers.

2. Experimental

In the case of polyamide-6/carbon nanotube nanocomposites, single-walled carbon nanotubes (CNTs) functionalized with carboxylic acid (CNT-COOH) supplied by Carbon Solutions, Inc. (USA) were used as a nanofiller. Nanotubes of this brand have specific end groups for chemical functionalization - they contain 3-4% carboxylic acid groups and have a relative carbon purity of 80-90%. All other necessary chemical reagents were obtained from Aldrich (USA) and used as supplied [3].

The following procedure was used to obtain nanocomposites based on polyamide-6 (PA-6) by *in situ* polymerization. Carbon nanotubes and caprolactam were loaded into a flask, and the mixture was sonicated at 353 K for 2 h to obtain a homogeneous CNTs dispersion. Then the flask was placed in an oil bath heated to 373 K, and 6-aminocaproic acid was added to the suspension. The suspension was heated for 6 h at 523 K with mechanical stirring in a nitrogen atmosphere. Then, the resulting mixture was poured into water, where a very rigid polymeric nanomaterial was deposited. The precipitate was cut into small pieces and washed with hot water at 353 K for an hour to remove the unreacted monomer and low molecular weight oligomers [3].

Fibres of PA-6/CNT nanocomposites were obtained by the extrusion of the material heated to 523 K in a nitrogen atmosphere through a hole with a diameter of 0.40 mm and subsequent cooling to room temperature in air. Mechanical tests for uniaxial tension of the fibres obtained by this method using samples with the diameter of ~ 1 mm and length of ~ 40 mm were performed using an Instron Universal Testing Machine (UTM, model 4455, USA) at a temperature of 293 K and a strain rate of ~ 10^{-3} s^{-1} [3].

Poly(ethylene terephthalate) (PET) manufactured by Toray Saehan with a weight-average molecular weight was used as a matrix polymer for polymer/graphene oxide nanocomposites. $\overline{M}_w = 1.92 \cdot 10^5$. The graphene oxide (GO), prepared according to the modified Hummers method, was used as a nanofiller. The functionalization of GO was performed using S_N2-type reaction with alkyl bromide, which easily reacts with hydroxyl and carboxyl groups on the surface of GO [4].

PET/GO nanocomposites were obtained by mixing the components (PET and GO) in 0-chlorophenyl and the subsequent sonication of the mixture for 1 h. After that, PET/GO nanocomposite films were obtained by pouring these solutions with different nanofiller contents onto a horizontal substrate. Then the solvent was slowly evaporated at room temperature during the day, and finally the films were dried under vacuum at a temperature of 343 K during the day. The content of graphene oxide in the studied nanocomposites varied within 0.5–3.0 wt%. % [4].

The mechanical properties of PET/GO nanocomposites under uniaxial tension were

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measured using an Instron-5543 universal testing machine using a 1 kN load cell at a temperature of 293 K and a slider speed of 3 mm/min [4].

3. Results and discussion

In the case of polymer nanocomposites, the rule of mixtures (equation (1)) can be rewritten as follows:

$$E_n = \left(\eta_{ef} E_{nan} - E_m\right)\varphi_n + E_m, \tag{2}$$

where E_n is the elastic modulus of the nanocomposite, E_{nan} is the nominal modulus of the nanofiller, taken for the considered nanomaterials equal to 750 GPa [3], η_{ef} is the efficiency indicator of the nanofiller when increasing the elastic modulus of the nanocomposite.

It should be noted that the most significant difference between equations (1) and (2) is the use of the nominal, rather than the effective value of the elastic modulus of the nanofiller E_{nan} in the last equation. In turn, this means that the efficiency indicator η_{ef} takes into account all factors leading to a decrease in the nominal value of the elastic modulus of the nanofiller (orientation, anisotropy, aggregation, etc.).

The fact that nanofiller aggregation is the strongest factor affecting the properties of nanocomposites is well known [5]. In this study, for the characterization of this process, we used the aggregation parameter χ defined as follows [6]:

$$\chi = \frac{\varphi_n}{\varphi_n + \varphi_{if}}, \tag{3}$$

where φ_{if} is the relative proportion of interfacial regions estimated using the following percolation relation [7]:

$$\frac{E_n}{E_m} = 1 + 11\left(\varphi_n + \varphi_{if}\right)^{1,7}, \tag{4}$$

where is the ratio En/Em is commonly referred to as reinforcement degree of the nanocomposite.

Attention should be paid to the physical meaning of the parameter χ, which is determined according to equation (3). As is known [8], the interfacial regions are the same reinforcing element of the nanocomposite structure as the nanofiller itself [8]. Thus, the parameter χ is determined by the growth of the actual proportion of the reinforcing element of the nanocomposite

structure ($\varphi_n + \varphi_{if}$) relative to the nominal φ_n. In other words, the degree of aggregation of a nanofiller is determined by its ability to generate interfacial regions.

In turn, the value of φ_n is determined according to the well-known formula [7]:

$$\varphi_n = \frac{W_n}{\rho_n}, \tag{5}$$

where W_n is the weight content of the nanofiller, ρ_n is its density, which for carbon nanotubes was estimated as follows [7]:

$$\rho_n = 188\left(d_{CNT}\right)^{1/3}, \text{kg/m}^3, \tag{6}$$

where d_{CNT} is the outer diameter of the carbon nanotube, specified in nanometers.

For graphene oxide, the value of ρ_n is taken as being equal to 1600 kg/m³ [9]. The dependence of the nanofiller efficiency indicator η_{ef} on the reciprocal value of aggregation parameter χ is shown in Fig. 1. It was linear and demonstrated an increase in the efficiency of the nanofiller as the degree of its aggregation decreased. This dependence can be analytically expressed by the following equation:

$$\eta_{ef} = 2,8 \cdot 10^{-3} \chi^{-1}. \tag{7}$$

It should be noted that the proposed model is adequate for nanofillers with very different forms of aggregation. For carbon nanotubes, which initially form bundles of collinearly arranged individual nanotubes, the emergence of ring-shaped formations in the polymer matrix is realized, structurally similar to macromolecular coils of branched polymer chains [10]. It should be noted that the emergence of such formations is a common effect for 1D nanofillers [11, 12]. Separate plates of graphene oxide in a polymer matrix form "packages" (tactoids) consisting of several collinearly stacked plates, the number of which varies from 1 to 100 [13]. Nevertheless, the various structural forms of nanofiller aggregation described above are correctly interpreted within the formalism of the proposed model (Fig. 1 and equation (7)).

For the studied PA-6/CNT and PET/GO nanocomposites, the calculation according to equations (3) and (4) showed an increase of χ in the interval 0.0143–0.330 at $\varphi_n \le 0.02$ (Fig. 1), which, according to equation (7), leads to the

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variation of η_{ef} = 0.195–0.009. Such a variation η_{ef} suggests for a hypothetical nanocomposite with E_{nan} = 1000 GPa, E_m = 2.5 GPa and φ_n = 0.02 change in magnitude E_n according to equation (2) from 2.68 to 6.40 GPa or a variation in the reinforcement degree E_n/E_m from 1.07 to 2.56, i.e., an increase of about 2.4 times, and this estimate clearly demonstrates the strong effect of nanofiller aggregation on the properties of polymer nanocomposites.

A comparison of the experimentally obtained dependences of the reinforcement degree E_n/E_m on the volume content of the nanofiller φ_n for PA-6/CNT and PET/OG nanocomposites, which were calculated according to the rule of mixtures (equations (2) and (7)), is shown in Fig. 2. As can be seen, in both cases, a good agreement between theory and experiment was obtained. Their average discrepancy was 6 %. This correspondence was obtained only by using the actual value of the elastic modulus of the nanofiller $\eta_{ef}E_{nan}$, instead of its nominal value E_{nan}. The same figure shows the theoretical curve calculated according to the base case, i.e., equation (1), which does not take into account nanofiller aggregation at h_0 = 0.38 [14] for a random orientation of anisotropic nanofillers. This curve provides overestimated values of the reinforcement degree and does not reflect the

actual shape of the dependence $E_n/E_m(\varphi_n)$ for PET/GO nanocomposites. It should be noted that the calculation according to the basic equation is in good agreement with the experimental data with low φ_n (< 0.002), where aggregation is negligible. The obtained correspondence means that the main factor influencing the properties of nanocomposites is the aggregation of the nanofiller, characterized by the parameter χ, and other factors (orientation, anisotropy, etc.) are only derivatives of the main process – aggregation. For example, the authors of [15] showed that the formation of ring-shaped structures of carbon nanotubes in a polymer matrix leads to a change in their anisotropy, namely, a decrease in the radius of these structures determines a decrease in the actual level of anisotropy of this nanofiller. Finally, it should be mentioned, that the change E_n/E_m with φ_n for the studied nanocomposites (Fig. 2), the authors of [3, 4] also explained by the increase in the degree of aggregation of the nanofiller as its content increased, without provision of any quantitative estimates to confirm this assumption.
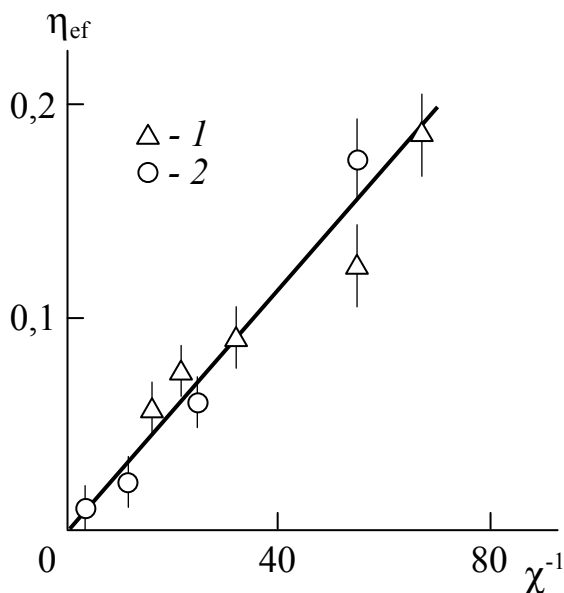

Fig. 1. The dependence of efficiency indicator of nanofiller η_{ef} on the reciprocal value of aggregation parameter с for nanocomposites PA-6/CNT (*1*) and PET/GO (*2*)
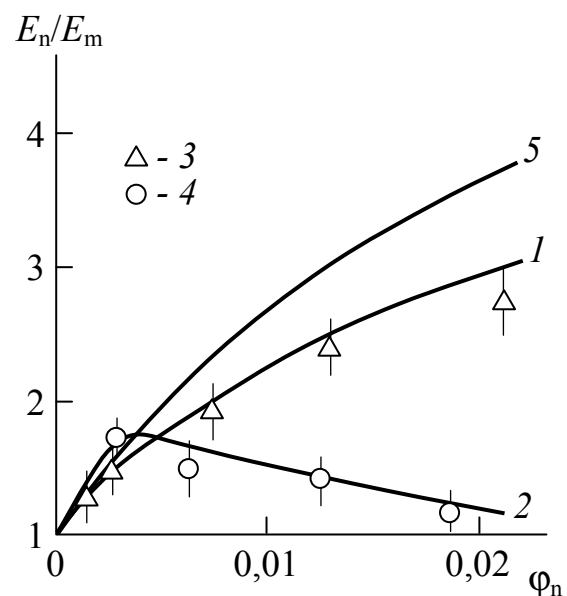

Fig. 2. Comparison of dependences of the reinforcement degree E_n/E_m on the volume content of the nanofiller φ_n for nanocomposites PA-6/CNT (*1, 3*) and PET/GO (*2, 4*) calculated according to the rule of mixtures (the equations (2) and (7)) (*1, 2*) and those experimentally obtained (*3, 4*). *5* – calculation according to the basic equation (1) at η_0 = 0.38

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4. Conclusions

Thus, the fundamental novelty of the obtained results consists of the following postulates. The effectiveness of a nanofiller in improving the properties of polymer nanocomposites is determined only by the degree of its aggregation. Other factors (orientation, anisotropy, etc.) are derivatives of this main process. The physical meaning of the aggregation parameter is the ratio of the nominal and actual content of the reinforcing component in the structure of the nanocomposite, i.e., the efficiency of the nanofiller is determined by its ability to generate high-modulus interfacial regions. The rule of mixtures provides a correct description of the elastic modulus (or reinforcement degree) only when using the actual (effective) elastic modulus of the nanofiller, and not its nominal value. The nanofiller efficiency indicator can serve as a complex characteristic of the quality of the resulting polymer nanocomposites.

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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