NANOCOMPOSITES POLYMER/GRAPHENE STIFFNESS DEPENDENCE ON THE NANOFILLER STRUCTURE: THE FRACTAL MODEL

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Abstract. The dependence of the elastic modulus of the nanofiller for polymer/graphene nanocomposites on the structure of graphene aggregates has been shown. It is established that this structure is defined by the dimension of Euclidean space, in which these aggregates are formed. The indicated structure is most accurately characterized by its fractal dimension.
Keywords: nanocomposite, graphene, structure, aggregation, fractal dimension, Euclidean space, modulus of elasticity

1. Introduction
It is assumed [1] that nanocomposites elastic modulus is defined by the nanofiller structure, forming in the polymer matrix. However, the explanation of this effect is given on the qualitative level exclusively, at that for specific cases of elastomeric matrices and for carbon nanotubes exclusively.

It is known [2] that nanofillers of any initial dimension (0D-, 1D- and 2D-nanofillers) form aggregates in the polymer matrix of the nanocomposite that are fractal objects. Their structure can be strictly physically characterized by the fractal dimension D_f. and it is expected that the real nanofiller's elastic modulus E_{nan} will increase in polymer matrix with the increasing of D_f in virtue of density and compactness growth of nanofiller aggregates.

It should be noted that the value E_{nan} can differ significantly (by orders of the magnitude) from the nominal modulus of nanofiller elasticity. Thus, in the work [3] it was discovered that in case of the rated elastic modulus of carbon nanotubes around 1000 GPa their real elastic modulus in nanocomposite polymer matrix is E_{nan}=71±55 GPa i.e. considerably lower. Application of the real elastic modulus of nanofiller allows us to calculate correctly the elastic modulus of the nanocomposite E_n according to the simple mixtures rule [4]:

$$E_n = E_{nan}\varphi_n + E_m(1-\varphi_n),\qquad(1)$$

where E_m is the elastic modulus of matrix polymer, φ_n is the nanofiller volume content.

Based on the above, the purpose of this work is to clarify the interconnection between the structure of the nanofiller aggregates in the polymer matrix, characterized by the fractal dimension D_f, and the real elastic modulus of nanofiller E_{nan}, i.e. its aggregates elastic modulus and subsequent calculation on this basis of nanocomposite elastic modulus E_n according to the mixtures rule by the example of nanocomposites polymer/graphene [5].

2. Methods

Necessary experimental data for 12 nanocomposites polymer/graphene with glassy amorphous and semicrystalline matrices are used for experimental justification and confirmation of a proposed theoretical model. Elastic modulus values of the matrix polymer E_m and graphene volume content were varied between 1.28 up to 2.45 GPa and 0.0005-0.031 respectively. Poly(methyl methacrylate) (twice), poly(vinyl acetate), poly(caproamide), epoxy polymer, poly(vinylydenfluoride), styreneacrylonyrile, polycarbonate, polyamide-6, polystyrene, polypropylene and polyacrylonytrile were used as matrix polymers. Nanocomposites were produced from solution, by the melt extrusion and polymerization in situ [5].

3. Results and discussion

The typical feature of fractal objects is the dependence of their dimension D_f on space dimension d, where they are formed. The indicated interconnection is described by a number of models, which gives the following relationship [6]:

$$D_f = \frac{8 + 5d^2}{6 + 5d}.$$
(2)

Figure 1 displays the reinforcement degree E_n/E_m dependences on volume contents of nanofiller φ_n according to the data [5] for polymer/graphene nanocomposites with different polymer matrices. As it follows from the figure 1 data, this dependence splits into two similar diagrams $E_n/E_m(\varphi_n)$ – for nanocomposites, produced from solution and by melt extrusion and thus the values E_n/E_m at the same φ_n are twice as much for the first than for second ones. It shows that nanocomposites production process affects their final properties. It is fair to assume that this influence is due to the following factors. There is its straight flow at enough high force in case of melt extrusion, which assumes approximately linear trajectory of nanofiller movement in space with $d \approx 1$. Nanofiller particle motion trajectory in the solution does not have a forced nature and is defined by an insignificant thickness of film sample in comparison with length and width, which assumes $d \approx 2$. Then according to equation (2), we obtain $D_f = 1.18$ for nanocomposites, produced by melt extrusion, and $D_f = 1.75$ – for produced from the solution. It should be noted that in this sense the production of nanocomposites by polymerization in situ and from the solution gives identical results.
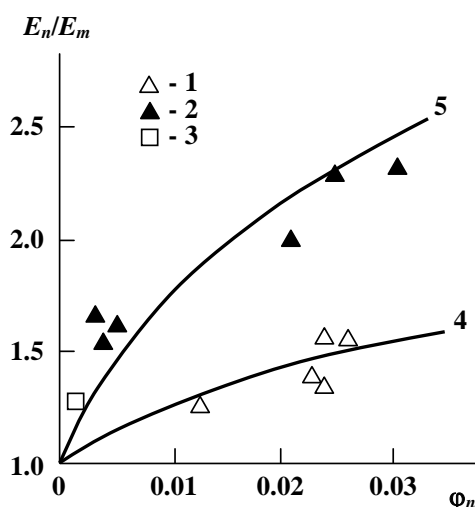

Fig. 1. The dependences of the reinforcement degree E_n/E_m on a volume content of the nanofiller φ_n for nanocomposites polymer/graphene, produced by melt extrusion (1), from the solution (2) and by polymerization in situ (3) at $d=1$, $D_f =1.18$ (4) and $d=2$, $D_f =1.75$ (5)

In terms of the percolation model of polymer nanocomposites reinforcement, the significance of increasing E_n/E_m is defined as follows [7]:

$$\frac{E_n}{E_m} = 1 + 11(\varphi_n)^{1/D_f} . \tag{3}$$

The above values $D_f = 1.18$ and $D_f = 1.75$ for nanocomposites, produced by melt extrusion and solution accordingly, theoretical curves, calculated according to equation (3) describe experimental results well. It should be noted that the dimension $D_f = 1.18$ characterizes the branched chain structure and $D_f = 1.75$ the graphene platelets clusters produced by aggregation mechanism cluster-cluster [8].

Further, we assumed that the value E_{nan} can be determined according to the equation (1) and the dimension D_f – according to the equation (3). Figure 2 presents the dependence of $E_{nan}(D_f)$ for the polymer/graphene nanocomposites that have expected nature, namely E_{nan} increase with the increasing of D_f that is analytically described by the following equation:

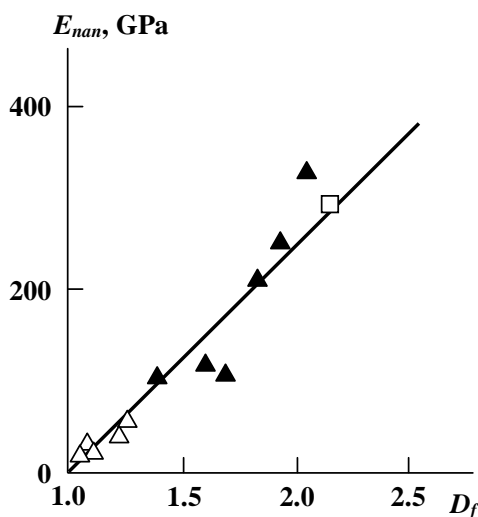$$E_{nan} = 15 + 245(D_f - 1), \text{GPa}. \tag{4}$$

Fig. 2. The dependence of elastic modulus of the nanofiller E_{nan} on fractal dimension of its aggregates D_f for polymer/graphene nanocomposites.
The designations are the same, that in Fig. 1

From equation (4) it follows, that within the range $D_f = 1$-3, i.e. within the most possible range from continuous chains up to Euclidean objects, the value $E_{nan} = 15$-495 GPa, that is much smaller rated value for graphene, which is equal to $\sim$ 1000 GPa [9]. This circumstance explains the overestimated value of elastic modulus of nanocomposites, determined according to the mixtures rule [10].

Further, when the E_{nan} value is determined according to equations (3) and (4) the elastic modulus of the nanocomposites polymer/graphene could be calculated according to the rule of mixtures (equation (1)).

Figure 3 presents a comparison of the calculated in accordance with the manner indicated and the experimentally obtained values of elastic modulus E_n for polymer/graphene nanocomposites under consideration. As it follows from the comparison, the conformity received between the theory and the experiment is good enough (their average discrepancy makes up $\sim$ 10 %). This conformity points out two important aspects: nanocomposites characteristics are defined by the real elastic modulus of a nanofiller i.e by the elastic modulus of its aggregates, but not by the rated value of this parameter, and the role of a nanofiller

structure consists in definition of the real elastic modulus of this component. At the indicated conditions fulfillment, the mixtures rule in its simplest form correctly described the experimental results for polymer nanocomposites.
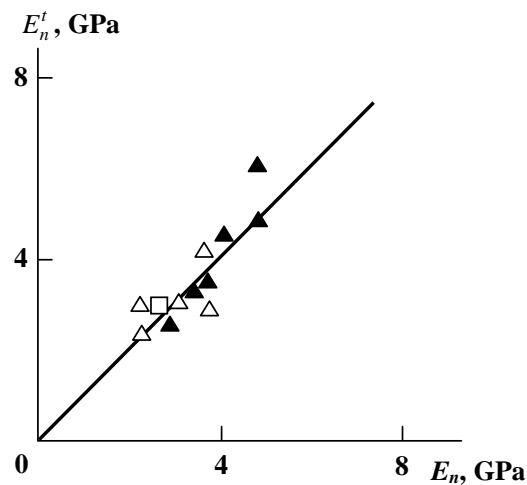

Fig. 3. The comparison of calculation according to the equation (1) E_n^t and experimentally produced E_n values of elastic modulus for polymer/graphene nanocomposites. The designations are the same, that in Fig. 1.

In conclusion, let us consider the causes of the observed experimentally reduction effect of the nanocomposite elasticity modulus below the value of this parameter for matrix polymer, which was observed for different nanofillers, for example, for graphene [11] and nanodiamonds [12]. From equation (1) it follows, that the condition $E_n=E_m$ is realized at $E_{nan}=E_m$. In its turn, for the polymer/graphene nanocomposites under consideration the value E_n is varied within the range of 1.28-2.45 GPa [5] and according to equation (4), we obtain in this case the variation of boundary value of $D_f=0.946-0.949$. Therefore the condition $E_n<E_m$ is realized for $D_f<0.946$, i.e., in that case, when the nanofiller structure in polymer matrix of nanocomposite represents as discrete chains, having ruptures between forming their particles.

4. Conclusions

Thus the results of this work demonstrate that the role of nanofiller structure or more accurately its aggregates in the polymer matrix of nanocomposite consists of the determination of the elastic modulus of mentioned aggregates. And in this case application of the real but not the nominal elastic modulus value of a nanofiller allows describing precisely this parameter for the nanocomposite as a whole framework of the simple mixtures rule. The nanofiller structure in polymer matrix could be correctly and physically strictly described with the aid of its fractal dimension. It is established that even the greatest magnitude of real elasticity modulus of a nanofiller twice as low as its nominal value. At realization of the nanofiller structure as discrete (interrupted) chains, the elastic modulus of nanocomposite reduces below the value of this parameter for matrix polymer.

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