

THE DESCRIPTION OF ELASTIC MODULUS OF NANOCOMPOSITES POLYURETHANE/GRAPHENE WITHIN THE FRAMEWORKS OF MODIFIED BLENDS RULE

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Abstract. For description of elastic modulus of nanocomposites polyurethane/graphene the modified mixtures rule was proposed, which takes into consideration two factors. First, this rule assumes, that in polymer nanocomposites interfacial regions are the same reinforcing element of their structure, as actually nanofiller. Secondly, real, but not nominal, characteristics values of nanocomposite components were used. This allows the quantitative description of elastic modulus of the considered nanocomposites exactly enough. Reaching of percolation threshold of graphene platelets results to the essential enhancement of elastic modulus for both structure components and nanocomposite as a whole.

Keywords: mixtures rule, nanocomposite, graphene, elastic modulus, interfacial regions

1. Introduction

As a rule, the efficiency of nanofiller loading in polymer matrix is estimated with the aid of such parameter as reinforcement degree E_n/E_m , where E_n and E_m are moduli of elasticity of nanocomposite and matrix polymer, respectively [1-4]. From the technological point of view this parameter is an ideal quantitative characteristic of nanofiller efficiency in the process of polymer stiffness enhancement, but at theoretical treatment of reinforcement process certain difficulties arise, which are due to structure and hence properties modification of both nanofiller and polymer matrix in nanofiller loading process [5]. In case of nanofiller the indicated modification of the structure is due to a high degree of aggregation of its initial particles and their anisotropy [1] and for polymer matrix this modification is expressed by the variation of its molecular and structural characteristics, crystallization, interfacial regions formation and so on [5]. The authors [6] proposed the methods for determination of real values of an elastic modulus for nanofiller E_{nf} and interfacial regions E_{if} for nanocomposites poly(vinyl alcohol)/carbon nanotubes and found out, that the value $E_{nf} = 71 \pm 55$ GPa at the nominal magnitude of elastic modulus of carbon nanotubes E_{CNT} of the order of 1000 GPa and $E_{if} = 46 \pm 5.5$ GPa at nominal elastic modulus of matrix poly(vinyl alcohol) $E_m \approx 2$ GPa.

For theoretical description of nanocomposites elastic modulus the mixture rule is often applied [7]:

$$E_n = (\eta_{or} E_{nf} - E_m) \varphi_n + E_m, \quad (1)$$

where η_{or} is a factor of length efficiency, φ_n is volume content of nanofiller.

However, the equation (1) application for determination of value E_n for polymer nanocomposites gives exact results rarely, that is due to the factors described above. Therefore the purpose of the present work is the development of modified analogue of a

mixture rule, taking into consideration real values of E_{nf} and E_{if} on the example of nanocomposites polyurethane/graphene (PU/Gr) [8].

2. Methods

Graphen sheets (flakes) of firm Sigma Aldridge production were dispersed in dimethylformamide (DMF) at the initial concentration 3 mg/ml and processed in a sonic bath Branson MT-1510 for 150 h. This dispersion was split into four portions which were centrifuged at 500 rpm for 22.5 and 45 min and at 750 and 1000 rpm for 45 min. After centrifugation, the supernatants were collected. However, after such procedure graphene dispersions in DMF with low concentrations only (no higher than ~ 1 mg/ml can be obtained). Therefore the authors [8] proposed a new methods for obtaining graphene suspensions, having high concentrations. The indicated supernate of graphene suspensions in DMF was filtered onto a nylon membranes of pore size of 0.45 mcm (Sterlitech). These membranes were immersed in suspension and sonicated in a bath Branson MT-1510 for 60 min. At such procedure graphene tends to come through the membrane, after that it becomes re-dispersed in DMF but at much higher concentrations (up to 20 mg/ml), that allows to obtain composites with high graphene contents [8].

The polyurethane (PU) from firm Hydrosize of mark U2-01 with an average particle size ~ 3 mcm was used as a matrix polymer. The polymer solution was produced by drying of dispersion PU in water at 333 K for 72 h and followed by dissolution of PU in DMF to obtain solution, having concentration of 50 mg/ml [8].

Then PU solution and graphene suspension in DMF were blended to create 10 dispersions with graphene concentrations 0-90 mass %, after that they were sonicated for 4 h to homogenize. Films of composites polyurethane/graphene (PU/Gr) are obtained by drop-casting method of suspensions on smooth surface of flat Teflon trays, after that they were dried in a vacuum oven at 333 K for 12 h and further dried at 333 K for 72 h in a normal oven. The thickness of the prepared films varies within the range of 35-40 microns [8].

Tensile tests were carried out by using an apparatus Zwick Roell with a 100 N load cell at a clip rate of 50 mm/min and temperature 298 K [8].

3. Results and Discussion

As it was noted above, in paper [6] the theoretical relationship, allowing to determine real values of elastic moduli of nanofiller E_{nf} and interfacial regions E_{if} was proposed, which has the look:

$$\frac{dE_n}{d\varphi_n} = (E_{if} - E_m) \frac{d\varphi_{if}}{d\varphi_n} + (\eta_{or} E_{nf} - E_m), \quad (2)$$

where φ_{if} is a relative fraction of interfacial regions and parameter η_{or} is accepted equal to 0.38.

The volume content of nanofiller (graphene) can be determined according to the well-known formula [1]:

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

where W_n is mass content of nanofiller, ρ_n is its density, which is equal to 1600 kg/m³ for graphene [9].

The value φ_{if} can be estimated with the aid of the following percolation relationship [1]:

$$\frac{E_n}{E_m} = 1 + 11(\varphi_n + \varphi_{if})^{1.7}. \quad (4)$$

This relationship takes into consideration, that interfacial regions are the same reinforcing (strengthening) element of nanofiller structure, as actually nanofiller, that follows directly from the comparison of values E_m and E_{if} , cited above [6-13].

Construction of the plots in coordinates $dE_n/d\varphi_n - d\varphi_{if}/d\varphi_n$ in case of their linearity together with using of the equation (2) allows to determine real values of elastic moduli of nanofiller and interfacial regions. In reference to the considered nanocomposites PU/Gr it was found out, that the indicated plot falls apart on two linear parts: for $W_n \leq 50$ mass % and for $W_n > 50$ mass %. These plots are adduced in Fig. 1 and Fig. 2, respectively. Since the relationship (4) allows to determine values φ_{if} only for the first from the indicated parts in virtue of the condition $E_n/E_m \leq 12$, then for the second part the following simple equation has been used:

$$\varphi_{if} = 1 - \varphi_n. \quad (5)$$

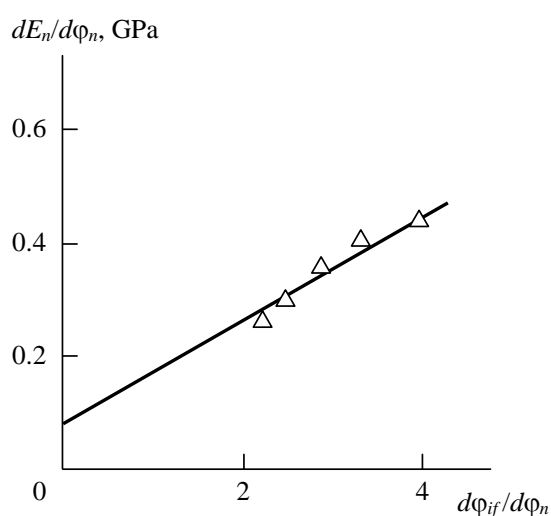


Fig. 1. The dependence of derivative $dE_n/d\varphi_n$ on derivative $d\varphi_{if}/d\varphi_n$, corresponding to the equation (2), for nanocomposites PU/Gr at $W_n \leq 50$ mass % (on the percolation threshold lower)

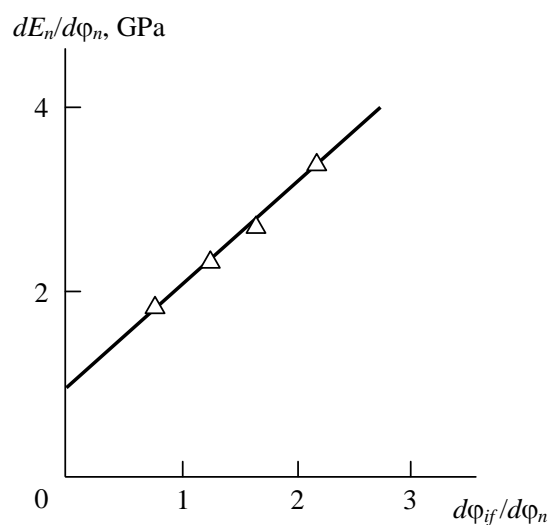


Fig. 2. The dependence of derivative $dE_n/d\varphi_n$ on derivative $d\varphi_{if}/d\varphi_n$, corresponding to the equation (2), for nanocomposites PU/Gr at $W_n > 50$ mass % (on the percolation threshold above)

The equation (5) assumes that at $W_n > 50$ mass % structure of nanocomposites PU/Gr consists of nanofiller and interfacial regions only.

The application of the described above methods showed that values E_{if} and E_{nf} are distinguished for the two indicated parts of the dependence $dE_n/d\varphi_n$ ($d\varphi_{if}/d\varphi_n$): for the first ($W_n \leq 50$ mass %) part $E_{if} = 0.124$ GPa and $E_{nf} = 0.236$ GPa and for the second one ($W_n > 50$ mass %) $E_{if} = 1.91$ GPa and $E_{nf} = 2.66$ GPa, i.e. more than one order above. Nevertheless, the values E_{if} and E_{nf} for both indicated parts essentially (also more than the order above) exceed elastic modulus of matrix polyurethane ($E_m = 10$ MPa [8]), that gives reasons to consider both nanofiller and interfacial regions as reinforcing element of nanocomposites PU/Gr structure. Then the modified mixtures rule can be written as follows:

$$E_n = E_{nf}\varphi_n + E_{if}\varphi_{if} . \quad (6)$$

In Fig. 3 the comparison of the calculated according to the modified mixtures rule, i.e. to the equation (6), and the obtained experimentally dependences of elastic modulus E_n on nanofiller mass contents W_n for nanocomposites PU/Gr is assumed. This comparison has shown both qualitative and quantitative good correspondence of theory and experiment (their average discrepancy makes up $\sim 7\%$), that confirms correctness of the proposed here modified mixtures rule. The equations (1) and (6) comparison demonstrates their main distinction: if the equation (1) operates by nominal values of elastic modulus of nanofiller and matrix polymer, then the equation (6) uses their real values and takes into consideration the formation of interfacial regions in polymer matrix at the introduction of nanofiller in matrix polymer.

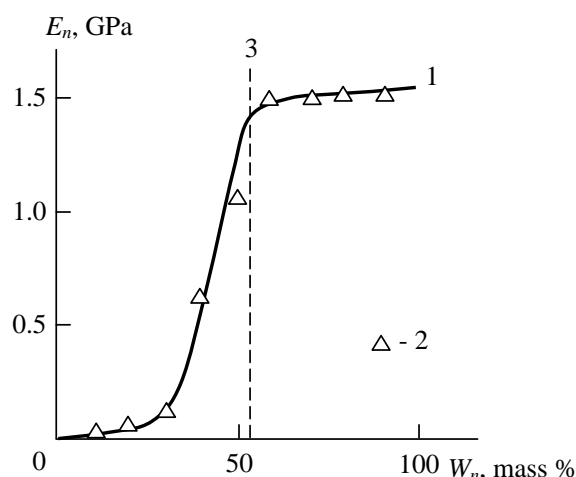


Fig. 3. The comparison of the calculated according to the modified mixture rule (the equation (6)) (1) and experimentally obtained (2) dependences of elastic modulus E_n on mass contents of nanofiller W_n for nanocomposites PU/Gr. The vertical shaded line 3 indicates percolation threshold $\varphi_c = 54.4$ mass %

And in conclusion let us consider the reason of the two linear parts appearance on the plot $dE_n/d\varphi_n$ ($d\varphi_{if}/d\varphi_n$). As it is known [14-16], for spherical particles two percolation thresholds φ_c are observed, corresponding to particles contact and interpenetration. If for such strongly anisotropic particles as carbon nanotubes and graphene the first from the indicated percolation thresholds is very small ($\varphi_c < 0.01$ [17-18]), then by analogy with spherical particles it can be supposed, that the interpenetration of graphene platelets is realized at $\varphi_n = \varphi_c = 0.34$ or $W_n \approx 54$ mass % according to the formula (3). As it was noted above, just this very threshold value W_n corresponds to the decay of the plot $dE_n/d\varphi_n$ ($d\varphi_{if}/d\varphi_n$) on two linear parts. In Fig. 3 this value W_n is indicated by vertical shaded line and it can be seen that it

divides two parts of the dependence $E_n(W_n)$: at $W_n \leq 50$ mass % fast growth E_n is observed and at $W_n > 50$ mass % the indicated dependence reaches plateau at $E_n \approx 1.5$ GPa. Let us note, that sharp enhancement of the parameters E_{if} and E_{nf} , indicated above, at percolation threshold reaching defines anomalously high values E_n of the order of 1.5 GPa. At conservation of the values E_{if} and E_{nf} , obtained up to percolation threshold, that value E_n , corresponding to the dependence $E_n(W_n)$ plateau, would make up 180 MPa only, i.e. about one order below.

4. Conclusions

Hence, in the present work the modified mixtures rule is proposed, which describes correctly elastic modulus of nanocomposites polyurethane/graphene. The mixtures rule modification is contained in using not nominal, but real characteristics of nanocomposites and accounting of interfacial regions properties, which are the same reinforcing (strengthening) element of nanocomposite structure, as actually nanofiller. Reaching percolation threshold of interpenetrating platelets of 2D-nanofiller (graphene) results to essential enhancement of elastic modulus of both nanofiller and interfacial regions and, as consequence, to increasing of elastic modulus of nanocomposite as a whole almost on one order of magnitude.

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References

- [1] Mikitaev AK, Kozlov GV, Zaikov GE. *Polymer Nanocomposites: Variety of Structural Forms and Applications*. New York: Nova Science Publishers Inc: 2008.
- [2] Schaefer DW, Justice RS. How nano are nanocomposites? *Macromolecules*. 2007;40(24): 8501-8517.
- [3] Mikitaev AK, Kozlov GV. Structural model for the reinforcement of polymethyl methacrylate/carbon nanotube nanocomposites at an ultralow nanofiller content. *Tech. Phys*. 2016;61(10): 1541-1545.
- [4] Kozlov GV, Dolbin IV. The fractal model of mechanical stress transfer in nanocomposites polyurethane/carbon nanotubes. *Lett. on Mater*. 2018;8(1): 77-80.
- [5] Kozlov GV. Polymer phase behavior in nanocomposites. In: Ehlers TP, Wilhelm JK (eds.) *Polymer Phase Behavior*. New York: Nova Science Publishers Inc.; 2011. p.123-169.
- [6] Coleman JN, Cadek M, Ryan KP, Fonseca A, Nady JB, Blau WJ, Ferreira MS. Reinforcement of polymers with carbon nanotubes. The role of an ordered polymer interfacial region. Experiment and modeling. *Polymer*. 2006;47(26): 8556-8561.
- [7] Khan U, May P, O'Neill A, Bell AP, Boussac E, Martin A, Semple J, Coleman JN. Polymer reinforcement using liquid-exfoliated boron nitride nanosheets. *Nanoscale*. 2013;5(2): 581-587.
- [8] Khan U, May P, O'Neill A, Coleman JN. Development of stiff, strong, yet tough composites by the addition of solvent exfoliated graphene to polyurethane. *Carbon*. 2010;48(14): 4035-4041.
- [9] Xu Y, Hong W, Bai H, Li C, Shi G. Strong and ductile poly(vinyl alcohol)/graphene oxide composite films with a layered structure. *Carbon*. 2009;45(15): 3538-3543.
- [10] Kim H, Abdala AA, Macosko CW. Graphene/Polymer Nanocomposites. *Macromolecules*. 2010;43(16): 6515-6530.
- [11] Jang BZ, Zhamu A. Processing of nanographene platelets (NGPs) and NGP nanocomposites: a review. *J. Mater. Sci*. 2008;43(15): 5092-5101.
- [12] Zhang Y, Mark JE, Zhu Y, Ruoff RS, Schaefer DW. Mechanical properties of polybutadiene reinforced with octadecylamine modified graphene oxide. *Polymer*. 2014;55(21): 5389-5395.

- [13] Yasmin A, Daniel IM. Mechanical and thermal properties of graphite platelet/epoxy composites. *Polymer*. 2004;45(24): 8211-8219.
- [14] Mikitaev AK, Kozlov GV. Description of the degree of reinforcement of polymer/carbon nanotube nanocomposites in the framework of percolation models. *Physics of the Solid State*. 2015;57(5): 974-977.
- [15] Kozlov GV, Burya AI, Dolbin IV. Fractal model of the heat conductivity of carbon plastics on the basis of phenylone. *J. Engn. Thermophysics*. 2005;13(2): 129-135.
- [16] Kozlov GV, Burya AI, Dolbin IV, Zaikov GE. Fractal Model of the Heat Conductivity for Carbon Fiber-Reinforced Aromatic Polyamide. *J. Appl. Polymer Sci*. 2006;100(5): 3828-3831.
- [17] Foygel M, Morris RD, Anez D, French S, Sobolev VL. Theoretical and computational studies of carbon nanotube composites and suspensions: Electrical and thermal conductivity. *Phys. Rev. B*. 2005;71(10): 104201
- [18] Celzard A, McRae E, Deleuze C, Dufort M, Furdin G, Mareche JF. Critical concentration in percolating systems containing a high-aspect-ratio filler. *Phys. Rev. B*. 1996;53(10): 6209-6214.