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# Prediction of Elastic Modulus for Polymer Composites

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**Abstract**

Elasticity of the composites was analyzed as inhomogeneous systems and their predictive estimation was provided using relevant models by Eshelby, nonlinear patterns of elastic deformation of bodies with rigid inclusions (Einstein, Guth-Smallwood, Eilers-van Dijck, Kerner, Mooney, Halpin-Tsai, Nielsen, Ishai equations). With the Shklovsky-De Gennes model the topological model was obtained in order to determine the fractal dimension of particulate filled polymer composites. The critical concentration of particulate filler in polymer composites was updated (percolation threshold $\upsilon=0, 15$) to reveal a structural transition from isolated clusters to a skeleton lattice which consists of dispersed particles and polymer film matrix. Using the percolation theory a value of critical exponent $t_3$ (universal exponent for state of structural topology of particulate filled polymer system) was found and defined. The universal critical exponent $t_3=1, 58$ was found, it determines a skeleton of fractal percolation cluster from fractal point of view, and it was revealed to have a pivotal effect on increasing the elasticity of composite materials. The prediction mathematical models (polynomial, exponential, etc.) were obtained for dynamic modulus and impact resistance of epoxy, polyether, epoxy-polyurethane composites according to the concentration of different hardeners. The optimum concentrations of matrix components (hardeners, modifiers) which provide high elasticity and impact resistance of the polymer matrices under study were defined. Based on the Kelvin-Voigt model a new structural mechanical model of particulate filled polymer composites was developed. It reflects the strain condition of matrix-mass, matrix-film and percolation lattice which consists of dispersed particles. With the Verhult's method the prediction models were obtained to describe the change in dynamic modulus according to volume content of reinforcing fillers. A two-component modifying agent was developed for epoxy-polyurethane composite materials with higher stress-strain properties. It consists of polyether and polyisocyanate in a ratio of 1 to 1. The formulas of effective filled epoxy, polyether and epoxy-polyurethane composites were specified.

**Keywords:** Elastic modulus, polymer composites, prediction, percolation model.

## BODY TEXT

The progress in mechanical engineering is closely associated with development and wide use of polymer composites. A wide range of possible applications of composites dictates the necessity of improving the current composites and developing new ones with required physical and engineering properties (elastic modulus, impact resistance, corrosion resistance, etc.) [1, 2].

The new materials which emerge as a result of efforts to improve the existing mechanical engineering products provide major opportunities for implementation of advanced design concepts, processes and for development of efficient property prediction methods. Design quality of the materials with specified properties (reliability, durability, etc.) depends on accuracy of the models for prediction of physical engineering properties of composite materials used in different loading

conditions. In this regard, the crucial and long-term task is to make new prediction models based on current theories of cluster formation, percolation, bifurcation, structural phase transition in order to give the most accurate predictions of the properties of new materials and products thereof [3].

There is no doubt that that effective moduli (dynamic modulus, stiffness) are the most important characteristics in the practice of materials science. Indeed, the mathematical representation of these parameters is a basis of strain calculation which ultimately justifies the application of engineering materials in the critical products and structures [4].

There are different approaches and models for prediction of stress-strain behavior of particulate filled composites [4, 5]:

- Eshelby model for analysis of inhomogeneous media used to calculate the strain energy of a composite;
- Guth-Smallwood equation $E_c=E_m(1 + 2,5\upsilon + 14,1\upsilon^2)$ where $E_c$ is the elastic modulus of the composite; $E_m$ is the elastic modulus of the matrix; $\upsilon$ is the volume fraction of the filler;
- Eilers-van Dijck equation

$$E_c = E_m\left\{1+\frac{1{,}25\upsilon}{1-\upsilon/0{,}74}\right\}^2;$$

- Kerner equation $E_c = E_m\dfrac{E_f A_k + B_k}{E_m A_k + B_k}$, where $E_f$ is the elastic modulus of the particulate filler; $A_k = \dfrac{\upsilon}{[(7-5\mu_m)E_m + (8-10\mu_m)E_f]}$; ;

$$B_k = \frac{(1-\upsilon)}{[15(1-\mu_m)]};\quad \mu_m \approx 0{,}5$$

- Mooney equation $E_c = E_m \exp\dfrac{2{,}5\upsilon}{1-\upsilon/0{,}74}$;
- Halpin-Tsai equation $E_C = E_m\dfrac{1+A_k B_k\upsilon}{1-B_k\upsilon}$;
- Nielsen equation $E_C = E_m\dfrac{1+2{,}5B_k\upsilon}{1-B_k\psi\upsilon}$, where $\psi = \dfrac{1+(1-\eta)}{\eta^2}\upsilon$, $\eta=0,74$ is the value of close packing for monodispersed spherical particles;
- Ishai equation $E_c = E_m\left\{\dfrac{\upsilon}{(n/(n-1)-\upsilon^{1/3}}+1\right\}$, where $n = E_f/E_m$.

The purpose of these studies was to create science-based prediction models for elastic modulus of polymer composite materials.

The experimental studies were conducted with epoxy, polyether, epoxy-polyurethane composites. The starting materials were epoxy resin ЭД-20 (ED-20) (standard GOST 10587-84), polyethylene polyamine (PEPA) (specification TU 2413-357-00203447-99), polyether resin 540-M 888, peroxide no1 (solution of methyl ethyl ketone peroxide in dimethyl phthalate), polyether (Сарэл А-04 (Sarel A-04)) and polyisocyanate (Сарэл Б-04 (Sarel B-04)). The fillers of composite materials were diabase (ρ=2900 kg/m$^3$, $S_{sp}$=80÷780 m$^2$/kg), marshallit (ρ=2650 kg/m$^3$, $S_{sp}$=80÷780 m$^2$/kg) where $S_{sp}$ is the specific surface area of the filler.

The elasticity and impact resistance of the composite materials were evaluated using not only the measured values of dynamic modulus $E_d$ and impact resistance $A$ but also existing GOST standards and regulatory documents.

The elasticity of the composite materials was measured with the tested Brüel & Kjær equipment (measuring instrument for dynamic modulus and loss factor, type 3930). The pendulum impact testing machine, type ПСБ-1, 5 (PSB-1, 5) (Russia) was used for impact testing of the polymer composites according to GOST 4647-80. The test data were processed using the methods of mathematical statistics.

The structural and topological features of highly condensed systems were observed from a present day perspective of cluster formation theory, percolation [6-8]. At the macrostructure level the elasticity of the composite materials is determined by stress-strain behavior of the matrix and filler, and at the microstructure level-by the phenomena that occur upon contact between the liquid and solid phases of the material.

Based on the analytical approach to calculation of percolation threshold in filled composites using the similarity theory and classic percolation model by touching spheres in polymer composites the percolation threshold of the composite was updated-it is equal to υ=0, 15 together with film matrix constituent [9-14].

Using the Hausdorff-Besicovitch model the fractal dimension of the composite percolation cluster with the film and volume constituents of the polymer matrix was determined [15-20]:

$$D_\infty = \frac{\ln p}{\ln(1/z)} = \frac{\ln 0{,}15}{\ln(1/2{,}12)} = 2{,}525, \qquad (1)$$

where $p$ is the percolation threshold; z is the self-similar relation.

By expressing subsets of the percolation cluster in increasing order using formula $1/z^n = p^{n/D}$ ($n$ is the order of the subset) the relation in the equality form was obtained for the fourth subset:

$n$=4, $1/z^4 = p^{4/D} = p^{1{,}58}$. (2)

From this relation it follows that the numerical value of index of parameter $p$ of the forth subset corresponds to the value of known critical exponent $t_3=1,5\div1,8$ which is provided by the percolation model for three dimensional systems proposed by B. I. Shklovsky and De Gennes [9, 14].

The relationship between structure and elasticity of the composite materials was revealed, and it was established that the basic mechanism for improving stress-strain properties is defined by the skeleton of fractal percolation cluster [13-14].

From the experiments using correlation and regression analysis the valid prediction models were obtained in the form of dependencies $E_d(k)$, $A(k)$:

-for epoxy matrix:

$$E_d(k) = -2{,}4306k^3 + 80{,}952k^2 - 766{,}47k + 5976{,}2, \qquad (3)$$

$$A(k) = 0{,}0004k^2 + 0{,}0144k + 0{,}0464, \qquad (4)$$

-for polyether matrix:

$$E_d(k) = -41{,}667k^3 + 344{,}64k^2 - 663{,}69k + 1750, \qquad (5)$$

$$A(k) = 0{,}1111e^{0{,}0986k}, \quad (6)$$

-for epoxy-polyurethane matrix:

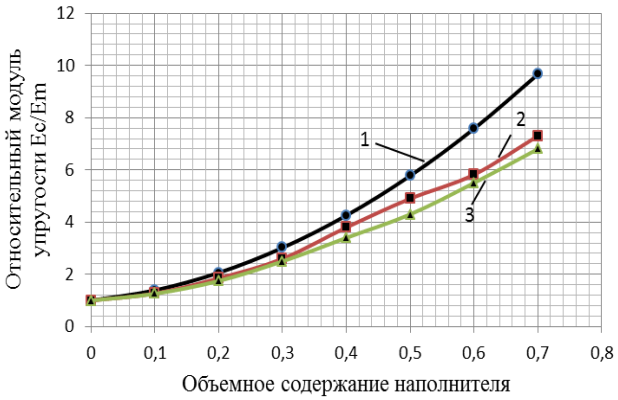
$$E_d(k) = 0{,}0165k^5 - 0{,}102k^4 - 8{,}2304k^3, +110{,}83k^2 - 243{,}74k + 4918 \quad (7)$$

$$A(k) = 1E - 0{,}5k^5 - 0{,}0003k^4 + 0{,}0003k^3, -0{,}0082k^2 + 0{,}0104k + 0{,}1889 \quad (8)$$

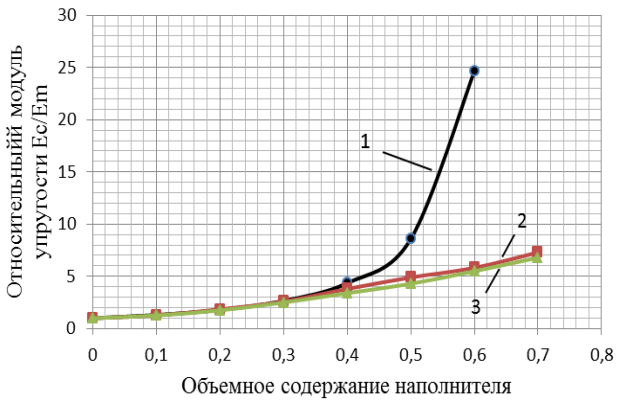
where $k$ is the concentration of hardener, weight fractions.

It was established that the molecule composite epoxy materials were effectively modified with the multicomponent agent made of polyether and polyisocyanate. It was revealed that $E_d$ and $A$ significantly increase when the multicomponent polymer agent is added to produce epoxy-polyurethane composites. It was established that optimum quantity of polyether and polyisocyanate which provides high elasticity and impact resistance of modified polymer matrix is 16 weight fractions of PEPA, 4 weight fractions of polyether Sarel A-04, 4 weight fractions of polyisocyanate Sarel B-04 per 100 weight fractions of epoxy resin ED-20.

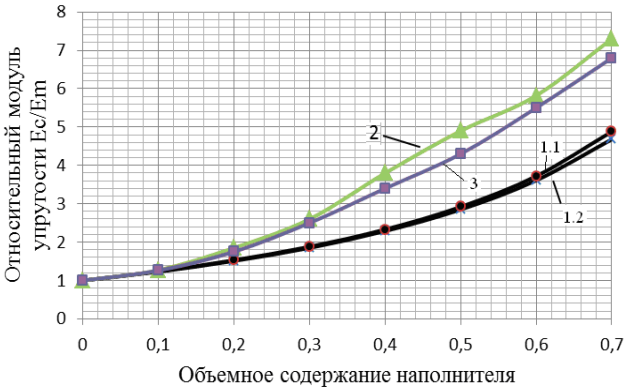
In the course of the study it was established that the elasticity (Figure 1) and impact strength of polyether, epoxy and epoxy-polyurethane materials increase considerably when high-modulus fillers (marshallit, diabase) are added to them.



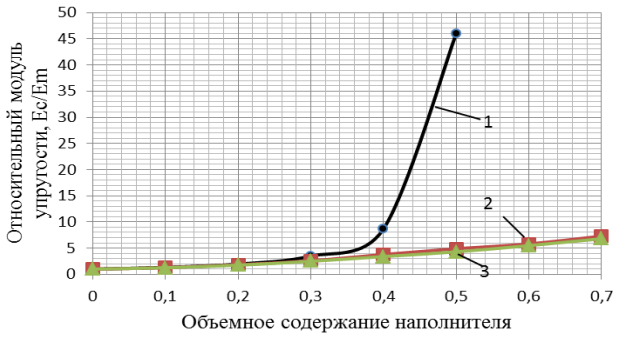

*a) Guth-Smallwood model



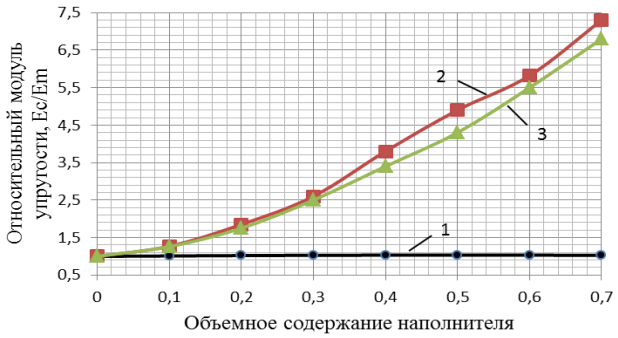

*b) Eilers-van Dijck model



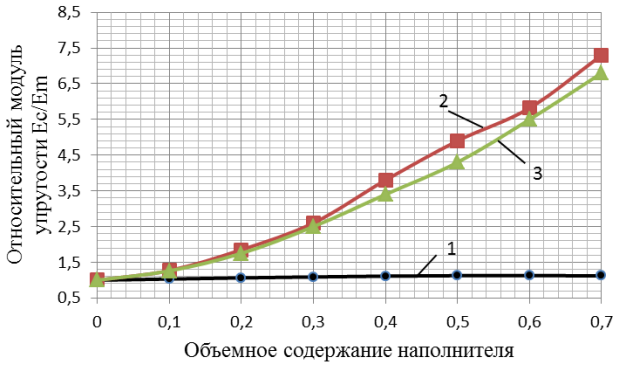

*c) Kerner model



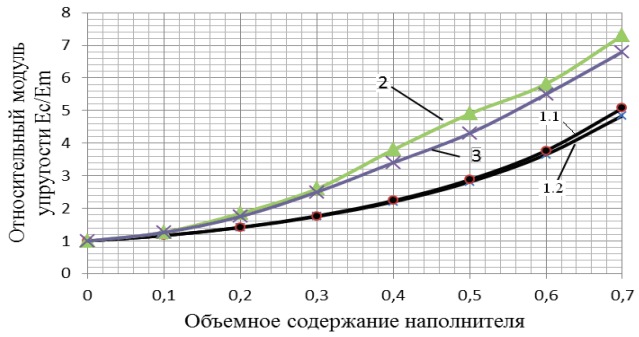

*d) Mooney model



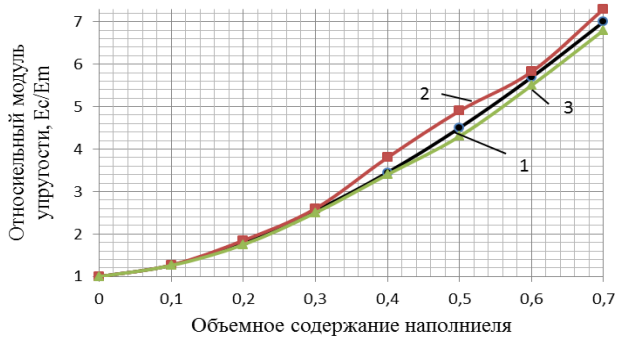

*e) Halpin-Tsai model




*f) Nielsen model




*g) Ishai model




*h) resulting percolation model

**Figure 1:** Behavior $E_c/E_m$ of epoxy-polyurethane composites (Sarel A-04-8 weight fractions, Sarel B-04-8 weight fractions, PEPA-16 weight fractions) versus $\upsilon$ of marshallit, diabase: 1) curve plotted from the reference data of the models* (1.1-for marshallit; 1.2-for diabase); 2) test results for epoxy-polyurethane marshallit-filled polymer; 3) test results for epoxy-polyurethane diabase-filled polymer

The results of the study revealed the optimum concentration of high-modulus fillers which gives higher stress-strain properties to composite materials *(υ=0, 7)*.

It was established that elasticity of filled epoxy-polyurethane composite forms as a result of kinetic transition, and its elasticity factor (dynamic modulus) is described by the Verhults's formula which enables to shape sigmoid curves effectively:

$$E_d = \frac{A}{1+10^{a+bx}} + C, \quad (9)$$

where $E_d$ is the function value; $x$ is the time; $A$ is the distance between upper and lower asymptotes; $C$ is the limiting value from which the function starts to grow; $a$, $b$ are the parameters which define slope, bend, point of inflection for the graph of the function.

Based on (9) the patterns and parameters for different epoxy-polyurethane composites were obtained:

-filled with marshallit

$$E(t) = \frac{39800}{1+10^{4,91-0,36t}} + 3900. \quad (10)$$

-filled with diabase

$$E(t) = \frac{37800}{1+10^{4,49-0,276t}} + 2900. \quad (11)$$

Based on Shklovsky-De Gennes model [9, 14] we obtained a two-dimensional model of the fractal structure for epoxy-polyurethane composite. It implies the formation of a superstructure of the infinite percolation cluster in polymer composite as the distorted spatial lattice which permeates the matrix and is made from chains of particulate filler particles interlinked by matrix interlayers, and formed from the lattice, dead-end branches of skeleton lattice, film matrix constituent-"matrix-film" and volume constituent-"matrix-mass".

The theoretical and experimental analysis established and confirmed that from the fractal point of view the exponent $t_3=1$, 58 defines a large-cell lattice of the fractal percolation cluster [16].

For reinforcing particulate filled polymer epoxy-polyurethane composites with (2) and the scaling relation for elastic modulus $E \propto (\upsilon - \upsilon_c)^{t_3}$ the universal prediction model with the scaling similarity of the structure is used:

$$E_c = E_m\left(1 + a \cdot \upsilon^{t_3}\right), \quad (12)$$

where $a = E_1 / E_m$; $E_1$ is the dynamic modulus of a single chain element of percolation lattice.

With all the empirical values used ($E_c / E_m$ and $\upsilon$) the correlation analysis of equation (12) was made and as a result it revealed that $a \approx 10, 618$, $t \approx 1, 58$. So, equation (12) can be written in the final form:

$$E_c = E_m\left(1 + 10{,}618 \cdot \upsilon^{1,58}\right). \quad (13)$$

As can be seen in Figure 1.h, percolation equation (13) gives the solutions which are nearest to the test data, including the high filler loading region, and that's why it can be effectively used in the predictive estimation of elastic modulus for new polymers under development [16-20].

The model for glass microsphere filled epoxy composites was used to obtain a structural mechanical model of epoxy-polyurethane composite with reinforcing filler [12]. In this model the strain $(\sigma)$ is taken simultaneously by three dimensional matrix with intrinsic viscoelasticity and rigid percolation lattice. Accordingly, the composite behavior under load can be defined using the Kelvin-Voigt model [13] in which, with the strain additivity rule, $\sigma$ is given by $\sigma = \sigma_m + \sigma_c$ where $\sigma_m = \sigma_{mas} + \sigma_{flm}$; where $\sigma_{mas}$ is the strain in matrix-mass; $\sigma_{flm}$ is the strain in matrix-film; $\sigma_c$ is the strain in the percolation lattice consisting of filler particles. In this case we can rewrite the equation for $\sigma$ as:

$$\sigma = \sigma_{mas} + \sigma_{flm} + \sigma_c. \quad (14)$$

In the resulting model an elastic element mostly corresponds to the rigid percolation lattice of composite system which the critical exponent $t_3$ matches with when a viscous element corresponds to polymer matrix.

## CONCLUSION

Elasticity of the composites was analyzed as inhomogeneous systems and their predictive estimation was provided using relevant models by Eshelby, nonlinear patterns of elastic deformation of bodies with rigid inclusions (Einstein, Guth-Smallwood, Eilers-van Dijck, Kerner, Mooney, Halpin-Tsai,

Nielsen, Ishai equations). It was established that these prediction models can be effectively used provided that $\upsilon=0\div0,3$. With the Shklovsky-De Gennes model the topological model was obtained in order to determine the fractal dimension of particulate filled polymer composites which is equal to $d=2,525$. The critical concentration of particulate filler in polymer composites was updated (percolation threshold $\upsilon=0,15$) to reveal a structural transition from isolated clusters to a skeleton lattice which consists of dispersed particles and polymer film matrix. Using the percolation theory a value of critical exponent $t_3$ (universal exponent for state of structural topology of particulate filled polymer system) was found and defined. The universal critical exponent $t_3=1,58$ was found, it determines a skeleton of fractal percolation cluster from fractal point of view, and it was revealed to have a pivotal effect on increasing the elasticity of composite materials. The prediction mathematical models (polynomial, exponential, etc.) were obtained for dynamic modulus and impact resistance of epoxy, polyether, epoxy-polyurethane composites according to the concentration of different hardeners. The optimum concentrations of matrix components (hardeners, modifiers) which provide high elasticity and impact resistance of the polymer matrices under study were defined. Based on the Kelvin-Voigt model a new structural mechanical model of particulate filled polymer composites was developed. It reflects the strain condition of matrix-mass, matrix-film and percolation lattice which consists of dispersed particles. With the Verhult's method the prediction models were obtained to describe the change in dynamic modulus according to volume content of reinforcing fillers. A two-component modifying agent was developed for epoxy-polyurethane composite materials with higher stress-strain properties. It consists of polyether and polyisocyanate in a ratio of 1 to 1. The optimum concentration of modifying agent in the composite is 8 weight fractions per 100 weight fractions of resin to improve significantly the physical and mechanical properties ($E_d$ by 50%, $A$ by 67%) as compared with epoxy matrix composite material. The formulas of effective filled epoxy, polyether and epoxy-polyurethane composites were specified. They increase their dynamic modulus and impact resistance by more than 15% in comparison to the matrix materials studied. It was established that the most effective composites are epoxy-polyurethane ones filled with marshallit and diabase $(\upsilon=0,7)$.

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