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Fractal-Percolation Approach for Determination of Structural and Mechanical Properties of Metal-Filled Polyurethane Auxetics

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The use of fractal and percolation approaches to the metal-filled polymer systems enables to analyze processes of their structure formation. The main aim of research paper is to define structural parameters and mechanical properties of metal-filled polyurethane systems based on results of ultrasonic study using fractal analysis and percolation approach. Polyurethanes auxetics filled with particles of iron (Fe), molybdenum (Mo) and wolfram (W) with radius between 0.3–1.0 μm are investigated. Polyurethane composites with polymer matrix are made of thermoplastic polyurethane synthesized from 4,4'-Methylenediphenyl diisocyanate, 1,4-Butanediol and Poly(tetramethylene ether)glycol with molecular weight 1500. Metal-filled polymer systems are obtained with the help of hot-pressing in T - p mode just after the components were all mixed. The results of acoustic research of investigated metal-filled thermoplastic polyurethane systems with 52% vol. Fe, 48% vol. W, 43% vol. Mo have proven to be with negative Poisson's constant. Based on percolation cluster model of metal-filled polyurethane auxetics their fractal dimensions and percolation indexes are distinguished. Usage of fractal-percolation ap-

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proach to the metal-filled polymer model enables us to estimate structural-microscopic (geometrics) dimensions of boundary and interface layers as well as mechanical properties of auxetics. Model calculations and experimental values of their properties are compared. As shown, the filler particles, boundary and interface layers take part in deformation processes conditioned by negative Poisson's constant. Models of application are demonstrated as to the referenced modelling in specifying operating features of polymer composite materials.

Key words: metal filler, polymer auxetic, Poisson's constant, percolation cluster, fractal dimension, modulus of deformation.

На основі моделі перколяційного кластера для металонаповнених поліуретанових ауксетиків визначено їхні фрактальні розмірності та індекси перколяції. Використання фрактально-перколяційного підходу до моделі металонаповненого полімеру дозволило розрахувати структурно-мікроскопічні (геометричні) параметри граничних та міжфазних шарів досліджуваних металонаповнених поліуретанів, а також механічні характеристики цих ауксетиків. Співставлено модельні розрахунки та експериментальні значення цих характеристик.

Ключові слова: металевий наповнювач, полімерний ауксетик, коефіцієнт Пуассона, перколяційний кластер, фрактальна розмірність, модулі деформації.

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1. INTRODUCTION

Creation, usage, modelling and investigation of auxetic materials have been a matter of many scientific and application-oriented research works [1–3]. Adding filler to polymer matrix causes changes of properties in newly formed systems. It is determined by interactions which take place in phase boundary filler–polymer matrix and depend on filler's potential. The filler causes changes in polymer's molecular and permolecular structures, macromolecular structural adjustments, modification of their relaxation spectrum, phase state and thermodynamical equilibrium. Metals and metal contained materials play a significant part among fillers [4]. Introduction of metal fillers into polymer matrix leads to thermophysical, electric, mechanical etc. properties of heterogeneous systems [5]. Adjustment of mechanical properties of filled polymers enables to obtain auxetics. It is preferably to modify macromolecular system in which permolecular formations and macromolecular structural elements will cause deformation reaction with negative Poisson's constant under condition of outer field of force. The processes of obtaining and implementation of polymer auxetics are analysed at nano-, micro-, meso- and macrolevels [6–8]. The promising direction of creation and usage of polymer auxetics is poly-

urethane and its composites [9–11]. As metal-filled polymers are thermodynamically unstable systems and processes of their structuring are not linear, so fractal analysis and synergetic approach should be used to investigate their properties. The main aim of the research paper is to define structural and mechanical properties of metal-filled polyurethane auxetics based on the usage of fractal analysis and percolation approach.

2. TARGET AND METHODS OF THE RESEARCH

Polyurethane composites with polymer matrix made of thermoplastic polyurethane that is synthesized from 4,4'-Methylen diphenyl diisocyanate, 1,4-Butanediol and Poly(tetramethylene ether)glycol with molecular weight 1500 have been investigated. High dispersed powders of iron (Fe), molybdenum (Mo) and wolfram (W) with particles' radius 0.3–1.0 μm are used as fillers.

Filled polymer systems are obtained with the help of hot-pressing in *T-p* mode just after the components were all mixed. The dilatational (v_l) and rotational (v_t) wave velocities in the samples are distinguished according to research [12]. The results of acoustic research of thermoplastic polyurethane enable to estimate dynamic Poisson's constant to

$$\nu = \frac{2 - v_l^2/v_t^2}{2(1 - v_l^2/v_t^2)}. \quad (1)$$

Thermoplastic polyurethane systems TPU + 52% vol. Fe, TPU + 48% vol. W, TPU + 43% vol. Mo had negative Poisson's constant (data presented in Table 1).

3. MAIN BODY. MODEL. FRACTAL DIMENSIONS

In a cluster model of amorphous polymer condition [13], where clusters are defined as areas of local order and clusters themselves form macromolecular cross-link connections, process of structuring could be analysed. Clusters in such model are regarded as structural defects that break the total chaos. And a segment, that is a part of a cluster, is considered as a linear defect. For such systems, according to synergetic approach fractal (Hausdorff) dimension of structuring is determined as [14]:

$$d_f = (d - 1)(1 + \nu), \quad (2)$$

where d is Euclidean dimension.

Taking into account research works [15, 16], we shall modify ther-

TABLE 1. Fractal dimensions, thermodynamic critical dimensions, ratio of μ/K for metal-filled polyurethane auxetics.

Composite type	ν	d_f	β	ν_0	t	μ/K			
						Experiment	$d=1$	$d=2$	$d=3$
TPU + 48% vol. W	-0.397	1.206	0.829	1.658	3.317	4.41	0.83	2.32	4.46
TPU + 43% vol. Mo	-0.365	1.270	0.787	1.575	3.150	4.10	0.79	2.15	4.09
TPU + 52% vol. Fe	-0.236	1.528	0.654	1.309	2.618	2.92	0.65	1.62	2.88

moplastic polyurethane systems as percolation clusters. In a percolation cluster model framework (a cluster model of amorphous polymer) we suppose looking at different levels of structuring of polymer auxetics. The amount of simply oriented areas in a polymer matrix (clusters) makes frame of a percolation cluster (cross-link connections) and distinguishes the first subset with critical index of percolation β . Chaos areas (open-packed polymer matrixes) represent the second subset with critical index of percolation ν_0 . Percolation indexes γ , t distinguish filler particles, its eternal branches and frame that is immersed into polymer. To define critical percolation index following relations have been used [17, 18]:

$$\beta = \frac{1}{d_f}, \quad \nu_0 = \frac{2}{d_f}, \quad \gamma = \frac{3}{d_f}, \quad t = \frac{4}{d_f}. \quad (3)$$

Filled polymers are modified as three-component systems: polymer matrix–interface layer–filler. The results of thermophysical researches [19] show that the content of the filler of investigated systems is critical. Having critical amount of filler in polymer matrix to distinguish structural properties we use a model suggested in the research paper [20]. Due to this model, polymer matrix under the action of filler's field of force turns into interface layer. Therewith thermoplastic polyurethane systems are modified as two-component: interface layer–filler. Let's consider the filler's interface as an object of fractal dimension d_F . Having known relation between filler's surface area S_F and filler particles radius r (nm) [21]:

$$d_F = d + \frac{\ln S_F - \ln 410}{\ln r}, \quad (4)$$

where $S_F = 1/(\rho r)$, ρ is density of filler, g/m^3 .

Size increase of filler particles (Fig. 1) leads to increase of its fractal

dimension.

Filler's surface particles ability and its fractality determine formation of interface layer and boundary layer as well. There are structural formations of thermoplastic polyurethane macromolecules in boundary layer that directly interfere with filler's surface field of force. Boundary layer structure is not only determined by force interaction but also by conformational and topological effects that are described by macromolecules flexibility.

Dimension that distinguishes flexibility is

$$\sigma = \frac{2d_f}{d(d-1)(d-d_f)} + \frac{4}{3}. \quad (5)$$

Fractal modelling of interface layer enables to calculate its geometric dimensions (l_{BL}) as

$$l_{BL} = l_0 \sigma \left(\frac{r}{l_0 \sigma} \right)^{2(d-d_f)/d}, \quad (6)$$

where l_0 is distance between neighbouring carbon atoms in polyurethane chain.

Dependence of geometric dimension of interface layer on particles radius can be observed on Fig. 2, l_{BL} dimension allows defining adhesion parameter of thermoplastic polyurethane-metal filler systems:

$$b = \left(\frac{l_{BL} + r}{r} \right)^3 - 1. \quad (7)$$

For thermoplastic polyurethane systems particles radius increase

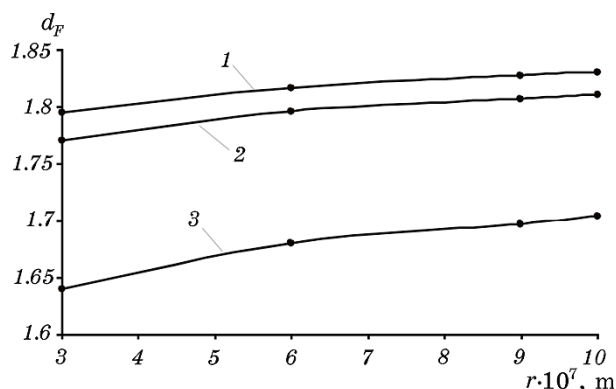


Fig. 1. Dependences of d_F on r for TPU-systems: 1—TPU + 52% vol. Fe; 2—TPU + 43% vol. Mo; 3—TPU + 48% vol. W.

leads to even b decrease (Fig. 2).

The following functional connection of b and r shows that there is nanoadhesion effect in polymer auxetics [21] that is of dimensional (fractal) nature.

To modify polymer auxetic as macrolattice we shall define its period

$$l_{\max} = D_F \left(\frac{\rho/\rho_p + \varphi_{cr}}{1.91 \varphi_{cr}} \right)^{1/3} \quad (8)$$

and interface layer dimension is

$$l_{IL} = D_F \left[\left(\frac{\rho/\rho_p + \varphi_{cr}}{1.91 \varphi_{cr}} \right)^{1/3} - 1 \right], \quad (9)$$

where D_F is filler's particles diameter, ρ_p is density of polyurethane, φ_{cr} is critical filler contents.

Dependences of l_{\max} , l_{IL} on r are shown in Fig. 3.

These structure dimensions are determined by the particle size of the filler and depend on the metal fillers nature (maximum value is common to TPU + W systems). Comparing l_{IL} and l_{BL} values allows simulating polymer matrix in thermoplastic polyurethane systems and form a system that consists of nanoformations. The system has two boundary layers that are formed because of nanoadhesion processes and in-between part of interface layer, where structural modifications are determined by conformational and topological effects. These processes in interface layer are possible because filler of surface field action transmission through boundary layer.

According to fractal approach interaction between filler particles at

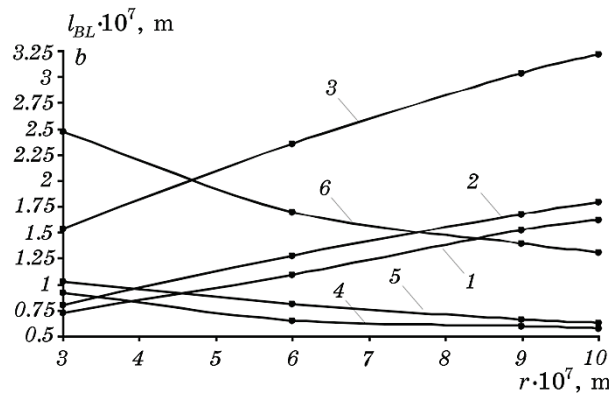


Fig. 2. Dependences of l_{BL} (1–3) and b (4–6) on r for TPU-systems: 1, 4—TPU + 52% vol. Fe; 2, 5—TPU + 43% vol. Mo; 3, 6—TPU + 48% vol. W.

this critical content could be explained as fractal interaction: filler’s surface–boundary layer–interface layer–filler’s surface.

4. STRUCTURAL AND MECHANICAL PROPERTIES

In elasticity theory Poisson’s constant is determined by correlation of modulus of volume strain (K) and shearing strain (μ):

$$\nu = \frac{1}{2} \left(\frac{3K - 2\mu}{3K + 2\mu} \right). \tag{10}$$

According to formula (2) correlation of modulus shearing strain and volume strain through the fractal dimension of thermoplastic polyurethane systems is:

$$\frac{\mu}{K} = \frac{d(d - d_f)}{d_f}. \tag{11}$$

Calculations for different d data of Euclidean space (Table 1) and comparison with testing data show that volume effects appear in thermoplastic polyurethane systems when strain by way of ultrasonic waves takes place. It is typical for the filler’s macrolattice to have not only longitudinal and shearing strain but volume strain as well. These types of strain are delivered by interacting fractals.

To prove our statement let’s determine polymer auxetic’s amplification ratio (correlation between modulus of system deformation E_s and modulus of polymer deformation E_p) using percolation approach.

If we suppose that polymer cluster grids with critical index of perco-

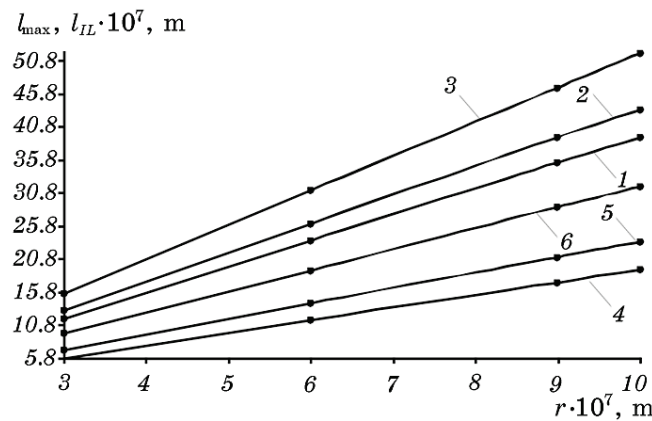


Fig. 3. Dependences of l_{max} (1–3) and l_{IL} (4–6) on r for TPU-systems: 1, 4—TPU+ 52% vol. Fe; 2, 5—TPU + 43% vol. Mo; 3, 6—TPU + 48% vol. W.

lation β take part in ultrasonic waves dissemination, so

$$E_S/E_P = 1 + 11(\varphi)^\beta. \tag{12}$$

If macrolattice takes part in the processes where strain is delivered through fractal chain with percolation index t , we will have

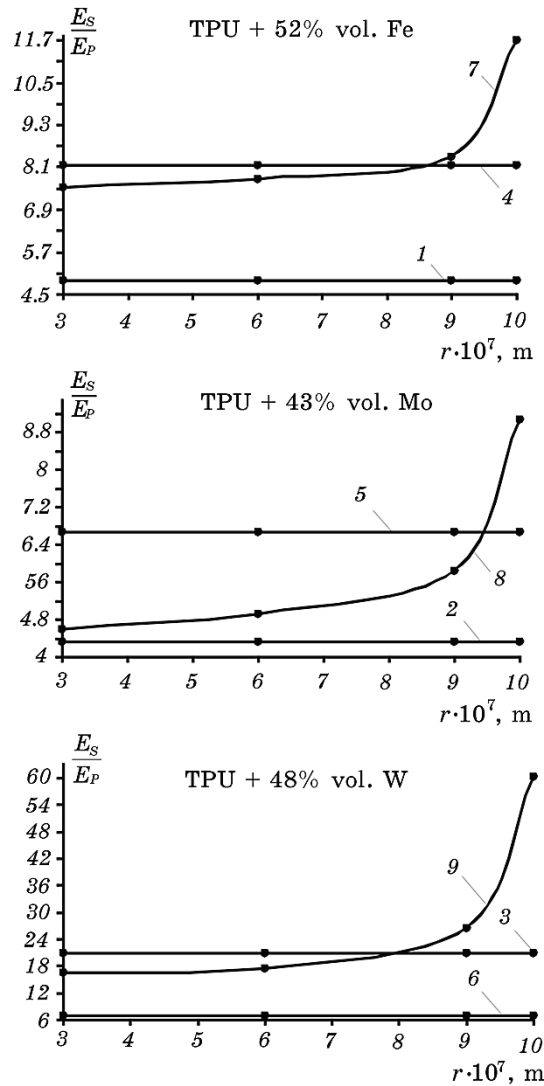


Fig. 4. Gain rate dependences of (E_S/E_P) on r for TPU-systems: 1, 4, 7—TPU + 52% vol. Fe; 2, 5, 8—TPU + 43% vol. Mo; 3, 6, 9—TPU + 48% vol. W [(1–3)—experiment, (4–6)—Eq. (12), (7–9)—Eq. (13)].

$$E_s/E_p = 1 + 11(\varphi_{IL} + \varphi)^t. \quad (13)$$

Comparing theoretical data value calculations as given by Eqs. (12), (13) and thermoplastic polyurethane systems reinforcement data based on research results (Fig. 4), it is stated that filler particles, boundary and interface layers take part in deformation processes conditioned by negative Poisson's constant. Predominate filler particles size in polymer auxetic in this case is 0.9–1.0 μm .

5. CONCLUSION

Fractal approach to metal-filled polymer auxetic structuring description enables to distinguish structural and microscopic properties of thermoplastic polyurethane systems and distinguish the effect of metal fillers (Fe, W, Mo) and their dimensions on the properties. Percolation critical index data value gives an opportunity to calculate mechanical data of such systems. Thermoplastic polyurethane systems with negative Poisson's constant could be simulated as macrolattice (percolation cluster) with nodes in the nature of massive metal parts where there is fractal interaction in cross-link-connections (metal particle surface–boundary layer–interface layer).

REFERENCES

1. V. V. Novikov and K. W. Wojciechowski, *FTT*, **41**, No. 12: 2147 (1999) (in Russian).
2. Y.-C. Wang and R. Lakes, *Int. J. Solids Structures*, **39**: 4825 (2002).
3. D. A. Konek, K. V. Voytsekhovskiy, Yu. M. Plaskachevskiy, and S. V. Shyl'ko, *Mekh. Komp. Mat. i Konstr.*, **10**, No. 1: 35 (2004) (in Russian).
4. A. L. Tolstov, V. F. Matyushov, D. A. Klymchuk, and E. V. Lebedev, *Polym. J.*, **41**, No. 1: 26 (2019) (in Ukrainian).
5. T. M. Shevchuk, M. A. Bordyuk, V. V. Krivtsov, and V. A. Mashchenko, *Polym. J.*, **41**, No. 4: 264 (2019) (in Ukrainian).
6. B. Brandel and R. S. Lakes, *J. Mater. Sci.*, **36**: 5885 (2001).
7. G. He, P. Liu, A. C. Griffin, C. W. Smith, and K. E. Evans, *Macromol. Chem. Phys.*, **206**: 233 (2005).
8. S. Xinchun and R. S. Lakes, *physica status solidi (b)*, **244**, No. 3: 1008 (2007).
9. E. O. Martz, R. S. Lakes, and J. B. Park, *Cell. Polym.*, **15**: 349 (1996).
10. A. Lowe and R. S. Lakes, *Cell. Polym.*, **19**: 157 (2000).
11. Y. J. Park and J. K. Rim, *Adv. Mater. Sci. Eng.*, **1** (2013).
12. B. S. Kolupaev, Yu. S. Lipatov, V. I. Nikitchuk, N. A. Bordyuk, and O. M. Voloshin, *Dopovidi AN Ukrayiny*, **3**: 130 (1993) (in Russian).
13. V. U. Novykov and H. V. Kozlov, *Uspekhi Khimii*, **69**, No. 6: 572 (2000) (in Russian).
14. A. S. Balankyn, *Sinergetika Deformiruemogo Tela* [Synergy of the Strained Body] (Moscow: Publ. by USSR Ministry of Defence: 1991) (in Russian).

15. V. U. Novykov and H. V. Kozlov, *Uspekhi Khimii*, **69**, No. 3: 378 (2000) (in Russian).
16. H. V. Kozlov, M. A. Hazaev, V. U. Novykov, and A. K. Mykytaev, *Pis'ma v ZhTF*, **22**, No. 16: 31 (1996) (in Russian).
17. A. Y. Olemskoy and A. Ya. Flat, *Usp. Fiz. Nauk*, **163**, No. 12: 1 (1993) (in Russian).
18. L. M. Zelenyi and A. V. Milovanov, *Usp. Fiz. Nauk*, **174**, No. 8: 809 (2004) (in Russian).
19. B. S. Kolupaev, Yu. S. Lypatov, V. Y. Nykytchuk, N. A. Bordyuk, and O. M. Voloshyn, *Inzh.-Fiz. Zhurnal*, **69**, No. 5: 726 (1996) (in Russian).
20. B. S. Kolupaev and N. A. Bordyuk, *Vysokomolek. Soed.*, **23**, No. 7: 1499 (1981) (in Russian).
21. H. V. Kozlov, *Usp. Fiz. Nauk*, **185**, No. 1: 35 (2015) (in Russian).