Yu. G. Yanovskii, G. V. Kozlov, G. E. Zaikov, Kh. S. Abzaldinov

THE STRUCTURE OF NANOFILLER

IN ELASTOMERIC PARTICULATE-FILLED NANOCOMPOSITES

Keywords: Nanocomposite, nanofiller, structure, "chains", fractal analysis.

It has been shown that nanofiller particles (aggregates of particles) "chains" in elastomeric nanocomposites are physical fractal within the self-similarity (and, hence, fractality) range ~500-1450 nm. The low dimensions of nanofiller particles (aggregates of particles) structure in elastomeric nanocomposites are due to high fractal dimension of nanofiller initial particles surface.

Ключевые слова: нанокомпозит, нанонаполнитель, структура, "цепи", фрактальный анализ.

Показано, что "цепи" частиц (агрегатов частиц) нанонаполнителя в эластомерных нанокомпозитах являются физическими фракталами в диапазоне самоподобия (и, следовательно, фрактальности) ~500-1450 нм. Небольшие размеры структуры частиц (агрегатов частиц) нанонаполнителя в эластомерных нанокомпозитах обусловлены большой фрактальной размерностью поверхности исходных частиц нанонаполнителя.

Introduction

It is well-known [1, 2], that in particulate-filled elastomeric nanocomposites (rubbers) nanofiller particles form linear spatial structures ("chains"). At the same time in polymer composites, filled with disperse microparticles (microcomposites) particles (aggregates of particles) of filler form a fractal network, which defines polymer matrix structure (analog of fractal lattice in computer simulation) [3, 4, 5]. This results to different mechanisms of polymer matrix structure formation in micro- and nanocomposites. If in the first filler particles (aggregates of particles) fractal network availability results to "disturbance" of polymer matrix structure, that is expressed in the increase of its fractal dimension d_f [3], then in case of polymer nanocomposites at nanofiller contents change the value d_f is not changed and equal to matrix polymer structure fractal dimension [6]. As it has to been expected, composites indicated classes structure formation mechanism change defines their properties change, in particular, reinforcement degree.

At present there are several methods of filler structure (distribution) determination in polymer matrix, both experimental [7, 8] and theoretical [3]. All the indicated methods describe this distribution by fractal dimension D_n of filler particles network. However, correct determination of any object fractal (Hausdorff) dimension includes three obligatory conditions. The first from them is the indicated above determination of fractal dimension numerical magnitude, which should not be equal to object topological dimension. As it is known [9], any real (physical) fractal possesses fractal properties within a certain scales range [10]. And at last, the third condition is the correct choice of measurement scales range itself. As it has been shown in papers [11, 12], the minimum range should exceed at any rate one self-similarity iteration.

The present paper purpose is dimension D_n estimation, both experimentally and theoretically, and checking two indicated above conditions fulfillment, i.e. obtaining of nanofiller particles (aggregates of particles) network ("chains") fractality strict proof in elastomeric nanocomposites on the example of particulate-filled butadiene-styrene rubber.

Experimental

The elastomeric particulate-filled nanocomposite on the basis of butadiene-styrene rubber (BSR) was an object of the study. The technical carbon of mark № 220 (TC) of industrial production, nano- and microshungite (the mean filler particles size makes up 20, 40 and 200 nm, accordingly) were used as a filler. All fillers content makes up 37 mass %. Nano- and microdimensional disperse shungite particles were obtained from industrially extractive material by processing according to the original technology. A size and polydispersity of the received in milling process shungite particles were monitored with the aid of analytical disk centrifuge (CPS Instruments, Inc., USA), allowing to determine with high precision the size and distribution by sizes within the range from 2 nm up to 50 mcm.

Nanostructure was studied on atomic-power microscopes Nano-DST (Pacific Nanotechnology, USA) and Easy Scan DFM (Nanosurf, Switzerland) by semi-contact method in the force modulation regime. Atomic-power microscopy results were processed with the aid of specialized software package SPIP (Scanning Probe Image Processor, Denmark). SPIP is a powerful programmes package for processing of images, obtained on SPM, AFM, STM, scanning electron microscopes, transmission electron microscopes, interferometers, confocal microscopes, profilometers, optical microscopes and so on. The given package possesses the whole functions number, which are necessary at images precise analysis, in the number of which the following are included:
1) the possibility of three-dimensional reflecting objects obtaining, distortions automatized leveling, including Z-error mistakes removal for examination separate elements and so on;
2) quantitative analysis of particles or grains, more than 40 parameters can be calculated for each found particle or pore: area, perimeter, average diameter, the ratio of

linear sizes of grain width to its height distance between grains, coordinates of grain center of mass a.a. can be presented in a diagram form or in a histogram form.

Results and Discussion

The first method of dimension D_n experimental determination uses the following fractal relationship [13, 14]:

$$D_n = \frac{\ln N}{\ln \rho} \qquad (1)$$

where N is a number of particles with size ρ.

Particles sizes were established on the basis of atomic-power microscopy data (see Fig. 1). For each from the three studied nanocomposites no less than 200 particles were measured, the sizes of which were united into 10 groups and mean values N and ρ were obtained.
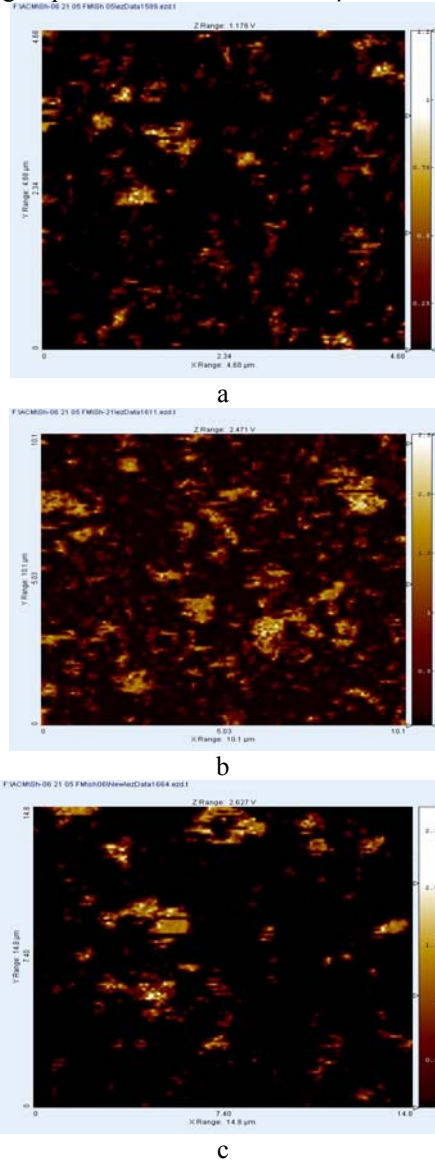

a

b

c

Fig. 1 - The electron micrographs of nanocomposites BSR/TC (a), BSR/nanoshungite (b) and BSR/microshungite (c), obtained by atomic-power microscopy in the force modulation regime

The dependences $N(\rho)$ in double logarithmic coordinates were plotted, which proved to be linear and

the values D_n were calculated according to their slope (see Fig. 2). It is obvious, that at such approach fractal dimension D_n is determined in two-dimensional Euclidean space, whereas real nanocomposite should be considered in three-dimensional Euclidean space. The following relationship can be used for D_n re-calculation for the case of three-dimensional space [15]:

$$D3 = \frac{d + D2 \pm \left[(d - D2)^2 - 2 \right]^{1/2}}{2} \qquad (2)$$

where $D3$ and $D2$ are corresponding fractal dimensions in three- and two-dimensional Euclidean spaces, $d=3$.
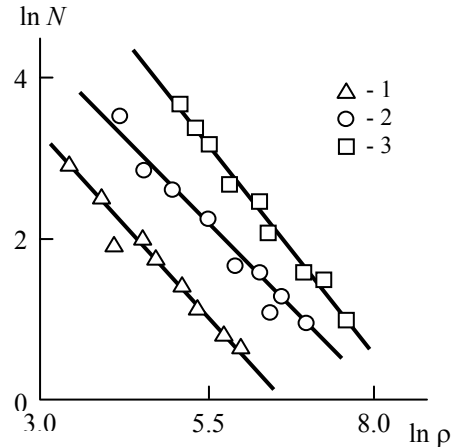

Fig. 2 - The dependence of nanofiller particles number N on their size ρ for nanocomposites BSR/TC (1), BSR/nanoshungite (2) and BSR/microshungite (3)

The calculated according to the indicated method dimensions D_n are adduced in table 1. As it follows from the data of this table, the values D_n for the studied nanocomposites are varied within the range of 1.10-1.36, i.e. they characterize more or less branched linear formations ("chains") of nanofiller particles (aggregates of particles) in elastomeric nanocomposite structure.

Table 1 - The dimensions of nanofiller particles (aggregates of particles) structure in elastomeric nanocomposites

The nano composite	D_n, the equations (1)	D_n, the equations (3)	d_0	d_{surf}	φ_n	D_n, the equations (7)
BSR/TC	1.19	1.17	2.86	2.64	0.48	1.11
BSR/nano shungite	1.10	1.10	2.81	2.56	0.36	0.78
BSR/micro shungite	1.36	1.39	2.41	2.39	0.32	1.47

Let us remind that for particulate-filled composites polyhydroxiether/graphite the value D_n changes within the range of $\sim$ 2.30-2.80 [7], i.e. for these materials filler particles network is a bulk object, but not a linear one [9].

Another method of D_n experimental determination uses the so-called "quadrates method" [16]. Its essence consists in the following. On the enlarged nanocomposite microphotograph (see Fig. 1) a

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net of quadrates with quadrate side size α_i, changing from 4.5 up to 24 mm with constant ratio $\alpha_{i+1}/\alpha_i=1.5$, is applied and then quadrates number N_i, in to which nanofiller particles hit (fully or partly), is calculated. Five arbitrary net positions concerning microphotograph were chosen for each measurement. If nanofiller particles network is fractal, then the following relationship should be fulfilled [16]:

$$N_i \sim S_i^{-D_n/2} \qquad (3)$$

where S_i is quadrate area, which is equal to α_i^2.

In Fig. 3 the dependences of N_i on S_i in double logarithmic coordinates for the three studied nanocomposites, corresponding to the relationship (3), is adduced.
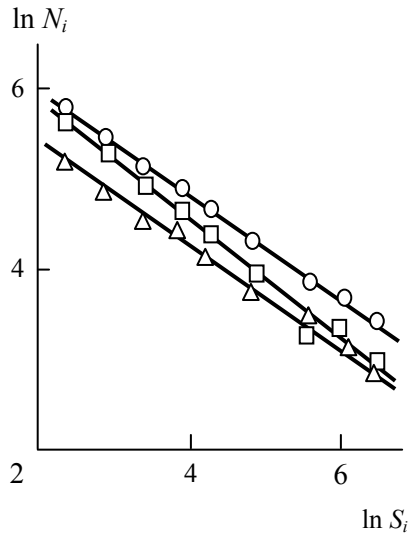
Fig. 3 - The dependences of covering quadrates number N_i on their area S_i, corresponding to the relationship (3), in double logarithmic coordinates for nanocomposites on the basis of BSR. The designations are the same, that in Fig. 2

As one can see, these dependences are linear, that allows to determine the value D_n from their slope. The determined according to the relationship (3) values D_n are also adduced in table 1, from which a good correspondence of dimensions D_n, obtained by the two described above methods, follows (their average discrepancy makes up 2.1 % after these dimensions re-calculation for three dimensional space according to the equation (2)).

As it has been shown in paper [17], at the relationship (3) the usage for self-similar fractal objects the condition should be fulfilled:

$$N_i - N_{i-1} \sim S_i^{-D_n} \qquad (4)$$

In Fig. 4 the dependence, corresponding to the relationship (4), for the three studied elastomeric nanocomposites is adduced. As one can see, this dependence is linear, passes through coordinates origin, that according to the relationship (4) is confirmed by nanofiller particles (aggregates of particles) "chains" self-similarity within the selected α_i range. It is obvious, that this self-similarity will be a statistical one [17].
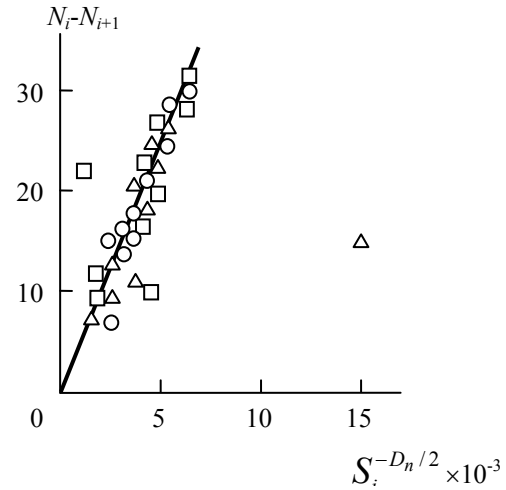
Fig. 4 - The dependences of $(N_i\text{-}N_{i+1})$ on the value $S_i^{-D_n/2}$, corresponding to the relationship (4), for nanocomposites on the basis of BSR. The designations are the same, that in Fig. 2

Let us note, that the points, corresponding to $\alpha_i=16$ mm for nanocomposites BSR/TC and BSR/microshungite, do not correspond to a common straight line. Accounting for electron microphotographs of Fig. 1 enlargement this gives the self-similarity range for nanofiller "chains" of 464-1472 nm. For nanocomposite BSR/nanoshungite, which has no points deviating from a straight line of Fig. 4, α_i range makes up 311-1510 nm, that corresponds well enough to the indicated above self-similarity range.

In papers [11, 12] it has been shown, that measurement scales S_i minimum range should contained at least one self-similarity iteration. In this case the condition for ratio of maximum S_{max} and minimum S_{min} areas of covering quadrates should be fulfilled [12]:

$$\frac{S_{max}}{S_{min}} > 2^{2/D_n} \qquad (5)$$

Hence, accounting for the defined above restriction let us obtain $S_{max}/S_{min}=121/20.25=5.975$, that is larger than values $2^{2/D_n}$ for the studied nanocomposites, which are equal to 2.71-3.52. This means, that measurement scales range is chosen correctly.

The self-similarity iterations number μ can be estimated from the inequality [12]:

$$\left(\frac{S_{max}}{S_{min}}\right)^{D_n/2} > 2^{\mu} \qquad (6)$$

Using the indicated above values of the included in the inequality (6) parameters, $\mu=1.42-1.75$ is obtained for the studied nanocomposites, i.e. in our experiment conditions self-similarity iterations number is larger than unity, that again is confirmed by the value D_n estimation correctness [8].

And let us consider in conclusion the physical grounds of smaller values D_n for elastomeric nanocomposites in comparison with polymer microcomposites, i.e. the causes of nanofiller particles

(aggregates of particles) "chains" formation in the first. The value D_n can be determined theoretically according to the equation [3]:

$$\varphi_{if} = \frac{D_n + 2.55d_0 - 7.10}{4.18} \tag{7}$$

where φ_{if} is interfacial regions relative fraction, d_0 is nanofiller initial particles surface dimension.

The dimension d_0 estimation can be carried out with the aid of the relationship [6]:

$$S_u = 410\left(\frac{D_p}{2}\right)^{d_0-d} \tag{8}$$

where S_u is nanofiller initial particles specific surface in m²/g, D_p is their diameter in nm, d is dimension of Euclidean space, in which a fractal is considered (it is obvious, in our case $d=3$).

The value S_u can be calculated according to the equation [18]:

$$S_u = \frac{6}{\rho_n D_p} \tag{9}$$

where ρ_n is nanofiller density, which is determined according to the empirical formula [6]:

$$\rho_n = 0.188\left(D_p\right)^{1/3} \tag{10}$$

The results of value d_0 theoretical estimation are adduced in table 1. The value φ_{if} can be calculated according to the equation [6]:

$$\varphi_{if} = \varphi_n\left(d_{surf} - 2\right) \tag{11}$$

where φ_n is nanofiller volume fraction, d_{surf} is fractal dimension of nanoparticles aggregate surface.

The value φ_n is determined according to the equation [6]:

$$\varphi_n = \frac{W_n}{\rho_n} \tag{12}$$

where W_n is nanofiller mass fraction and dimension d_{surf} is calculated according to the equations (8)-(10) at diameter D_p replacement on nanoparticles aggregate diameter D_{agr}, which is determined experimentally (see Fig. 5).
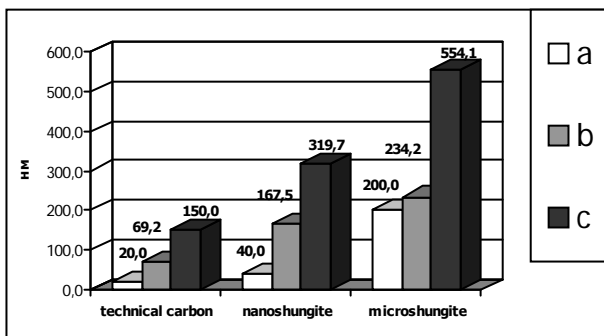

Fig. 5 - The initial particles diameter (a), their aggregates size in nanocomposite (b) and distance between nanoparticles aggregates (c) for nanocomposites on the basis of BSR, filled with technical carbon, nano- and microshungite

The results of dimension D_n theoretical calculation according to the equations (7)-(12) are adduced in table 1, from which theory and experiment good correspondence follows. The equation (7) indicates unequivocally the cause of filler in nano- and microcomposites different behaviour. The high (close to 3, see table 1) values d_0 for nanoparticles and relatively small ($d_0=2.17$ for graphite) values d_0 for microparticles at comparable values φ_{if} for composites of the indicated classes [3, 6].

Conclusions

Therefore, the present paper results have shown, that nanofiller particles (aggregates of particles) "chains" in elastomeric nanocomposites are physical fractal within self-similarity (and, hence, fractality [14]) range of ~ 500-1450 nm. In this range their dimension D_n can be estimated according to the equations (1), (3) and (7). The cited examples demonstrate the necessity of the measurement scales range correct choice. As it has been noted earlier [19], linearity of the plots, corresponding to the equations (1) and (3), and D_n nonintegral value do not guarantee object self-similarity (and, hence, fractality). The nanofiller particles (aggregates of particles) structure low dimensions are due to the initial nanofiller particles surface high fractal dimension.

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