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THE DESCRIPTION OF NANOFILLER PARTICLES AGGREGATION WITHIN THE FRAMEWORKS OF IRREVERSIBLE AGGREGATION MODELS

Keywords: Nanocomposite, elastomer, nanoparticle, aggregation, diffusion.

A nanofiller disperse particles aggregation process in elastomeric matrix has been studied. The modified model of irreversible aggregation particle-cluster was used for this process theoretical analysis. The modification necessity is defined by simultaneous formation of a large number of nanoparticles aggregates. The offered approach allows to predict nanoparticles aggregates final parameters as a function of the initial particles size, their contents and other factors number.

Ключевые слова: нанокомпозит, эластомер, наночастица, агрегация, диффузия.

Исследован процесс агрегации дисперсных частиц нанонаполнителя в эластомерной матрице. Для теоретического анализа процесса была использована модифицированная модель необратимой агрегации частица-кластер. Необходимость модификации определяется одновременным образованием большого количества агрегатов наночастиц. Предложенный подход позволяет предсказать конечные параметры агрегатов наночастиц как функцию размера начальных частиц, их содержания и ряда других факторов.

Introduction

The aggregation of the initial nanofiller powder particles in more or less large particles aggregates always occurs in the course of technological process of making particulate-filled polymer composites in general [1, 2, 3] and elastomeric nanocomposites in particular [4]. The aggregation process tells on composites (nanocomposites) macroscopic properties [1, 5]. For nanocomposites nanofiller aggregation process gains special significance, since its intensity can be the one, that nanofiller particles aggregates size exceeds 100 nm – the value, which assumes (although and conditionally enough [6]) as an upper dimensional limit for nanoparticle. In other words, the aggregation process can result to the situation, when primordially supposed nanocomposite ceases to be the one. Therefore at present several methods exist, which allowed to suppress nanoparticles aggregation process [4, 7]. Proceeding from this, in the present paper theoretical treatment of disperse nanofiller aggregation process in butadiene-styrene rubber matrix within the frameworks of irreversible aggregation models was carried out.

Experimental

The elastomeric particulate-filled nanocomposite on the basis of butadiene-styrene rubber was an object of the study. Mineral shungite nanodimensional and microdimensional particles and also industrially produced technical carbon with mass contents of 37 mass % were used as a filler. The analysis 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 μm .

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 scanning probe microscopy (SPM), atomic forced microscopy (AFM), scanning tunneling microscopy (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 reflected 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

For theoretical treatment of nanofiller particles aggregate growth processes and final sizes traditional irreversible aggregation models are inapplicable, since it is obvious, that in nanocomposites aggregates a large number of simultaneous growth takes place. Therefore the model of multiple growth, offered in paper [8], was used for nanofiller aggregation description.

In Fig. 1 the images of the studied nanocomposites, obtained in the force modulation regime, and corresponding to them nanoparticles aggregates fractal dimension d_f distributions are adduced. As it follows from the adduced values d_f ($d_f=2.40-2.48$), nanofiller particles aggregates in the studied nanocomposites are formed by a mechanism particle-cluster (P-Cl), i.e. they are Witten-Sander clusters [9]. The variant A, was chosen which according

to mobile particles are added to the lattice, consisting of a large number of “seeds” with density of c_0 at simulation beginning [8]. Such model generates structures, which have fractal geometry on length short scales with value $d_f \approx 2.5$ (see Fig. 1) and homogeneous structure on length large scales. A relatively high particles concentration c is required in the model for uninterrupted network formation [8].

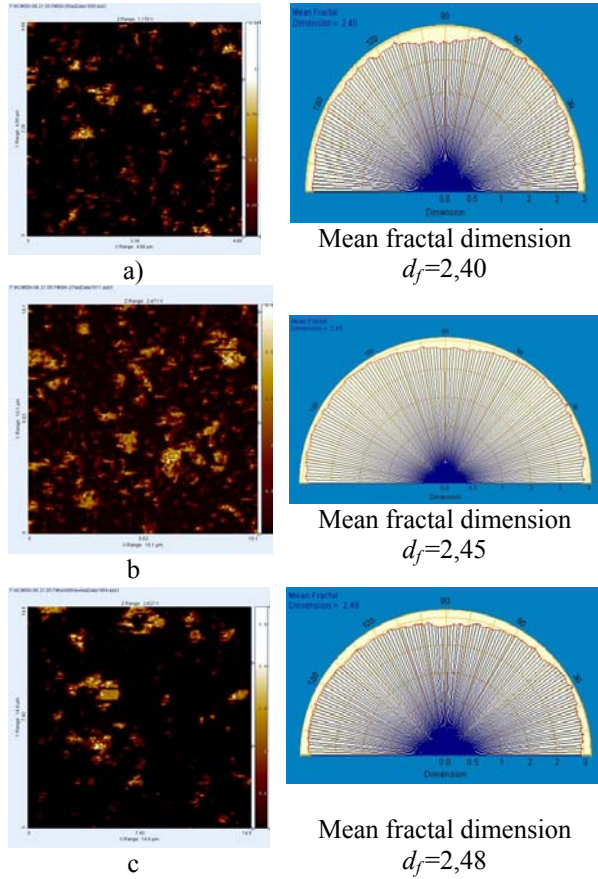


Fig. 1 - The images, obtained in the force modulation regime, for nanocomposites, filled with technical carbon (a), nanoshungite (b), microshungite (c) and corresponding to them fractal dimensions d_f .

In case of “seeds” high concentration c_0 for the variant A the following relationship was obtained [8]:

$$R_{\max}^{d_f} = N = c / c_0 \quad (1)$$

where R_{\max} is nanoparticles cluster (aggregate) greatest radius, N is nanoparticles number per one aggregate, c is nanoparticles concentration, c_0 is “seeds” number, which is equal to nanoparticles clusters (aggregates) number.

The value N can be estimated according to the following equation [10]:

$$2R_{\max} = \left(\frac{S_n N}{\pi \eta} \right)^{1/2} \quad (2)$$

where S_n is cross-sectional area of nanoparticles, from which aggregate consists, η is packing coefficient, equal to 0.74.

The experimentally obtained nanoparticles aggregate diameter $2R_{agr}$ was accepted as $2R_{\max}$ (table 1) and the value S_n was also calculated according to the

experimental values of nanoparticles radius r_n (table 1). In table 1 the values N for the studied nanofillers, obtained according to the indicated method, were adduced. It is significant that the value N is a maximum one for nanoshungite despite larger values r_n in comparison with technical carbon.

Table 1 - The parameters of irreversible aggregation model of nanofiller particles aggregates growth

Filler	R_{agr} , nm	r_n , nm	N	R_{\max}^T , nm	R_{agr}^T , nm	R_c , nm
Technical carbon	34.6	10	35.4	34.7	34.7	33.9
Nanoshungite	83.6	20	51.8	45.0	90.0	71.0
Microshungite	117.1	100	4.1	15.8	158.0	255.0

R_{agr} , nm - experimental radius of nanofiller aggregate

r_n , nm - radius of nanofiller particle

N - number of particles in one aggregate

R_{\max}^T , nm - radius of nanofiller aggregate (the equation (1))

R_{agr}^T , nm - radius of nanofiller aggregate (the equation (3))

R_c , nm - radius of nanofiller aggregate (the equation (8))

Further the equation (1) allows to estimate the greatest radius R_{\max}^T of nanoparticles aggregate within the frameworks of the aggregation model [8]. These values R_{\max}^T are adduced in table 1, from which their reduction in a sequence of technical carbon-nanoshungite-microshungite, that fully contradicts to the experimental data, i.e. to R_{agr} change (table 1). However, we must not neglect the fact that the equation (1) was obtained within the frameworks of computer simulation, where the initial aggregating particles sizes are the same in all cases [8]. For real nanocomposites the values r_n can be distinguished essentially (table 1). It is expected, that the value R_{agr} or R_{\max}^T will be the higher, the larger is the radius of nanoparticles, forming aggregate, is i.e. r_n . Then theoretical value of nanofiller particles cluster (aggregate) radius R_{agr}^T can be determined as follows:

$$R_{agr}^T = k_n r_n N^{1/d_f} \quad (3)$$

where k_n is proportionality coefficient, in the present work accepted empirically equal to 0.9.

The comparison of experimental R_{agr} and calculated according to the equation (3) R_{agr}^T values of the studied nanofillers particles aggregates radius shows their good correspondence (the average discrepancy of R_{agr} and R_{agr}^T makes up 11.4 %). Therefore, the

theoretical model [8] gives a good correspondence to the experiment only in case of consideration of aggregating particles real characteristics and, in the first place, their size.

Let us consider two more important aspects of nanofiller particles aggregation within the frameworks of the model [8]. Some features of the indicated process are defined by nanoparticles diffusion at nanocomposites processing. Specifically, length scale, connected with diffusible nanoparticle, is correlation length ξ of diffusion. By definition, the growth phenomena in sites, remote more than ξ , are statistically independent. Such definition allows to connect the value ξ with the mean distance between nanofiller particles aggregates L_n . The value ξ can be calculated according to the equation [8]:

$$\xi^2 \approx c^{-1} R_{agr}^{d_f-d+2} \quad (4)$$

where c is nanoparticles concentration, d is dimension of Euclidean space, in which a fractal is considered (it is obvious, that in our case $d=3$).

The value c should be accepted equal to nanofiller volume contents ϕ_n , which is calculated as follows [11]:

$$\phi_n = \frac{W_n}{\rho_n} \quad (5)$$

where W_n is nanofiller mass contents, ρ_n is its density, determined according to the equation [5]:

$$\rho_n = 0.188(2r_n)^{1/3} \quad (6)$$

The values r_n and R_{agr} were obtained experimentally (see histogram of Fig. 2). In Fig. 3 the relation between L_n and ξ is added, which, as it is expected, proves to be linear and passing through coordinates origin. This means, that the distance between nanofiller particles aggregates is limited by mean displacement of statistical walks, by which nanoparticles are simulated. The relationship between L_n and ξ can be expressed analytically as follows:

$$L_n = 9.6\xi \quad (7)$$

The second important aspect of the model [6] in reference to nanofiller particles aggregation simulation is a finite nonzero initial particles concentration c or ϕ_n effect, which takes place in any real systems. This effect is realized at the condition $\xi \approx R_{agr}$, that occurs at the critical value $R_{agr}(R_c)$, determined according to the relationship [8]:

$$c \sim R_c^{d_f-d} \quad (8)$$

The relationship (8) right side represents cluster (particles aggregate) mean density. This equation establishes that fractal growth continues only, until cluster density reduces up to medium density, in which it grows. The calculated according to the relationship (8) values R_c for the considered nanoparticles are added in table 1, from which it follows, that they give reasonable correspondence with this parameter experimental values R_{agr} (the average discrepancy of R_c and R_{agr} makes up 24 %).

Since the treatment [8] was obtained within the frameworks of a more general model of diffusion-

limited aggregation, then its correspondence to the experimental data indicated unequivocally, that aggregation processes in these systems were controlled by diffusion. Therefore let us consider briefly nanofiller particles diffusion. Statistical walkers diffusion constant ζ can be determined with the aid of the relationship [8]:

$$\xi \approx (\zeta t)^{1/2} \quad (9)$$

where t is walk duration.

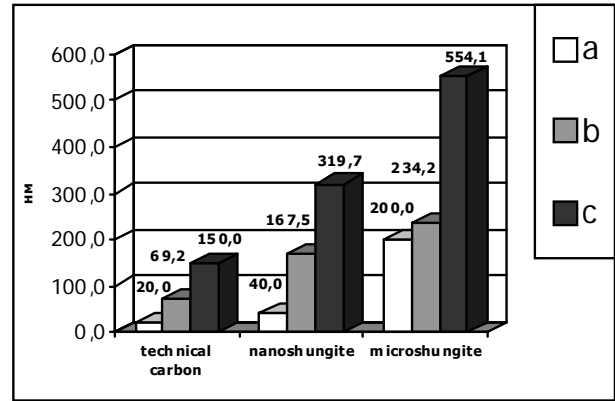


Fig. 2 - The initial particles diameter (a), their aggregates size in nanocomposite (b) and distance between nanoparticles aggregates (c) for nanocomposites, filled with technical carbon, nano- and microshungite

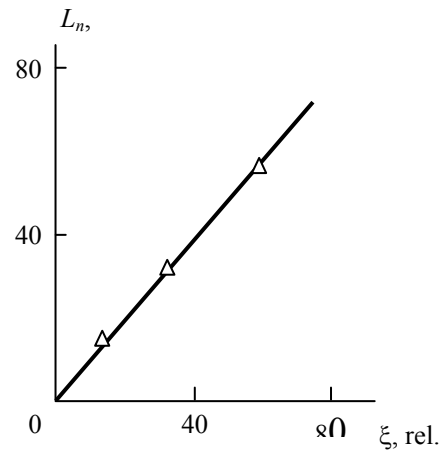


Fig. 3 - The relation between diffusion correlation length ξ and distance between nanoparticles aggregates L_n for studied nanocomposites

The equation (9) supposes (at $t=\text{const}$) ξ increase in a number technical carbon-nanoshungite-microshungite as 196-1069-3434 relative units, i.e. diffusion intensification at diffusible particles size growth. At the same time diffusivity D for these particles can be described by the well-known Einstein's relationship [12]:

$$D = \frac{kT}{6\pi\eta r_n \alpha} \quad (10)$$

where k is Boltzmann constant, T is temperature, η is medium viscosity, α is numerical coefficient, which further is accepted equal to 1.

In its turn, the value η can be estimated according to the equation [13]:

$$\frac{\eta}{\eta_0} = 1 + \frac{2.5\varphi_n}{1 - \varphi_n} \quad (11)$$

where η_0 and η are initial polymer and its mixture with nanofiller viscosity, accordingly, φ_n is nanofiller volume contents.

The calculation according to the equations (10) and (11) shows, that within the indicated above nanofillers number the value D changes as 1.32-1.14-0.44 relative units, i.e. reduces in three times, that was expected. This apparent contradiction is due to the choice of the condition $t = \text{const}$ (where t is nanocomposite production duration) in the equation (9). In real conditions the value t is restricted by nanoparticle contact with growing aggregate and then instead of t the value t/c_0 should be used, where c_0 is seeds concentration, determined according to the equation (1). In this case the value ζ for the indicated nanofillers changes as 0.288-0.118-0.086, i.e. it reduces in 3.3 times, that corresponds fully to the calculation according to the Einstein's relationship (the equation (10)). This means, that nanoparticles diffusion in polymer matrix obeys classical laws of Newtonian rheology [12].

Conclusions

Disperse nanofiller particles aggregation in elastomeric matrix can be described theoretically within the frameworks of a modified model of irreversible aggregation particle-cluster. The obligatory consideration of nanofiller initial particles size is a feature of the indicated model application to real systems description. The indicated particles diffusion in polymer matrix obeys classical laws of Newtonian liquids hydrodynamics. The offered approach allows to predict nanoparticles aggregates final parameters as a function of the initial particles size, their contents and other factors number.

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