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 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 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 df distributions are adduced. As it follows from the adduced values df (df=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 c0 at simulation beginning [8]. Such model generates structures, which have fractal geometry on length short scales with value df»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]. a) Mean fractal dimension df =2,40 b Mean fractal dimension df =2,45 c Mean fractal dimension df =2,48 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 df. In case of “seeds” high concentration c0 for the variant A the following relationship was obtained [8]: (1) where Rmax is nanoparticles cluster (aggregate) greatest radius, N is nanoparticles number per one aggregate, c is nanoparticles concentration, c0 is “seeds” number, which is equal to nanoparticles clusters (aggregates) number. The value N can be estimated according to the following equation [10]: (2) where Sn is cross-sectional area of nanoparticles, from which aggregate consists, h is packing coefficient, equal to 0.74. The experimentally obtained nanoparticles aggregate diameter 2Ragr was accepted as 2Rmax (table 1) and the value Sn was also calculated according to the experimental values of nanoparticles radius rn (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 rn in comparison with technical carbon. Table 1 - The parameters of irreversible aggregation model of nanofiller particles aggregates growth Filler Ragr, nm rn, nm N nm , nm Rc, 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 Ragr, nm - experimental radius of nanofiller aggregate rn, nm - radius of nanofiller particle N - number of particles in one aggregate , nm - radius of nanofiller aggregate (the equation (1)) , nm - radius of nanofiller aggregate (the equation (3)) Rc, nm - radius of nanofiller aggregate (the equation (8)) Further the equation (1) allows to estimate the greatest radius of nanoparticles aggregate within the frameworks of the aggregation model [8]. These values 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 Ragr 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 rn can be distinguished essentially (table 1). It is expected, that the value Ragr or will be the higher, the larger is the radius of nanoparticles, forming aggregate, is i.e. rn. Then theoretical value of nanofiller particles cluster (aggregate) radius can be determined as follows: (3) where kn is proportionality coefficient, in the present work accepted empirically equal to 0.9. The comparison of experimental Ragr and calculated according to the equation (3) values of the studied nanofillers particles aggregates radius shows their good correspondence (the average discrepancy of Ragr and 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 x of diffusion. By definition, the growth phenomena in sites, remote more than x, are statistically independent. Such definition allows to connect the value x with the mean distance between nanofiller particles aggregates Ln. The value x can be calculated according to the equation [8]: (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 jn, which is calculated as follows [11]: (5) where Wn is nanofiller mass contents, rn is its density, determined according to the equation [5]: (6) The values rn and Ragr were obtained experimentally (see histogram of Fig. 2). In Fig. 3 the relation between Ln and x is adduced, 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 Ln and x can be expressed analytically as follows: (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 jn effect, which takes place in any real systems. This effect is realized at the condition x»Ragr, that occurs at the critical value Ragr(Rc), determined according to the relationship [8]: (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 Rc for the considered nanoparticles are adduced in table 1, from which it follows, that they give reasonable correspondence with this parameter experimental values Ragr (the average discrepancy of Rc and Ragr 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 z can be determined with the aid of the relationship [8]: (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 x and distance between nanoparticles aggregates Ln for studied nanocomposites The equation (9) supposes (at t=const) z 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]: (10) where k is Boltzmann constant, T is temperature, h is medium viscosity, a is numerical coefficient, which further is accepted equal to 1. In its turn, the value h can be estimated according to the equation [13]: (11) where h0 and h are initial polymer and its mixture with nanofiller viscosity, accordingly, jn 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=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/c0 should be used, where c0 is seeds concentration, determined according to the equation (1). In this case the value z 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.