

The object of the study is the sealing elements of the packer.

The fundamental principle of the cluster model is the assumption that the sum of the relative volume fractions of two structural elements of a natural nanocomposite (loosely packed matrix and nanoclusters) is equal to one – $\varphi_{l.m.} + \varphi_{cl} = 1$. This approach is incorrect because it is violated when the nanoclusters are immersed in a loosely packed matrix. In this regard, a new relationship is proposed that relates the relative volume fractions of the loosely packed matrix and the part of nanoclusters immersed in it – $\varphi_{l.m.} + \hat{\varphi}_{cl} = 1$. Calculation formulas are obtained for the relative fractions of the loosely packed matrix and the interphase region.

The paper shows that such an assumption is unfounded due to the indispensable immersion of clusters in a loosely packed matrix, and in this regard, a new relationship is proposed linking the relative volume fractions of the loosely packed matrix and the part of nanoclusters immersed in it.

For a composite with a matrix, a mixture of synthetic butadiene nitrile and hydrogenated butadiene nitrile rubber and the addition of a copper nanoparticle, it is shown that in a natural nanocomposite, which is the polymer under study in an amorphous state, the time dependences of the relative volume fractions of the regions of inter-component adhesion and the loosely packed matrix coincide quite well with each other.

The application of the above relationship between the volume fractions of a loosely packed matrix and nanoclusters allows to reformulate the known equations of parallel and sequential micromechanical models, as well as the Kerner equation for a more complex micromechanical model used to describe the effect of strengthening the elastic modulus of nanocomposites

Keywords: cluster model, natural nanocomposite, interfacial region, inter-component adhesion, loosely packed matrix, nanoclusters

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IDENTIFYING OF THE MECHANISM FORMATION OF A NATURAL NANOCOMPOSITE IN POLYMER COMPOSITE MATERIALS

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1. Introduction

Among the modern methods of oil production intensification, various methods of influencing oil formations are of significant practical interest, which requires reliable operation of well equipment, primarily packers, which consist of a housing with a set of rubber seals and other components [1, 2]. This is especially important in connection with the transition to a new technology of deep and ultra-deep drilling, for which there was a need for sealing elements (SE) with high physical and mechanical properties.

As noted above, the object of research in this work is a packer – a device designed to disconnect two zones of the borehole and isolate the internal space of the production column from the impact of the borehole environment. The tightness of the packers is achieved thanks to sealing ele-

ments (SE), for the manufacture of which various rubbers based on butadiene-nitrile rubbers (BNC) are used.

In this work, a new composite with the composition: a mixture of synthetic butadiene nitrile and hydrogenated butadiene nitrile rubber (BNC+HBNC), vulcanizer, stabilizer, technological additives and copper nanoparticles was adopted as the material for the manufacture of the SE packer [3].

According to the cluster model, a mesh polymer consists of two components – a loosely packed (or, what is the same, weakly packed) matrix and nanoclusters, the latter playing the role of a nanofiller, and a loosely packed matrix – the role of a matrix of a natural nanocomposite. In [4], based on fractal estimates of the surface of nanoclusters, the dependence of the volume fraction of the loosely packed matrix on the temperature of the composite was found. It is shown that the dimensional effect of nanoclusters is identical to the

corresponding effect of dispersed filler in artificial polymer nanocomposites, namely, a decrease of the number of statistical segments in one cluster or the radius of clusters increases the degree of amplification (modulus of elasticity) of the artificial nanocomposite [5].

With the results of practical research, it can be concluded that increasing the service life of the packer sealing unit is determined by the correct choice of material for their manufacture, as well as the study of the formation of physical and mechanical properties is an important and urgent task. Therefore, studies aimed at identifying the mechanism of formation of clusters and loosely packed matrix in a natural nanocomposite have scientific significance.

2. Literary analysis and problem statement

In oil wells that are in the last stage of operation, the frequency of operations and impacts on the reservoir are increasing. Various methods are used to influence the oil reservoir, among which hydraulic fracturing occupies a special place [6]. This technology is used to increase the reservoir throughput [7]. With the multi-stage completion of hydraulic fracturing, the analysis of the production results after the operation of impact on the formation shows that production at different stages is very uneven, and up to 30 % may not be extracted at all due to a combination of geomechanical and design factors of hydraulic fracturing [8]. The authors [9] propose a data-driven model for optimizing hydraulic fracturing design, in which the workflow is essentially divided into two stages. As a result of the first stage, efforts to create a digital database of field data from several thousand multi-stage high-frequency operations on vertical, inclined and almost horizontal wells are summarized, and at the second stage, the optimal set of design parameters of hydraulic fracturing is selected to maximize production. This allows not to damage the well and increase the reservoir throughput and production levels. In [10], it is proposed to carry out a comprehensive technology for restoring the productivity of only wells with a wave hydromonitor, which is characterized by high efficiency.

It is known from the theory of operation of packer sealing elements that for reliable sealing of the inter-tube space, it is necessary that the contact stresses on the casing wall $\sigma_k > \sigma_p$ exceed the hydraulic fracturing pressure [11].

The authors [12] found that in order to reduce the reliability of the packer sealing assembly, it is necessary to use composite materials filled with metal nanoparticles for their manufacture. In their research, the authors achieved an improvement in their performance by regulating the structure of sealing elements. However, their behavior in various environments, including sandy, chemical, corrosion-active, etc., is not specified.

In [13], the authors conducted research in two directions in order to improve the physical and mechanical characteristics of sealing elements: constructive and technological. By adjusting the structural changes, the strength and deformability of the sealing elements are increased. There are three types of rubber with an optimal design that allows uniform distribution of contact voltage with different wall thicknesses.

Composite materials based on polytetrafluoroethylene (PTFE) have been widely used in sealing devices, combining high rates of deformation-strength, tribotech-

nical, physico-chemical and thermophysical characteristics that favorably distinguish them from other types of polymer composite materials. The authors [14] introduced a polymer matrix of various fillers-modifiers: fibrous, dispersed, metallic and other materials, significantly affect the formation of structuring in the material and achieved a significant increase in wear resistance and physico-mechanical properties of the resulting polymer composite materials. However, there is no unambiguous answer about their behavior in oil and chemical environments, which makes it difficult to use them in these industries.

Thus, research in the field of improving the reliability and durability of the packer sealing unit is relevant and requires extensive research in both structural and materials science areas.

3. The aim and objectives of the study

The aim of the study is to identifying the mechanism of formation of clusters and a loosely packed matrix in a natural nanocomposite formed in the amorphous state of polymers with a description of the effect of strengthening the elastic modulus of the nanocomposite as a whole for the manufacture of packer sealing elements.

To achieve this aim, the following objectives are accomplished:

- to establish the main causes of packer parts failures and develop recommendations on the choice of composite material for the manufacture of packer sealing elements;
- to study the process of structure formation in a nanocomposite and the nature of deformation of a loosely packed matrix and tightly packed nanoclusters.

4. Materials and methods of research

As noted above, the sealing elements of the packer were accepted as the object of research. For their manufacture, a composite material, where the matrix is a mixture of synthetic butadiene nitrile and hydrogenated butadiene nitrile rubber (BNR+HBNR) and filler – nanomedium.

It is known [10] that rubbers based on butadiene-nitrile rubbers are used in the manufacture of sealing elements of oil and gas field equipment. Currently, more than 20 brands of this elastomer with various properties are produced. Their bearing properties are determined by the ratio of acrylonitrile (NAC) and butadiene (DB). NAC affects the glass transition temperature and wear resistance. To impart specific properties, BNCs are carboxylated [11].

In order to give the composite material a high resistance, hydrogenated butadiene nitrile rubber (HBNA) was included in the composite matrix. The method of peroxide vulcanization was adopted for crosslinking the selected elastomers [12]. A nanomedium with dimensions of 60–80 nm was added to the composition of the second position.

Determination of the physical and mechanical characteristics of the composite material was carried out:

- GOST 4651-2014 (ISO 604:2002) Plastics. Compression test method; GOST 12020 Plastics. Methods for determining resistance to chemical media; GOST 15139 Plastics. Methods for determining density; GOST 15173 Plastics. Method for determining the average coefficient of linear thermal expansion; GOST 32658-2014 (ISO 14129:1997)

Polymer composites. Determination of mechanical characteristics during shear in the reinforcement plane by tensile testing at an angle=45°.

5. Results of research on the choice of composite material for sealing elements and the process of structure formation in nanocomposite

5.1. Results of the study on the choice of composite material and for sealing elements of the packer

Table 1 shows the results of monitoring to establish the main causes of packer failures at 100 oil wells for 2020–2022.

Table 1

The main reasons for packer failures

Reasons for packer failures	Years		
	2020	2021	2022
Damage to sealing elements (cuffs)	65	67	64
Clutch mechanism failure (failure of the dies of the lower and upper anchoring node)	28	30	30
Damage to threaded surfaces	5	3	4
Other	2	–	2

As can be seen from the analysis of the data given in Table 1, most of the package failures are associated with the failure of their sealing elements. Therefore, one of the directions of research was related to the choice of the material of sealing cuffs.

As a material for the manufacture of sealing elements of the packer, a composite material was adopted, where the matrix is a mixture of synthetic butadiene nitrile and hydrogenated butadiene nitrile rubber (BNR+HBNR). The composition of the composite material is shown in Table 2.

Table 2

Composition of the composition selected for the study.

Name of indicators	Composition of prototypes, %		
	K-1	K-2	K-3
Matrix (BNC+BNC)	30/34	32/32	34/30
The mass fraction of the antioxidant	1.0	1.0	1.0
m isooctane-toluene vulcanizer	30	30	30
Carbon black	1.5	1.5	1.5
Stabilizer (Novantox)	1.0	1.0	1.0
Technological additive (Softener PC-1)	1.5	1.5	1.5
Nanoparticle	1.0	1.0	1.0

The following components were included in the structure of the composite material: a mixture of synthetic butadiene-nitrile and hydrogenated butadiene-nitrile rubber (BNR+HBNR), vulcanizer, stabilizer, technological additives and copper and iron nanoparticles. The content of acrylic acid nitrile (NACL) in nitrile butadiene rubber was 17–19 %.

It has been experimentally established that a composite material with a formulation corresponding to K-1 is characterized by high physico-mechanical and elastic properties, as well as increased resistance of rubbers to aggressive media, which makes it possible to use it as a material for the manufacture of sealing elements for packers. The factor of

nanoparticles in the composite material contributes to the formation of a stable structure with increased characteristics.

5.2. Results of the study of the process of structure formation in nanocomposite

In the field of elastic deformation in the form of a loosely packed matrix and inelastic (plastic) deformations in the form of tightly packed nanoclusters, as well as clarifying the relationship linking the relative volumetric roles of the structural elements of a natural nanocomposite, taking into account the immersion of part of the clusters in the matrix and based on a new relationship between the above fractions, within the fractal approach, corresponding expressions for the equations of parallel and sequential micromechanical models are obtained.

To describe the structural features of the nanocomposite under study, a cluster model of the structure of the amorphous state of polymers was used [4]. This model assumes that in the amorphous state of the polymer, along with a grid of macromolecular “entanglements”, there is a cluster mesh of meshes consisting of regions of local order (clusters) immersed in a loosely packed (or, what is the same, loosely packed) matrix. A schematic representation of the cluster structure of the amorphous state of polymers is given in Fig. 1.

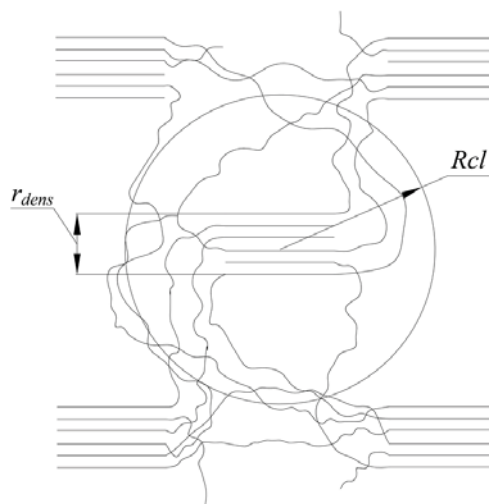


Fig. 1. Schematic representation of the cluster structure of the amorphous state of polymers [5]

The relationship between the concepts of “local order” and “fractality” in the case of glassy-like polymers has fundamental physical foundations and is expressed by analytical relations [4]:

$$d_f = 3 - 6.44 \times 10^{-10} \left(\frac{\varphi_{cl}}{SC_\infty} \right)^{1/2}, \tag{1}$$

or

$$d_f = 3 - 6.44 \times 10^{-10} (l_0 v_{cl})^2. \tag{2}$$

Here d_f – the fractal dimension of the polymer; φ_{cl} – the volume fraction of clusters; S – the cross-sectional area of the macromolecule, l_0 – the length of the skeletal bond of the chain, C_∞ – the characteristic ratio, which is an indicator of the statistical flexibility of the polymer chain and is determined from the ratio $T_g = 129(S/C_\infty)^{1/2}$ where T_g – the

glass transition temperature of the polymer matrix, v_{cl} – the density of the cluster grid of macromolecular meshes:

$$v_{cl} = \frac{\Phi_{cl}}{C_{\infty} \cdot I_0 \cdot S}. \quad (3)$$

The interpretation of the amorphous state of polymers as natural nanocomposites is associated with a very important problem of adhesion loosely packed matrix nanoclusters (inter-component adhesion). In a natural nanocomposite, there are the following main types of dependences of the degree of reinforcement $E_c/E_m(\Phi_{cl})$ (where E_c and E_m are the elastic modulus of the composite and matrix polymer) on the degree of filler Φ_n , characterizing the inter-component adhesion [6]:

1) ideal adhesion between the polymer matrix and the filler, described by the Kerner equation:

$$\frac{E_c}{E_m} = 1 + 11,6 \cdot \Phi_n - 44,4 \cdot \Phi_n^2 + 96,3 \cdot \Phi_n^3, \quad (4)$$

provided $E_c = E_m$, $E_m = E_{l.m.}$ and $\Phi_n = \Phi_{cl}$ where E_m and $E_{l.m.}$ are the elastic modulus of a poly-dimensional matrix and a loosely packed matrix in a natural nanocomposite, Φ_{cl} – is the relative volume fraction of nanoclusters in the polymer matrix.

2) zero adhesive strength at a high coefficient of friction between the filler and the polymer matrix, described by the equation:

$$\frac{E_c}{E_m} = 1 + \Phi_n. \quad (5)$$

3) complete absence of interaction and perfect slippage between the filler and the matrix in the case when the elastic modulus of the composite is determined by the cross-section of the polymer matrix and E_c is related to the degree of filling by the equation:

$$\frac{E_c}{E_m} = 1 - \Phi_n^{2/3}. \quad (6)$$

Dependencies (4) and (5) are called perfect adhesion and strong friction. In relation to natural composites, formulas (4)–(6) assume $E_c = E_m$, $E_m = E_{l.m.}$ and $\Phi_n = \Phi_{cl}$ and write them as:

$$\frac{E_m}{E_{l.m.}} = 1 + 11,6 \cdot \Phi_{cl} - 44,4 \cdot \Phi_{cl}^2 + 96,3 \cdot \Phi_{cl}^3, \quad (7)$$

$$\frac{E_m}{E_{l.m.}} = 1 + \Phi_{cl}, \quad (8)$$

$$\frac{E_m}{E_{l.m.}} = 1 - \Phi_{cl}^{2/3}. \quad (9)$$

To describe the modulus of elasticity (or the degree of amplification) of natural nanocomposites, two of the simplest models (parallel and sequential) are used [6] to describe the modulus of elasticity of natural composites (polymers), giving the upper and lower bounds of this parameter [7]. The parallel model is defined as:

$$E_m = E_{cl} \cdot \Phi_{cl} + E_{l.m.} \cdot \Phi_{l.m.}, \quad (10)$$

and the sequential model is like:

$$E_m = \frac{E_{cl} \cdot E_{l.m.}}{E_{cl} \cdot \Phi_{l.m.} + E_{l.m.} \cdot \Phi_{cl}}. \quad (11)$$

At comparable values E_m and $E_{l.m.}$ for a glassy-like loosely packed matrix, parallel stress transfer is realized through both structural components of a natural nanocomposite, and for a non-glazed loosely packed matrix ($E_m = E_{l.m.}$ at $E_{l.m.} \rightarrow 0$), only sequential stress transfer through nanoclusters is possible.

In most works on natural nanocomposites, the assumption is accepted:

$$\Phi_{l.m.} + \Phi_{cl} = 1, \quad (12)$$

where $\Phi_{l.m.}$ and Φ_{cl} is understood to be the relationships, $\Phi_{l.m.} = V_{cl}/V_m$, and $V_m = V_{l.m.} + V_{cl}$. Equality (12) is obviously violated when nanoclusters are immersed in a loosely packed matrix. Clarification of the relationship between the volume fractions of structural elements of amorphous glassy polymers, considered as natural nanocomposites, will be given at the end of this section. It follows from assumption (12) that:

$$\Phi_{l.m.} = 1 - \Phi_{cl}. \quad (13)$$

Then formulas (10) and (11) take a known form of writing (for example [6]):

$$E_m = E_{cl} \cdot \Phi_{cl} + E_{l.m.} \cdot (1 - \Phi_{cl}), \quad (14)$$

$$E_m = \frac{E_{cl} \cdot E_{l.m.}}{E_{cl} (1 - \Phi_{cl}) + E_{l.m.} \cdot \Phi_{cl}}. \quad (15)$$

The paper [6] uses a more complex micromechanical model of Takayanagi that more complex than (10) and (11), which allows an empirical description of the response of the composite to mechanical action:

$$\frac{G_c}{G_m} = \frac{\Phi_m \cdot G_m + (\alpha + \Phi_n) \cdot G_n}{(1 + \alpha \Phi_n) G_m + \alpha \cdot \Phi_m \cdot G_n}, \quad (16)$$

where, G_c , G_m and G_n are the shear modules of the composite, polymer matrix Φ_m and filler, respectively; and Φ_n are the relative volume fractions of the polymer matrix and filler, respectively; α – fitting parameter. A generalization of the Takayanagi model is the Kerner equation, which is identical to relation (17), but for it the parameter α is not a fitting one and is defined as:

$$\alpha_m = \frac{2(4 - 5\nu_m)}{(7 - 5\nu_m)}, \quad (17)$$

where α_m and ν_m – the parameter and the Poisson's ratio for the polymer matrix. To apply equations (16) and (17) in the case of natural nanocomposites, one should take $G_c = G_m$, $G_m = G_{l.m.}$, $G_n = G_{cl}$; where, G_m , $G_{l.m.}$ and G_{cl} are the shear modules of the polymer, loosely packed matrix and nanoclusters, respectively; and $\Phi_n = \Phi_{cl}$. The corresponding shift modules are calculated according to the expression [8]:

$$G = \frac{E}{d_f}, \quad (18)$$

where d_f – the corresponding fractal dimension.

However, the calculation according to equations (16) and (17) does not give a good correspondence with the experiment. Taking into account the fact that in the Kerner equation with the parameter it is α_m usually assumed that the nominal concentration scale differs from the mechanically effective fraction of the filler φ_n^{ef} (φ_{cl}^{ef} in the case of a natural nanocomposite), the above ratio (16) can be written as follows [9]:

$$\varphi_{cl}^{ef} = \frac{(G_m - G_{l.m.})(G_{l.m.} + \alpha_{l.m.} G_{cl})}{(G_{cl} - G_{l.m.})(G_{l.m.} + \alpha_{l.m.} G_n)} \quad (19)$$

The value $\alpha_{l.m.}$ is determined according to equation (17), assuming $\alpha = \alpha_{l.m.}$ and $v_m = v_{l.m.}$, the estimate of the Poisson's ratio of the loosely packed matrix $v_{l.m.}$ is calculated from known values according $d_f^{l.m.}$ to equation [4]:

$$d_f = (d - 1)(1 + v), \quad (20)$$

assuming $d_f = d_f^{l.m.}$, $v = v_{l.m.}$.

The relative volume fraction of the interphase region in a composite φ_{iph} consisting of a matrix and a filler is determined by the expression [12]:

$$\varphi_{iph} = \frac{D_{sp} + 2.55d_n - 7.10}{4.18}, \quad (21)$$

where D_{sp} – the fractal dimension of the space (analogous to a fractal lattice in computer modeling) in which the matrix structure is formed, d_n – the fractal dimension of the surface of filler particles. When applied to a natural nanocomposite, D_{sp} is a dimension of the fractal space in which the nanocluster structure is formed and φ_{iph} is determined by the interfacial (intercomponent) region between the loosely packed matrix and nanoclusters. Since the formation of the nanocluster structure occurs in a loosely packed matrix below the glass transition temperature of the polymer T_c [13] during the curing of the crosslinking agent/oligomerin mixture, the fractal dimension of the loosely packed matrix $d_f^{l.m.}$ can be considered as D_{sp} in (21), which can be calculated according to the rule of mixtures $d_f^{l.m.}$ (the calculation formula for $d_f^{l.m.}$ will be given in the next section), i. e. $D_{sp} = d_f^{l.m.}$.

To calculate the fractal dimension of the surface of nanoclusters $d_n = d_f^{cl}$, the method [6] is used, according to which $d_n = d_f^{cl}$ it is calculated using the following equation:

$$S_u = 5270 \cdot r_{cl}^{d_f^{cl} - d}, \quad (22)$$

where S_u – the specific surface of the nanocluster, r_{cl} – its radius, d – the dimension of the Euclidean space in which the fractal is considered (in our case $d=3$):

$$S_u = \frac{G}{\rho_{cl} D_{cl}}, \quad (23)$$

where $D_{cl} = 2r_{cl}$ – the diameter of the cluster, ρ_{cl} is the density of the nanocluster. The radius r_{cl} of the nanoclass is determined according to the equation:

$$r_{cl} = [FS / (2\pi\eta)]^{1/2},$$

where S – the cross-sectional area of the polymer macromolecule; η is the packing coefficient, which in the case of dense

packing is 0.868; F – the functionality of the cluster (the number of chains coming out of it), determined by the equation:

$$F = 43 \cdot \frac{v_{cl}}{l_0 \cdot S} \cdot C_{\infty}^2, \quad (24)$$

where v_{cl} – the density of the cluster grid of macromolecular meshes. Taking into account equality $v_{cl} = \varphi_{cl} / (C_{\infty} l_0 S)$, formula (24) is written as:

$$F = 43 \cdot \frac{\varphi_{cl}}{(l_0 \cdot S)^2} \cdot C_{\infty}. \quad (25)$$

The process of fluidity of glassy-like polymers is realized in densely packed regions [14], these densely packed regions are precisely clusters [13]. The process of fluidity in polymers is unambiguously associated with the loss of stability by clusters in the shear stress field and it is realized in densely packed regions of the polymer structure [5]. Within the framework of the fractal concept of plasticity, the value of the Poisson's ratio v_{fl} at the point of fluidity can be estimated as [15]:

$$v_{fl} = v \cdot \chi + 0.5(1 - \chi), \quad (26)$$

where v – the value of the Poisson's ratio in the field of elastic deformations, χ – the relative fraction of the elastically deformed polymer. Experimental comparison of the values χ and $\varphi_{l.m.}$ for amorphous glassy-like polymers also showed their good correspondence [4].

So, a loosely packed matrix can be identified as an area of elastic deformation, and clusters as an area of inelastic (plastic) deformations, and that inelastic deformation processes occur in areas of dense packing of amorphous glassy-like polymers. According to the model of two-stage glass transition of polymers [5], loosely packed regions (in the cluster model, this is a loosely packed matrix) are non-glassy formed at a temperature $T'_g = T_g - 50K$, where T_g is the glass transition temperature. But the nonglossy form of a loosely packed matrix is only a consequence, and not a criterion for the implementation of the fluidity process. A sufficient condition for the fluidity of amorphous glassy-like polymers is the loss of stability of local order regions in the field of external mechanical stress. This conclusion can be reached [4] on the basis of the above description of the implementation of the fluidity process of amorphous glassy-like polymers, taking into account the approximate equality:

$$\chi \cong \varphi_{l.m.} \quad (27)$$

The structure of mesh polymers is modeled by a set of a large number of Witten-Sander clusters with a fractal dimension of each approximately equal to 2.5 [5]. For each class of mesh polymers, there is a boundary value $D_{sp} = D_{sp}^{bn}$ corresponding to a change in the mechanism of formation of the structure of a loosely packed polymer matrix according to the model of diffusion-limited aggregation – from the mechanism of DOA P-Cl (particle-cluster) occurring at $D_{sp} > D_{sp}^{bn}$, to the mechanism of DOA Cl-Cl (cluster-cluster), at $D_{sp} < D_{sp}^{bn}$ [6]. Consequently, with a sufficiently high density of chemical crosslinking (lower values D_{sp}), the formation of the structure of the loosely packed matrix occurs not by joining statistical segments, but by combining

groups of these segments. The inequality $D_{sp} < D_{sp}^{bn}$ implies the formation of discontinuities or defects (breachs) in the structure of the loosely packed matrix. The formation of such discontinuities (and, therefore, the magnitude D_{sp}) is affected by both the application of pressure and the type of crosslinking agent).

The cluster model of the amorphous state of the polymer assumes that in this state the polymer is divided into a loosely packed matrix and nanoclusters immersed in it. This means that the elastic part of the polymer coincides completely with the loosely packed matrix, since nanoclusters are an inelastic part of the matrix. Therefore, the parameter χ in equality (26) coincides with the value $\varphi_{l.m.}$ and this equality will be written as:

$$v_{fl} = v \cdot \varphi_{l.m.} + 0,5(1 - \varphi_{l.m.}). \quad (28)$$

It is shown that using the relation (28) it is possible to find $\varphi_{l.m.}$ the dependence of the magnitude $\varphi_{l.m.}$ on the fractal dimension of the matrix d_f^m . From (18) and the equation for the critical shear stress, which in the case of polymer fluidity is written as [4]:

$$\tau_{cr} = G / (\pi\sqrt{3}), \quad (29)$$

it follows:

$$\tau_{cr.fl} = \frac{E_{fl}}{\pi\sqrt{3} \cdot d_f^{l.m.}}. \quad (30)$$

Taking into account the general relationship between the normal stress σ and the shear stress $\tau = \sigma / \sqrt{3}$ from (30) obtain the equation:

$$\sigma_T = \frac{E_{fl}}{\pi \cdot d_f^{l.m.}}. \quad (31)$$

From (31) and the equation for the Poisson's ratio [9]:

$$\frac{\sigma_{fl}}{E_{fl}} = \frac{1 - 2\nu_{fl}}{6(1 + \nu_{fl})}, \quad (32)$$

where ν_{fl} is the Poisson's ratio of the polymer matrix at the point of flow, follows:

$$\frac{1 - 2\nu_{fl}}{6(1 + \nu_{fl})} = \frac{1}{\pi \cdot d_f^m}. \quad (33)$$

Solving equation (33) with respect to ν_{fl} , let's find:

$$\nu_{fl} = \frac{\pi \cdot d_f^m}{2(3 + \pi d_f^m)}. \quad (34)$$

From the equation $d_f^m = (d - 1)(1 + \nu_f)$ (ν_f Poisson's ratio for the polymer) let's find:

$$\nu_f = \frac{d_f^m}{d - 1} - 1. \quad (35)$$

Then from (28), (34), (35) let's obtain the equation:

$$\frac{\pi \cdot d_f^m - 6}{2(3 + \pi \cdot d_f^m)} = \left(\frac{d_f^m}{d - 1} - 1 \right) \cdot \varphi_{l.m.} + 0,5(1 - \varphi_{l.m.})\nu_{fl}, \quad (36)$$

solving which is $\varphi_{l.m.}$ relative, let's find the dependence $\varphi_{l.m.}$ on d_f^m :

$$\varphi_{l.m.} = \frac{1}{1,5 - \frac{d_f^m}{d - 1}} \left[\frac{\pi \cdot d_f^m - 6}{2(3 + \pi \cdot d_f^m)} + 0,5 \right]. \quad (37)$$

Equality (12), as mentioned above, is valid only if there is no immersion of clusters in a loosely packed matrix. In the case when the clusters are immersed in a loosely packed matrix, the volume of the matrix V_m is represented as a sum $V_m = V_{l.m.} + V_{cl}$, where $V_{l.m.}$ and V_{cl} is the volume of the loosely packed matrix and parts of the nanoclusters not loaded into the loosely packed matrix and located outside it. Then by introducing the notation $\varphi_{l.m.} = \frac{V_{l.m.}}{V_m}$, $\hat{\varphi}_{cl} = \frac{V_{cl}}{V_m}$, let's obtain an obvious equality:

$$\varphi_{l.m.} + \hat{\varphi}_{cl} = 1, \quad (38)$$

what is a refinement of the relationship between the volume fractions of the loosely packed matrix and nanoclusters in the amorphous state of the polymer matrix, considered as a natural nanocomposite.

From the mixture equation:

$$d_f^m = d_f^{l.m.} \cdot \varphi_{l.m.} + d_f^{cl} (1 - \varphi_{l.m.}), \quad (39)$$

let's define the fractal dimension of the loosely packed matrix:

$$d_f^{l.m.} = \frac{1}{\varphi_{l.m.}} [d_f^m - d_f^{cl} (1 - \varphi_{l.m.})]. \quad (40)$$

Usually, the fractal dimension of a nanocluster, due to their dense packaging, is assumed to be equal to the fractal dimension of real solids, i. e. $d_f^{cl} = 2.95$. The value $d_f^{l.m.}$ calculated by formula (40) is taken into account as the value of the value $d_f^{l.m.}$ in formula (21) for φ_{iph} .

Taking into account the equality of (38), formulas (14) and (15) take the form, respectively:

$$E_m = E_{cl} \cdot \varphi_{cl} + E_{l.m.} \cdot \varphi_{l.m.}, \quad (41)$$

$$E_m = \frac{E_{cl} \cdot E_{l.m.}}{E_{cl} \cdot \varphi_{l.m.} + E_{l.m.} \cdot \varphi_{cl}}. \quad (42)$$

Taking into account the equality of (38), formulas (14) and (15) take the corresponding form:

$$E_m = E_{cl} \cdot \varphi_{cl} + E_{l.m.} \cdot \varphi_{l.m.}, \quad (43)$$

$$E_m = \frac{E_{cl} \cdot E_{l.m.}}{E_{cl} \cdot \varphi_{l.m.} + E_{l.m.} \cdot \varphi_{cl}}, \quad (44)$$

where $\varphi_{l.m.} = 1 - \hat{\varphi}_{cl}$.

Fig. 2 shows a comparison the dependences of the fractions of the interphase (inter-component) region φ_{iph} and the loosely packed matrix $\varphi_{l.m.}$ on the test temperature T for the cross-linked polymer under consideration, calculated according to forms (21) and (38), respectively.

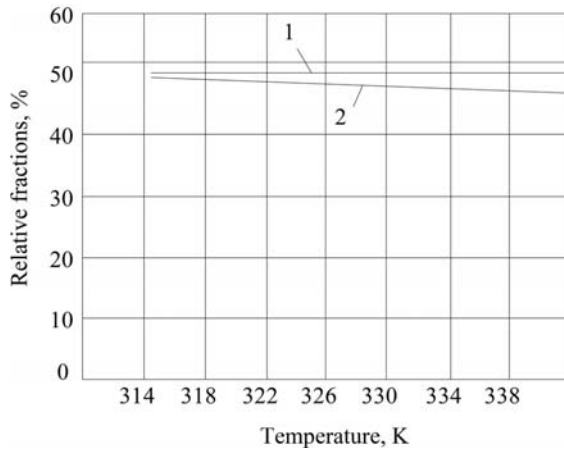


Fig. 2. Dependence of relative fractions on polymer temperature: 1 – loosely packed matrix; 2 – interfacial region

6. Discussions of the results of studies of the cluster model of the nanocomposite

According to the results of the analysis of the operating conditions of packers and the main causes of their failures, it was found that the failure of sealing elements is dominant and amounts to approximately 65–67 %. The reason is both design flaws and non-improvement of the technology of their manufacture of sealing elements, as well as the composition of the composite material.

It has been experimentally established that a composite material with a formulation corresponding to K–1 is characterized by high physico-mechanical, chemical and elastic properties. The presence of nanoparticles contributes to the formation of a stable structure with increased characteristics.

It is shown that a mixture of synthetic butadiene-nitrile and hydrogenated butadiene-nitrile rubber (NBR+HBNR) filling with nanoparticles contributes to an increase in the physical and mechanical characteristics of the sealing elements of the packer.

Studies have established that (Fig. 2) there is a good correspondence between the values $\varphi_{l.m.}$ and φ_{iph} , since the discrepancy between the graphs of the functions $\varphi_{l.m.}(T)$ and $\varphi_{iph}(T)$ does not exceed the measurement error. For comparison, let's note that under the condition $\varphi_{l.m.} + \varphi_{cl} = 1$ on the example of polycarbonate (PC), the average discrepancy between $\varphi_{l.m.}$ and φ_{cl} was 7 % [4, 5], and under the same condition on the example of polymer ED-20/BSK, this discrepancy was about 5 %. Consequently, it can be stated with great certainty that in a natural composite, which is considered polymer, there are no interfacial regions and regions structurally different from the loosely packed matrix, except for the natural presence of nanoclusters. In addition, the relative volume fractions of the loosely packed matrix $\varphi_{l.m.}$ and the part of the nanoclusters immersed in it $\hat{\varphi}_{cl}$ are related by the ratio (40), which plays an essential role in determining the relative volume fraction $\varphi_{l.m.}$ and fractal dimension $d_f^{l.m.}$ of the loosely packed matrix.

The results of the study of the cluster model of a natural nanocomposite are:

- it is shown that the loosening of a loosely packed matrix at a temperature of $T_c' = T_c - 50K$ (T_c is the glass transition temperature of the polymer) is only a consequence, and not a criterion for the implementation of the fluidity

process, and that a sufficient condition for the fluidity of amorphous glassy polymers is the loss of stability of local order regions (nanoclusters) in the field of external mechanical stress;

- is normally used for natural nanocomposite ratio $\varphi_{p.m.} + \varphi_{cl} = 1$, where $\varphi_{p.m.}$ and φ_{cl} refers to the relationship $\varphi_{p.m.} = V_{p.m.}/V_m$, $\varphi_{cl} = V_{cl}/V_m$, $V_m = V_{p.m.} + V_{cl}$ is encouraged to correct the ratio $j_{p.m.} + \hat{V}_{cl} = 1$, where $\varphi_{p.m.} = V_{p.m.}/V_m$, $\hat{\varphi}_{cl} = \hat{V}_{cl}/V_m$, \hat{V}_{cl} – the volume of the part of clusters not loaded into the matrix;

- in accordance with the proposed fractal approach to the description of the mechanism of formation of a natural nanocomposite in the amorphous state of glassy polymers, using the example of BNR/HBNR, it is shown that in the natural nanocomposite, which is the polymer under study, the time dependences of the relative volume fractions of the regions of inter-component adhesion, φ_{mf} and the loosely packed matrix, $\varphi_{p.m.}$, coincide approximately with the measurement error of the data.

The paper shows that the process of fluidity of glassy polymers forming densely packed regions in the form of clusters in the amorphous state is associated with the loss of cluster stability when the stress in the natural nanocomposite reaches the macroscopic yield strength σ_T . As a result, at a temperature of $T_c = T_c - 50K$ (T_c is the glass transition temperature of the polymer), a mechanical interpretation of the loosely packed matrix occurs within the framework of the two-stage polymer glass transition model. Beyond the yield point, a plateau of forced elasticity (cold flow) begins, associated with the deformation of the uncovered loosely packed matrix, in which clusters seem to “float”. In the theory of rubber high elasticity, in which the behavior of a mesh polymer on a cold flow plateau is well described, the grid of stable clusters is preserved and only the decay of unstable clusters occurs, which determines the loosening of the loosely packed matrix.

The formation of the nanocluster structure of a natural nanocomposite is realized only in the fractal space created by the loosely packed matrix. The dimension of this space D_{sp} is affected by the crosslinking density. This influence is not unambiguous and is determined by the aggregation mechanism.

It should be noted that the formula (21) used in the work for the relative volume fraction of the interfacial region $\varphi_{p.m.}$ in a nanocomposite consisting of a loosely packed matrix and nanoclusters relies on information about the maximum possible value of the elastic modulus of this nanocomposite in order to obtain the maximum possible value of the elastic modulus of this nanocomposite. the modulus of elasticity of a natural nanocomposite E_n . To obtain such information, it is necessary to develop a polymer structure with a higher D_{sp} size, which to some extent limits the range of the formula (21).

The generally accepted opinion that the stitching density increases is incorrect. The prospect of developing an approach to describing the mechanism of formation of the structure of a natural nanocomposite is associated with a deeper study of the fractal mechanics of polymers and requires the use of mathematical and physical modeling of the process.

7. Conclusions

1. It is shown that the most vulnerable elements of packers are sealing elements used to seal the well and differ in the

failure rate. The main reasons for failures of sealing elements are design flaws, not improving the technology of their manufacture, as well as the composition of the composite material. A new composite material is proposed: a mixture of synthetic butadiene-nitrile and hydrogenated butadiene-nitrile rubber (BNR+HBNR), vulcanizer, stabilizer, technological additives and copper nanoparticles, which is highly effective for the manufacture of packer sealing elements.

2. In contrast to the cluster model of the amorphous state of glassy polymers, the polymer structure is considered as a natural nanocomposite, in which a loosely packed matrix plays the role of a matrix polymer, and nanoclusters play the role of a filler. It is assumed that the sum of the relative volume fractions of these two structural elements is equal to one, which is not correct. A new relation is proposed that relates the relative volume fractions of a loosely packed matrix and a part of nanoclusters immersed in it. In accordance with the proposed approach to the description of the cluster model of a natural nanocomposite, calculation formulas for the relative fractions of a loosely packed matrix and an interfacial region characterizing the inter-component adhesion between the constituent elements of the structure are obtained, and expressions for parallel and sequential models in the case of a natural nanocomposite, nanocomposites are reformulated. It is shown that in a natural nanocomposite, the

temperature dependences of the relative volume fractions of the regions of inter-component adhesion and loosely packed matrix approximately coincide with the measurement error of the data. Thus, it can be stated with great confidence that in a natural nanocomposite there are no interfacial regions and regions structurally different from a loosely packed matrix, except for the natural presence of nanoclusters in it.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

Data will be made available on reasonable request.

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