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POLYMERS AS NATURAL COMPOSITES: STRUCTURE AND PROPERTIES

Ключевые слова: структура, свойства, природные композиты, полимеры, модели, полукристаллы, механизм, компоненты, гибридные полимерные системы.

Аннотация Приведенные в настоящей статье результаты дают чисто практический аспект таких теоретических понятий, как кластерная модель структуры аморфного состояния полимеров и применений фрактального анализа для описания структуры и свойств полимеров, рассматриваемых как натуральные нанокompозиты. Целенаправленное создание необходимых наноструктур позволит получать полимеры, не уступающие (и даже превосходящие) по своим свойствам композиты, полученные на их основе. "Бесструктурные" (бездефектные) полимеры являются наиболее перспективными в этом отношении. Такие полимеры могут быть естественной заменой для большого количества разработанных в настоящее время полимерных нанокompозитов. Применение "бесструктурных" полимеров в качестве искусственных нанокompозитных полимерных матриц может дать гораздо больший эффект. Такой подход позволяет получать полимерные материалы, сравнимые по своим характеристикам с металлами (например, алюминием).

Keywords: structure, properties, natural composites, polymers, models, semicrystalline, mechanism, components, hybride polymer systems.

The stated in the present article results give purely practical aspect of such theoretical concepts as the cluster model of polymers amorphous state structure and fractal analysis application for the description of structure and properties of polymers, treated as natural nanocomposites. The necessary nanostructure goal-directed making will allow to obtain polymers, not yielding (and even exceeding) by their properties to the composites, produced on their basis. Structureless (defect-free) polymers are imagined the most perspective in this respect. Such polymers can be natural replacement for a large number of elaborated at present polymer nanocomposites. The application of structureless polymers as artificial nanocomposites polymer matrix can give much larger effect. Such approach allows to obtain polymeric materials, comparable by their characteristics with metals (for example, with aluminium).

The idea of different classes polymers representation as composites is not new. Even 35 years ago Kardos and Raison [1] offered to use composite models for the description of semicrystalline polymers properties number and obtained prediction of the indicated polymers stiffness and thermal strains to a precision of $\pm 20\%$. They considered semicrystalline polymer as composite, in which matrix is the amorphous and the crystallites are a filler. The authors [1] also supposed that other polymers, for example, hybride polymer systems, in which two components with different mechanical properties were present obviously, can be simulated by a similar method.

In paper [2] it has been pointed out, that the most important consequence from works by supramolecular formation study is the conclusion, that physical-mechanical properties depend in the first place on molecular structure, but are realized through supramolecular formations. At scales interval and studies methods resolving ability of polymers structure the nanoparticle size can be changed within the limits of $1\div 100$ and more nanometers. The polymer crystallites size makes up $10\div 20$ nm. The macromolecule can be included in several crystallites, since at molecular weight of order of 6×10^4 its length makes up more than 400 nm. These reasonings point out, that macromolecular formations and polymer systems in virtue of their structure features are always nanostructural systems.

However, in the cited above works the amorphous glassy polymers consideration as natural composites (nanocomposites) is absent, although they are one of the most important classes of polymeric materials. This gap reason is quite enough i.e. polymers amor-

phous state quantitative model absence. However, such model appearance lately [3-5] allows to consider the amorphous glassy polymers (both linear and cross-linked ones) as natural nanocomposites, in which local order regions (clusters) are nanofiller and surrounded them loosely-packed matrix of amorphous polymers structure is matrix of nanocomposite. Proceeding from the said above, in the present chapter description of amorphous glassy polymers as natural nanocomposites, their limiting characteristics determination and practical recommendation by the indicated polymers properties improvement will be given.

1. Natural Nanocomposites Structure

The synergetics principles revealed structure adaptation mechanism to external influence and are universal ones for self-organization laws of spatial structures in dynamical systems of different nature. The structure adaptation is the reformation process of structure, which loses stability, with the new more stable structure self-organization. The fractal (multifractal) structure, which is impossible to describe within the framework of Euclidean geometry, are formed in reformation process. A wide spectrum of natural and artificial topological forms, the feature of which is self-similar hierarchically organized structure, which amorphous glassy polymers possessed [6], belongs to fractal structures.

The authors [7, 8] considered the typical amorphous glassy polymer (polycarbonate) structure change within the frameworks of solid body synergetics.

The local order region, consisting of several densely-packed collinear segments of various polymer chains (for more details see previous paper) according

to a signs number should be attributed to the nanoparticles (nanoclusters) [9]:

- 1) their size makes up 2÷5 nm;
- 2) they are formed by self-assemble method and adapted to the external influence (for example, temperature change results to segments number per one nanocluster change);
- 3) the each statistical segment represents an atoms group and boundaries between these groups are coherent owing to collinear arrangement of one segment relative to another.

The main structure parameter of cluster model-nanoclusters relative fraction ϕ_{cl} , which is polymers structure order parameter in strict physical sense of this term, can be calculated according to the equation (see previous paper). In its turn, the polymer structure fractal dimension d_f value is determined according to the equations (see previous paper).

In Fig 1. the dependence of ϕ_{cl} on testing temperature T for PC is shown, which can be approximated by the broken line, where points of folding (bifurcation points) correspond to energy dissipation mechanism change, coupling with the threshold values ϕ_{cl} reaching. So, in Fig. 1. T_1 corresponds to structure “freezing” temperature T_0 [4], T_2 to loosely-packed matrix glass transition temperature T_g [11] and T_3 to polymer glass transition temperature T_g .

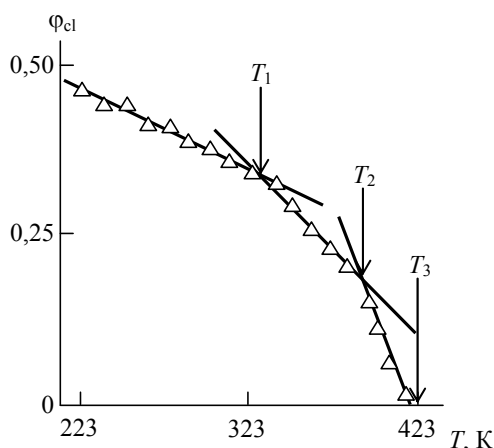


Fig. 1 - The dependence of nanoclusters relative fraction ϕ_{cl} on testing temperature T for PC. The critical temperatures of bifurcation points are indicated by arrows (explanations are given in the text) [18]

Within the frameworks of solid body synergetics it has been shown [12], that at structures self-organization the adaptation universal algorithm [12] is realized at transition from previous point of structure instability to subsequent one. The value $m = 1$ corresponds to structure minimum adaptivity and $m = m^*$ to maximum one. In paper [12] the table is added, in which values A_m , m and Δ_i are given, determined by the gold proportion rule and corresponding to spectrum of structure stability measure invariant magnitudes for the alive and lifeness nature systems. The indicated table usage facilitates determination of the interconnected by the power law stability and adaptivity of structure to external influence [12].

Using as the critical magnitudes of governing parameter the values ϕ_{cl} in the indicated bifurcation

points T_0 , T_g' and T_g (ϕ_{cl}' and T_{cl}^* , accordingly) together with the mentioned above table data [12], values A_m , Δ_i and for PC can be obtained, which are added in table 1. As it follows from the data of this table, systematic reduction of parameters A_m and Δ_i at the condition $m = 1 = \text{const}$ is observed. Hence, within the frameworks of solid body synergetics temperature T_g' can be characterized as bifurcation point ordering-degradation of nanostructure and T_g – as nanostructure degradation-chaos [12].

It is easy to see, that Δ_i decrease corresponds to bifurcation point critical temperature increase.

Table 1 - The critical parameters of nanocluster structure state for PC [8]

The temperature range	ϕ_{cl}'	ϕ_{cl}^*	A_m	Δ_i	m	m^*
213÷333 K	0,528	0,330	0,623	0,618	1	1
333÷390 K	0,330	0,153	0,465	0,465	1	2
390÷425 K	0,153	0,049	0,324	0,324	1	8

Therefore, critical temperatures T_{cr} (T_0 , T_g' and T_g) values increase should be expected at nanocluster structure stability measure Δ_i reduction. In Fig 2 the dependence of T_{cr} in Δ_i reciprocal value for PC is added, on which corresponding values for polyarylate (PAr) are also plotted. This correlation proved to be linear one and has two characteristic points. At $\Delta_i = 1$ the linear dependence $T_{cr}(\Delta_i^{-1})$ extrapolates to $T_{cr} = 293K$, i.e., this means, that at the indicated Δ_i value glassy polymer turns into rubber-like state at the used testing temperature $T = 293K$. From the data of the determined by gold proportion law $\Delta_i = 0,213$ at $m = 1$ follows [12]. In the plot of Fig. 2 the greatest for polymers critical temperature $T_{cr} = T_{ll}$. (T_{ll} is the temperature of “liquid 1 to liquid 2” transition), defining the transition to “structureless liquid” [13], corresponds to this minimum Δ_i magnitude. For polymers this means the absence of even dynamical short-lived local order [13].

Hence, the stated above results allow to give the following interpretation of critical temperatures T_g'

and T_g of amorphous glassy polymers structure within the frameworks of solid body synergetics. These temperatures correspond to governing parameter (nanocluster contents) ϕ_{cl} critical values, at which reaching one of the main principles of synergetics is realized-subordination principle, when a variables set is controlled by one (or several) variable, which is an order parameter. Let us also note reformations number $m = 1$ corresponds to structure formation mechanism particle-cluster [4, 5].

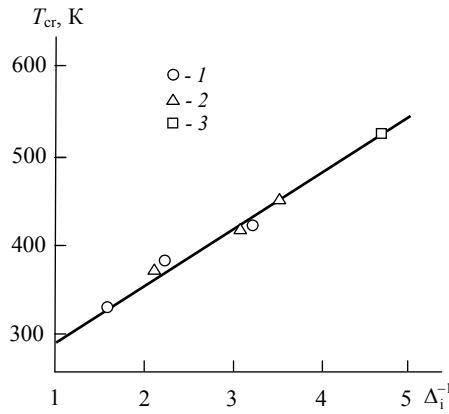


Fig. 2 - The dependence of critical temperatures T_{cr} on reciprocal value of nanocluster structure stability measure Δ_i for PC (1) and PAr(2), 3 – T_{II} value for PC [19]

The authors [14, 15] considered synergetics principles application for the description of behaviour of separate nanocluster structure, characterized by the integral parameter ϕ_{cl} nanoclusters in the system for the same amorphous glassy polymers. This aspect is very important, since, as it will be shown in subsequent sections, just separate nanoclusters characteristics define natural nanocomposites properties by critical mode. One from the criterions of nanoparticle definition has been obtained in paper [16]: atoms number N_{at} in it should not exceed $10^3 \div 10^4$. In paper [15] this criterion was applied to PC local order regions, having the greatest number of statistical segments $n_{cl} = 20$. Since nanocluster is amorphous analogue of crystallite with the stretched chains and at its functionality F a number of chains emerging from it is accepted, then the value n_{cl} is determined as follows [4]:

$$n_{cl} = \frac{F}{2}, \quad (1)$$

where the value F was calculated according to the equation (1.7) in previous publication.

The statistical segment volume simulated as a cylinder, is equal to $l_{st}S$ and further the volume per one atom of substance (PC) a^3 can be calculated according to the equation [17]:

$$a^3 = \frac{M}{\rho N_A p}, \quad (2)$$

where M is repeated link molar mass, ρ is polymer density, N_A is Avogadro number, p is atoms number in a repeated link.

For PC $M = 264$ g/mole, $\rho = 1200$ kg/m³ and $p = 37$. Then $a^3 = 9,54$ Å³ and the value N_{at} can be estimated according to the following simple equation [17]:

$$N_{at} = \frac{l_{st} \cdot S \cdot n_{cl}}{a^3} \quad (3)$$

For PC $N_{at} = 193$ atoms per one nanocluster (for $n_{cl} = 20$) is obtained. It is obvious that the indicated value N_{at} corresponds well to the adduced above nanoparticle definition criterion ($N_{at} = 10^3 \div 10^4$) [9, 17].

Let us consider synergetics of nanoclusters formation in PC and PAr. Using in the equation (3) as governing parameter critical magnitudes n_{cl} values at

testing temperature T consecutive change and the indicated above the table of the determined by gold proportion law values A_m , m and Δ_i , the dependence $\Delta_i(T)$ can be obtained, which is adduced in Fig 3. As it follows from this figure data, the nanoclusters stability within the temperature range of $313 \div 393$ K is approximately constant and small ($\Delta_i \approx 0,232$ at minimum value $\Delta_i \approx 0,213$) and at $T > 393$ K fast growth Δ_i (nanoclusters stability enhancement) begins for both considered polymers.

This plot can be explained within the frameworks of a cluster model [3-5]. In Fig 3 glass transition temperatures of loosely-packed matrix T'_g , which are approximately 50 K lower than polymer macroscopic glass transition temperature T_g , are indicated by vertical shaded lines. At T'_g instable nanoclusters, i.e., having small n_{cl} decay occurs. At the same time stable and, hence, more steady nanoclusters remain as a structural element, that results to Δ_i growth [14].

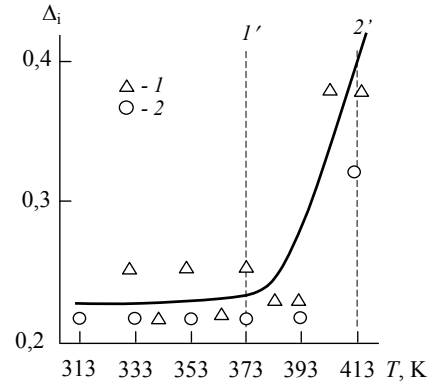


Fig 3 - The dependence of nanoclusters stability measure Δ_i on testing temperature T for PC(1) and PAr(2). The vertical shaded lines indicate temperature T'_g for PC (1') and PAr (2') [14]

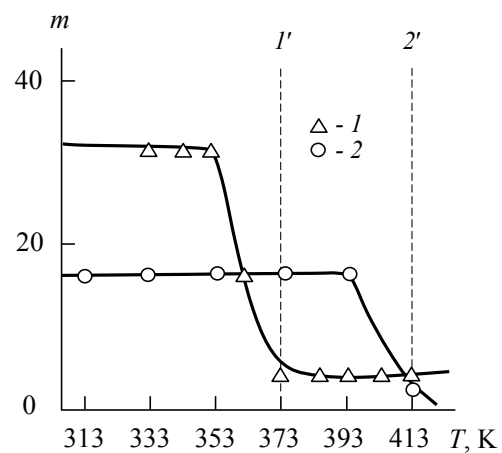


Fig. 4 - The dependences of reformations number m for nanoclusters on testing temperature T . The designations are the same as in Fig. 3 [14]

In Fig. 4 the dependences of reformations number m on testing temperature T for PC and PAr are adduced. At relatively low temperatures ($T < T'_g$) segments number in nanoclusters is large and segment join-

ing (separation) to nanoclusters occurs easily enough, that explains large values m . At $T \rightarrow T'_g$ reformations number reduces sharply and at $T > T'_g$ $m \approx 4$. Since at $T > T'_g$ in the system only stable clusters remain, then it is necessary to assume, that large m at $T < T'_g$ are due to reformation of just instable nanoclusters [15].

In Fig. 5 the dependence of n_{cl} on m is adduced. As one can see, even small m enhancement within the range of 2÷16 results to sharp increasing in segments number per one nanocluster. At $m \approx 32$ the dependence $n_{cl}(m)$ attains asymptotic branch for both studied polymers. This supposes that $n_{cl} \approx 16$ is the greatest magnitude for nanoclusters and for $m \geq 32$ this term belongs equally to both joining and separation of such segment from nanocluster.

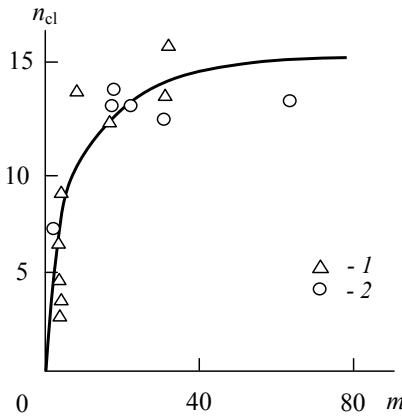


Fig. 5 - The dependence of segments number per one nanocluster n_{cl} on reformations number m for PC (1) and PAR (2) [14]

In Fig 6 the relationship of stability measure Δ_i and reformations number m for nanoclusters in PC and PAR is adduced. As it follows from the data of this figure, at $m \geq 16$ (or, according to the data of Fig 5, $n_{cl} \geq 12$) Δ_i value attains its minimum asymptotic magnitude $\Delta_i = 0.213$ [12]. This means, that for the indicated n_{cl} values nanoclusters in PC and PAR structure are adopted well to the external influence change ($A_m \geq 0.91$).

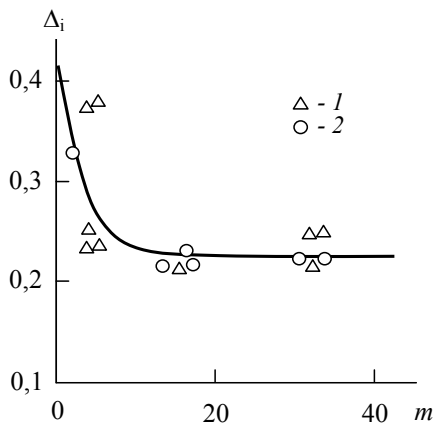


Fig 6 - The dependence of stability measure Δ_i on reformation number m for PC (1) and PAR (2) [14]

Nanoclusters formation synergetics is directly connected with the studied polymers structure macroscopic characteristics. As it has been noted above, the fractal structure, characterized by the dimension d_f , is formed as a result of nanoclusters reformations. In Fig. 7 the dependence $d_f(\Delta_i)$ for the considered polymers is adduced, from which d_f increase at Δ_i growth follows. This means, that the increasing of possible reformations number m , resulting to Δ_i reduction (Fig. 6), defines the growth of segments number in nanoclusters, the latter relative fraction ϕ_{cl} enhancement and, as consequence, d_f reduction [3-5].

And let us note in conclusion the following aspect, obtaining from the plot $\Delta_i(T)$ (Fig. 3) extrapolation to maximum magnitude $\Delta_i \approx 1.0$. The indicated Δ_i value is reached approximately at $T \approx 458$ K that corresponds to mean glass transition temperature for PC and PAR. Within the frameworks of the cluster model T_g reaching means polymer nanocluster structure decay [3-5] and, in its turn, realization at T_g of the condition $\Delta_i \approx 1.0$ means, that the “degenerated” nanocluster, consisting of one statistical segment or simply statistical segment, possesses the greatest stability measure. Several such segments joining up in nanocluster mains its stability reduction (see Figs. 5 and 6), that is the cause of glassy polymers structure thermodynamical nonequilibrium [14].

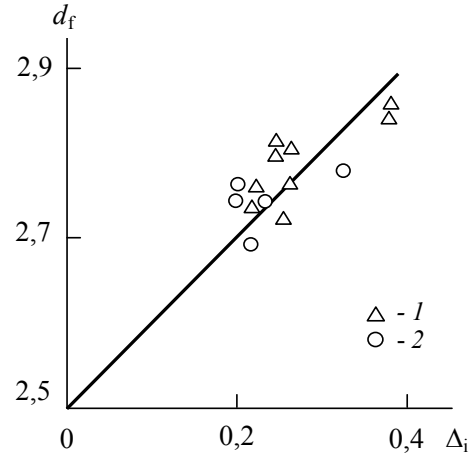


Fig 7 - The dependence of structure fractal dimension d_f on stability measure of nanoclusters Δ_i for PC (1) and PAR (2) [14]

Therefore, the stated above results showed synergetics principles applicability for the description of association (dissociation) processes of polymer segments in local order domains (nanoclusters) in case of amorphous glassy polymers. Such conclusion can be a priori, since a nanoclusters are dissipative structures [6]. Testing temperature increase rises nanoclusters stability measure at the expence of possible reformations number reduction [14, 15].

As it has been shown lately, the notion “nanoparticle” (nanocluster) gets well over the limits of purely dimensional definition and means substance state specific character in sizes nanoscale. The nanoparticles, sizes of which are within the range of order of 1 ÷ 100 nm, are already not classical macroscopic objects. They represent themselves the boundary state between macro- and microworld and in virtue of this they have specific features number, to which the following ones are attrib-

uted:

1. nanoparticles are self-organizing nonequilibrium structures, which submit to synergetics laws;
2. they possess very mature surface;
3. nanoparticles possess quantum (wave) properties.

For the nanoworld structures in the form of nanoparticles (nanoclusters) their size, defining the surface energy critical level, is the information parameter of feedback [19].

The first from the indicated points was considered in detail above. The authors [20, 21] showed that nanoclusters surface fractal dimension changes within the range of $2,15 \div 2,85$ that is their well developed surface sign. And at last, let us consider quantum (wave) aspect of nanoclusters nature on the example of PC [22]. Structural levels hierarchy formation and development "scenario" in this case can be presented with the aid of iterated process [23]:

$$l_k = \langle a \rangle B_\lambda^k; \lambda_k = \langle a \rangle B_\lambda^{k+1}; k = 0, 1, 2, \dots \quad (4)$$

where l_k is specific spatial scale of structural changes, λ_k is length of irradiation sequence, which is due to structure reformation, k is structural hierarchy sublevel number, $B_\lambda = \lambda_b / \langle a \rangle = 2,61$ is discretely-wave criterion of microfracture, λ_b is the smallest length of acoustic irradiation sequence.

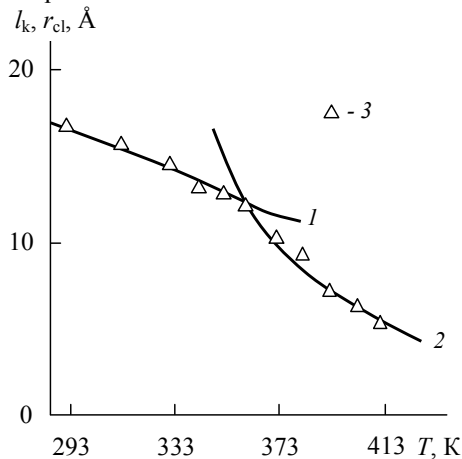


Fig. 8 - The dependences of structural changes specific spatial scale l_k at $B_\lambda = 1,06$ (1) and $1,19$ (2) and nanoclusters radius r_{cl} (3) on testing temperature T for PC [22]

In Fig. 8 the dependences of l_k and nanoclusters radius r_{cl} on T are adduced, where l_k was determined according to the equation (4) and the value r_{cl} was calculated according to the formula (in previous paper). As it follows from the data of Fig. 8, the values l_k and r_{cl} agree within the whole studied temperatures range. Let us note, that if in paper [23] the value $B_\lambda = 2,61$, then for PC the indicated above agreement was obtained at $B_\lambda = 1,19$ and $1,06$. This distinction confirms the thesis about distinction of synergetics laws in reference to nanomicroworld objects (let us remind, that the condition $B_\lambda = 2,61$ is valid even in the case of earthquakes [14]). It is interesting to note, that B_λ change occurs at glass transition temperature of loosely-packed matrix, i.e., approximately at $T_g - 50$ K [11].

Hence, the stated above results demonstrated

that the nanocluster possessed all nanoparticles properties, i.e., they belonged to substance intermediate state-nanoworld.

And in completion of the present section let us note one more important feature of natural nanocomposites structure. In papers [24, 25] the interfacial regions absence in amorphous glassy polymers, treated as natural nanocomposites, was shown. This means, that such nanocomposites structure represents a nanofiller (nanoclusters), immersed in matrix (loosely-packed matrix of amorphous polymer structure), i.e., unlike polymer nanocomposites with inorganic nanofiller (artificial nanocomposites) they have only two structural components.

2. The Natural Nanocomposites Reinforcement

As it is well-known [26], very often a filler introduction in polymer matrix is carried out for the last stiffness enhancement. Therefore the reinforcement degree of polymer composites, defined as a composite and matrix polymer elasticity moduli ratio, is one of their most important characteristics.

At amorphous glassy polymers as natural nanocomposites treatment the estimation of filling degree or nanoclusters relative fraction ϕ_{cl} has an important significance. Therefore the authors [27] carried out the comparison of the indicated parameter estimation different methods, one of which is EPR-spectroscopy (the method of spin probes). The indicated method allows to study amorphous polymer structural heterogeneity, using radicals distribution character. As it is known [28], the method, based on the parameter d_1/d_c – the ratio of spectrum extreme components total intensity to central component intensity-measurement is the simplest and most suitable method of nitroxil radicals local concentrations determination. The value of dipole-dipole interaction ΔH_{dd} is directly proportional to spin probes concentration C_w [29]:

$$\Delta H_{dd} = A \cdot C_w, \quad (5)$$

where $A = 5 \times 10^{-20}$ Ersted-cm³ in the case of radicals chaotic distribution.

On the basis of the equation (5) the relationship was obtained, which allows to calculate the average distance r between two paramagnetic probes [29]:

$$r = 38(\Delta H_{dd})^{-1/3}, \text{ Å} \quad (6)$$

where ΔH_{dd} is given in Ersted.

In Fig. 9 the dependence of d_1/d_c on mean distance r between chaotically distributed in amorphous PC radicals-probes is adduced. For PC at $T = 77$ K the values of $d_1/d_c = 0,38 \div 0,40$ were obtained. One can make an assumption about volume fractions relation for the ordered domains (nanoclusters) and loosely-packed matrix of amorphous PC. The indicated value d_1/d_c means, that in PC at probes statistical distribution 0,40 of its volume is accessible for radicals and approximately 0,60 of volume remains unoccupied by spin probes, i.e., the nanoclusters relative fraction ϕ_{cl} according to the EPR method makes up approximately 0,60÷0,62.

This result corresponds well to the experimental data of Yech [30] and Perepechko [31], who obtained the values 0,60 and 0,63 for densely-packed re-

gions relative fraction in amorphous polymers.

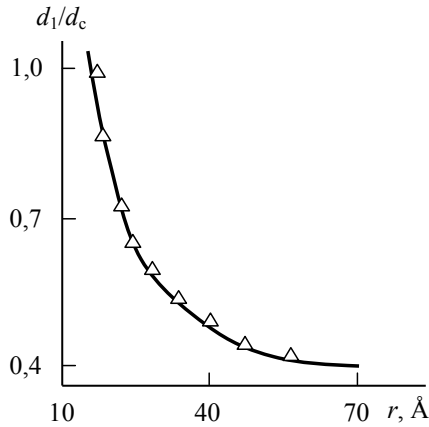


Fig. 9 - The dependence of parameter d_1/d_c of EPR spectrum on the value of mean distance r between radicals for PC [27]

The authors of paper [11] fulfilled ϕ_{cl} estimation with the aid of reversed gas chromatography and obtained the following magnitudes of this parameter for PC, poly (methyl methacrylate) and polysulfone: 0,70, 0,60 and 0,65, accordingly (Tabl. 2).

Within the frameworks of the cluster model ϕ_{cl} estimation can be fulfilled by the percolation relationship (in previous paper) usage. Let us note, that in the given case the temperature of polymers structure quasiequilibrium state attainment, lower of which ϕ_{cl} value does not change, i.e., T_0 [32], is accepted as testing temperature T . The calculation ϕ_{cl} results according to the equation (in previous paper) for the mentioned above polymers are adduced in Tabl. 2, which correspond well to other authors estimations.

Proceeding from the circumstance, that radicals-probes are concentrated mainly in intercluster regions, the nanocluster size can be estimated, which in amorphous PC should be approximately equal to mean distance r between two paramagnetic probes, i.e., ~ 50 Å (Fig. 9). This value corresponds well to the experimental data, obtained by dark-field electron microscopy method ($\approx 30 \div 100$ Å) [33].

Within the frameworks of the cluster model the distance between two neighbouring nanoclusters can be estimated according to the equation (in previous paper) as $2R_{cl}$. The estimation $2R_{cl}$ by this mode gives the value 53,1 Å (at $F = 41$), that corresponds excellently to the method EPR data.

Thus, the paper [27] results showed, that the obtained by EPR method natural nanocomposites (amorphous glassy polymers) structure characteristics corresponded completely to both the cluster model theoretical calculations and other authors estimations. In other words, EPR data are experimental confirmation of the cluster model of polymers amorphous state structure.

The treatment of amorphous glassy polymers as natural nanocomposites allows to use for their elasticity modulus E_p (and, hence, the reinforcement degree $E_p/E_{l.m.}$, where $E_{l.m.}$ is loosely-packed matrix elasticity modulus) description theories, developed for polymer composites reinforcement degree description [9, 17].

The authors [34] showed correctness of particulate-filled polymer nanocomposites reinforcement of two concepts on the example of amorphous PC. For theoretical estimation of particulate-filled polymer nanocomposites reinforcement degree E_n/E_m two equations can be used. The first from them has the look [35]:

$$\frac{E_n}{E_m} = 1 + \phi_n^{1,7}, \quad (7)$$

where E_n and E_m are elasticity moduli of nanocomposites and matrix polymer, accordingly, ϕ_n is nanofiller volume contents.

The second equation offered by the authors of paper [36] is:

$$\frac{E_n}{E_m} = 1 + \frac{0,19W_n l_{st}}{D_p^{1/2}}, \quad (8)$$

where W_n is nanofiller mass contents in mas. %, D_p is nanofiller particles diameter in nm.

Let us consider included in the equations (7) and (8) parameters estimation methods. It is obvious, that in the case of natural nanocomposites one should accept: $E_n = E_p$, $E_m = E_{l.m.}$ and $\phi_n = \phi_{cl}$, the value of the latter can be estimated according to the equation (in previous paper).

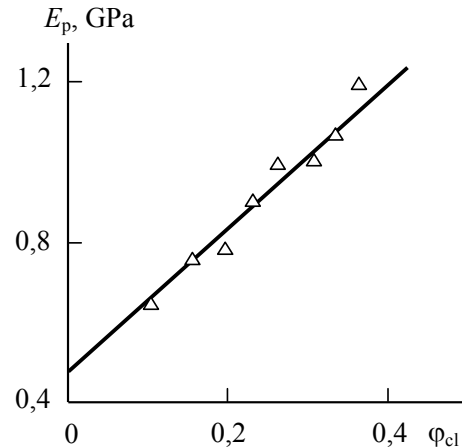


Fig. 10 - The dependence of elasticity modulus E_p on nanoclusters relative fraction ϕ_{cl} for PC [34]

The mass fraction of nanoclusters W_{cl} can be calculated as follows [37]:

$$W_{cl} = \rho \phi_{cl}, \quad (9)$$

where ρ is nanofiller (nanoclusters) density which is equal to 1300 kg/m³ for PC.

The value $E_{l.m.}$ can be determined by the construction of $E_p(\phi_{cl})$ plotting, which is adduced in Fig. 10. As one can see, this plot is approximately linear and its extrapolation to $\phi_{cl} = 0$ gives the value $E_{l.m.}$ And at last, as it follows from the nanoclusters definition (see chapter 1) one should accept $D_p \approx l_{st}$ for them and then the equation (8) accepts the following look [34]:

In Fig 11 the comprasion of theoretical calculation according to the equations (7) and (10) with experimental values of reinforcement degree $E_p/E_{l.m.}$ for PC is adduced. As one can see, both indicated equations give a good enough correspondence with the experiment: their average discrepancy makes up 5,6% in the equation (7) case and 9,6 % for the equation (10). In other words, in both cases the average discrepancy does

not exceed an experimental error for mechanical tests. This means, that both considered methods can be used for PC elasticity modulus prediction. Besides, it is necessary to note, that the percolation relationship (7) qualitatively describes the dependence $E_p/E_{l.m.}(\varphi_{cl})$ better, than the empirical equation (10).

$$\frac{E_n}{E_m} = 1 + 0,19\rho\varphi_{cl}^{1/2} \quad (10)$$

The obtained results allowed to make another important conclusion. As it is known, the percolation relationship (7) assumes, that nanofiller is percolation system (polymer composite) solid-body component and in virtue of this circumstance defines this system elasticity modulus. However, for artificial polymer particulate-filled nanocomposites, consisting of polymer matrix and inorganic nanofiller, the equation (7) in the cited form gives the understated values of reinforcement degree. The authors [9, 17] showed, that for such nanocomposites the sum $(\varphi_n + \varphi_{if})$, where φ_{if} was interfacial regions relative fraction, was a solid-body component. The correspondence of experimental data and calculation according to the equation (7) demonstrates, that amorphous polymer is the specific nanocomposite, in which interfacial regions are absent [24, 25]. This important circumstance is necessary to take into consideration at amorphous glassy polymers structure and properties description while simulating them as natural nanocomposites. Besides, one should note, that unlike micromechanical models the equations (7) and (10) do not take into account nanofiller elasticity modulus, which is substantially differed for PC nanoclusters and inorganic nanofillers [34].

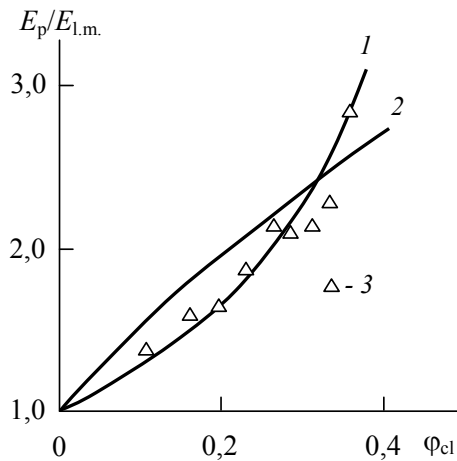


Fig. 11 - The dependences of reinforcement degree $E_p/E_{l.m.}$ on nanoclusters relative fraction φ_{cl} for PC. 1 – calculation according to the equation (7); 2 – calculation according to the equation (10); 3 – the experimental data [34]

Another mode of natural nanocomposites reinforcement degree description is micromechanical models application, developed for polymer composites mechanical behaviour description [1, 37-39]. So, Takayanagi and Kerner models are often used for the description of reinforcement degree on composition for the indicated materials [38, 39]. The authors [40] used the mentioned models for theoretical treatment of natural

nanocomposites reinforcement degree temperature dependence on the example of PC.

Takayanagi model belongs to a micromechanical composite models group, allowing empirical description of composite response upon mechanical influence on the basis of constituent it elements properties. One of the possible expressions within the frameworks of this model has the following look [38]:

$$\frac{G_c}{G_m} = \frac{\varphi_m G_m + (\alpha + \varphi_f) G_f}{(1 + \alpha \varphi_f) G_m + \alpha \varphi_m G_f}, \quad (11)$$

where G_c , G_m and G_f are shear moduli of composite, polymer matrix and filler, accordingly, φ_m and φ_f are polymer matrix and filler relative fractions, respectively, α is a fitted parameter.

Kerner equation is identical to the formula (11), but for it the parameter α does not fit and has the following analytical expression [38]:

$$\alpha_m = \frac{2(4 - 5\nu_m)}{(7 - 5\nu_m)}, \quad (12)$$

where α_m and ν_m are parameter α and Poisson's ratio for polymer matrix.

Let us consider determination methods of the equation (11) and (12) parameters, which are necessary for the indicated equations application in the case of natural nanocomposites. Firstly, it is obvious, that in the last case one should accept: $G_c = G_p$, $G_m = G_{l.m.}$, $G_f = G_{cl}$, where G_p , $G_{l.m.}$ and G_{cl} are shear moduli of polymer, loosely-packed matrix and nanoclusters, accordingly, and also $\varphi_f = \varphi_{cl}$, where φ_{cl} is determined according to the percolation relationship (in previous paper). Young's modulus for loosely-packed matrix and nanoclusters can be received from the data of Fig. 10 by the dependence $E_p(\varphi_{cl})$ extrapolation to $\varphi_{cl} = 1,0$, respectively. The corresponding shear moduli were calculated according to the general equation (in previous paper).

The value of nanoclusters fractal dimension d_f^{cl} in virtue of their dense package is accepted equal to the greatest dimension for real solids ($d_f^{cl} = 2,95$ [40]) and

loosely-packed matrix fractal dimension $d_f^{l.m.}$ can be estimated.

However, the calculation according to the equations (11) and (12) does not give a good correspondence to the experiment, especially for the temperature range of $T = 373 \div 413$ K in PC case. As it is known [38], in empirical modifications of Kerner equation it is usually supposed, that nominal concentration scale differs

from mechanically effective filler fraction φ_f^{ef} , which can be written accounting for the designations used above for natural nanocomposites as follows [41].

$$\varphi_f^{ef} = \frac{(G_p - G_{l.m.})(G_{l.m.} + \alpha_{l.m.} G_{cl})}{(G_{cl} - G_{l.m.})(G_{l.m.} + \alpha_{l.m.} G_p)}, \quad (13)$$

where $\alpha_{l.m.} = \alpha_m$. The value $\alpha_{l.m.}$ can be determined according to the equation (12), estimating Poisson's ratio of loosely-packed matrix $\nu_{l.m.}$ by the known values $d_f^{l.m.}$ according to the equation (in previous paper).

Besides, one more empirical modification Φ_f^{ef} exists, which can be written as follows [41]:

$$\Phi_{cl_2}^{ef} = \Phi_{cl} + c \left(\frac{\Phi_{cl}}{2r_{cl}} \right)^{2/3}, \quad (14)$$

where c is empirical coefficient of order one r_{cl} is nano-cluster radius, determined according to the equation (in previous paper).

At the value $\Phi_{cl_2}^{ef}$ calculation according to the equation (14) magnitude c was accepted equal to 1,0 for the temperature range of $T = 293 \div 363$ K and equal to 1,2 – for the range of $T = 373 \div 413$ K and $2r_{cl}$ is given in nm. In Fig. 12 the comparison of values Φ_{cl}^{ef} , calculated according to the equations (13) and (14) ($\Phi_{cl_1}^{ef}$ and $\Phi_{cl_2}^{ef}$, accordingly) is added. As one can see, a

good enough conformity of the values Φ_{cl}^{ef} , estimated by both methods, is obtained (the average discrepancy of $\Phi_{cl_1}^{ef}$ and $\Phi_{cl_2}^{ef}$ makes up slightly larger than 20%).

Let us note, that the effective value Φ_{cl} exceeds essentially the nominal one, determined according to the relationship (in previous paper): within the range of $T = 293 \div 363$ K by about 70% and within the range of $T = 373 \div 413$ K – almost in three times.

In Fig. 13 the comparison of experimental and calculated according to Kerner equation (the equation (11)) with the formulas (13) and (14) using values of reinforcement degree by shear modulus $G_p/G_{l.m.}$ as a function of testing temperature T for PC is added. As one can see, in this case at the usage of nanoclusters effective concentration scale (Φ_{cl}^{ef} instead of Φ_{cl}) the good conformity of theory and experiment is obtained (their average discrepancy makes up 6%).

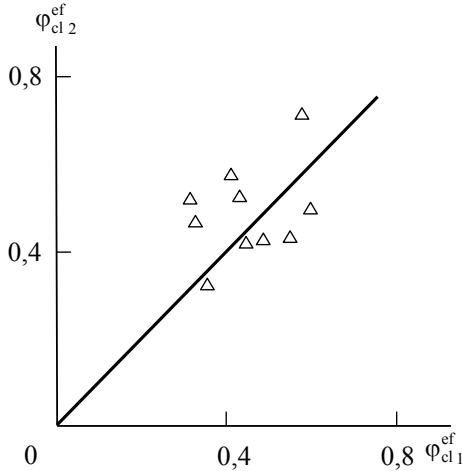


Fig. 12 - The comparison of nanoclusters effective concentration scale $\Phi_{cl_1}^{ef}$ and $\Phi_{cl_2}^{ef}$, calculated according to the equation (13) and (14), respectively, for PC. A straight line shows the relation 1:1 [41]

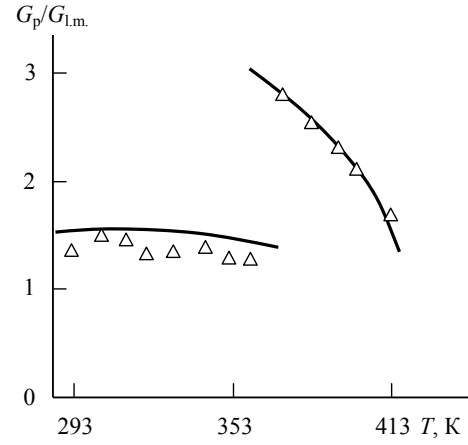


Fig. 13 - The comparison of experimental (points) and calculated according to the equations (11), (13) and (14) (solid lines) values of reinforcement degree by shear modulus $G_p/G_{l.m.}$ as a function of testing temperature T for PC. [41]

Hence, the stated above results have shown the modified Kerner equation application correctness for natural nanocomposites elastic response description. Really this fact by itself confirms the possibility of amorphous glassy polymers treatment as nanocomposites. Microcomposite models usage gives the clear notion about factors, influencing polymers stiffness.

3. Intercomponent Adhesion in Natural Nanocomposites

Amorphous glassy polymers as natural nanocomposites puts forward to the foreground their study intercomponent interactions, i.e., interactions nanoclusters – loosely-packed matrix. This problem plays always one of the main roles at multiphase (multicomponent) systems consideration, since the indicated interactions or interfacial adhesion level defines to a great extent such systems properties [42]. Therefore the authors [43] studied the physical principles of intercomponent adhesion for natural nanocomposites on the example of PC.

The authors [44] considered three main cases of the dependence of reinforcement degree E_c/E_m on Φ_f . In this work the authors have shown, that there are the following main types of the dependences $E_c/E_m(\Phi_f)$ exist:

1) the ideal adhesion between filler and polymer matrix, described by Kerner equation (perfect adhesion), which can be approximated by the following relationship:

$$\frac{E_c}{E_m} = 1 + 11,64\Phi_f - 44,4\Phi_f^2 + 96,3\Phi_f^3, \quad (15)$$

2) zero adhesional strength at a large friction coefficient between filler and polymer matrix, which is described by the equation:

$$\frac{E_c}{E_m} = 1 + \Phi_f, \quad (16)$$

3) the complete absence of interaction and ideal slippage between filler and polymer matrix, when composite elasticity modulus is defined practically by polymer cross-section and connected with the filling degree by the equation:

$$\frac{E_c}{E_m} = 1 - \varphi_f^{2/3}, \quad (17)$$

In Fig. 14 the theoretical dependences $E_p/E_{l.m.}(\varphi_{cl})$ plotted according to the equations (15) ÷ (17), as well as experimental data (points) for PC are shown. As it follows from the adduced in Fig. 14 comparison at $T = 293 \div 363$ K the experimental data correspond well to the equation (16), i.e., in this case zero adhesional strength at a large friction coefficient is observed. At $T = 373 \div 413$ K the experimental data correspond to the equation (15), i.e., the perfect adhesion between nanoclusters and loosely-packed matrix is observed. Thus, the adduced in Fig. 14 data demonstrated, that depending on testing temperature two types of interactions nanoclusters – loosely-packed matrix are observed: either perfect adhesion or large friction between them. For quantitative estimation of these interactions it is necessary to determine their level, which can be made with the help of the parameter b_m , which is determined according to the equation [45]:

$$\sigma_f^c = \sigma_f^m K_s - b_m \varphi_f, \quad (17)$$

where σ_f^c and σ_f^m are fracture stress of composite and polymer matrix, respectively, K_s is stress concentration coefficient. It is obvious, that since b_m increase results to σ_f^c reduction, then this means interfacial adhesion level decrease.

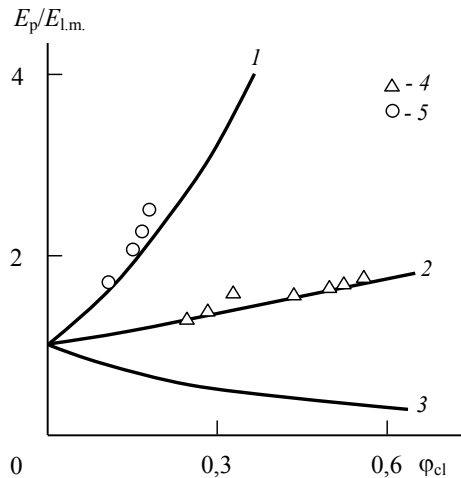


Fig. 14 - The dependences of reinforcement degree $E_p/E_{l.m.}$ on nanoclusters relative fraction φ_{cl} . 1÷3 – the theoretical dependences, corresponding to the equation (15) ÷ (17), accordingly; 4, 5 – the experimental data for PC within the temperature ranges: 293÷363K(4) and 373÷413K(5) [43]

The true fracture stress σ_f^{tr} for PC, taking into account sample cross-section change in a deformation process, was used as σ_f^c for natural nanocomposites, which can be determined according to the known formula:

$$\sigma_f^{\text{tr}} = \sigma_f^n (1 + \varepsilon_f) \quad (19)$$

where σ_f^n is nominal (engineering) fracture stress, ε_f is

strain at fracture.

The value σ_f^m , which is accepted equal to loosely-packed matrix strength $\sigma_f^{\text{l.m.}}$, was determined by graphic method, namely, by the dependence $\sigma_f^{\text{tr}}(\varphi_{cl})$ plotting, which proves to be linear, and by subsequent extrapolation of it to $\varphi_{cl} = 0$, that gives $\sigma_f^{\text{l.m.}} = 40$ MPa [43].

And at last, the value K_s can be determined with the help of the following equation [39]:

$$\sigma_f^{\text{tr}} = \sigma_f^{\text{l.m.}} (1 - \varphi_{cl}^{2/3}) K_s, \quad (20)$$

The parameter b_m calculation according to the stated above technique shows its decrease (intercomponent adhesion level enhancement) at testing temperature raising within the range of $b_m \approx 500 \div 130$.

For interactions nanoclusters – loosely-packed matrix estimation within the range of $T = 293 \div 373$ K the authors [48] used the model of Witten-Sander clusters friction, stated in paper [46]. This model application is due to the circumstance, that amorphous glassy polymer structure can be presented as an indicated clusters large number set [47]. According to this model, Witten-Sander clusters generalized friction coefficient f can be written as follows [46]:

$$f = \ln c + \beta \ln n_{cl}, \quad (21)$$

where c is constant, β is coefficient, n_{cl} is statistical segments number per one nanocluster.

The coefficient β value is determined as follows [46]:

$$\beta = (d_f^{\text{cl}})^{-1} \quad (22)$$

where d_f^{cl} is nanocluster structure fractal dimension, which is equal, as before, to 2,95 [40].

In Fig. 15 the dependence $b_m(f)$ is adduced, which is broken down into two parts. On the first of them, corresponding to the range of $T = 293 \div 363$ K, the intercomponent interaction level is intensified at f decreasing (i.e., b_m reduction is observed and on the second one, corresponding to the range of $T = 373 \div 413$ K, $b_m = \text{const}$ independent on value f . These results correspond completely to the data of Fig. 14, where in the first from the indicated temperature ranges the value $E_p/E_{l.m.}$ is defined by nanoclusters friction and in the second one by adhesion and, hence, it does not depend on friction coefficient.

As it has been shown in paper [48], the interfacial (or intercomponent) adhesion level depends on a number of accessible for the formation interfacial (intercomponent) bond sites (nodes) on the filler (nanocluster) particle surface N_u , which is determined as follows [49]:

$$N_u = L^{d_u} \quad (23)$$

where L is filler particle size, d_u is fractal dimension of accessible for contact (“nonscreened”) indicated particle surface.

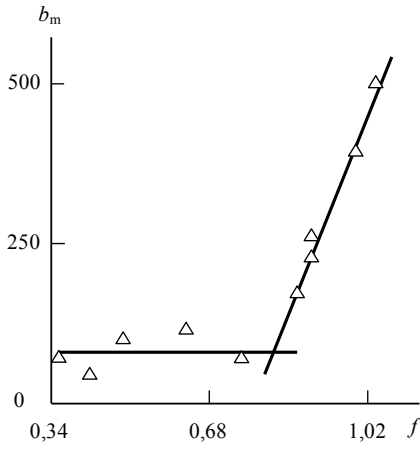


Fig. 15 - The dependence of parameter b_m on generalized friction coefficient f for PC [43]

One should choose the nanocluster characteristic size as L for the natural nanocomposite which is equal to statistical segment l_{st} , determined according to the equation (in previous paper), and the dimension d_u is determined according to the following relationship [49]:

$$d_u = (d_{surf} - 1) + \left(\frac{d - d_{surf}}{d_w} \right), \quad (24)$$

where d_{surf} is nanocluster surface fractal dimension, d_w is dimension of random walk on this surface, estimated according to Aarony-Stauffer rule [49]:

$$d_w = d_{surf} + 1, \quad (25)$$

The following technique was used for the dimension d_{surf} calculation. First the nanocluster diameter $D_{cl} = 2r_{cl}$ was determined according to the equation (in previous paper) and then its specific surface S_u was estimated [35]:

$$S_u = \frac{6}{\rho_{cl} D_{cl}}, \quad (26)$$

where ρ_{cl} is the nanocluster density, equal to 1300 kg/m³ in the PC case.

And at last, the dimension d_{surf} was calculated with the help of the equation [20]:

$$S_u = 5,25 \times 10^3 \left(\frac{D_{cl}}{2} \right)^{d_{surf} - d}, \quad (27)$$

In Fig. 16 the dependence $b_m(N_u)$ for PC is added, which is broken down into two parts similarly to the dependence $b_m(f)$ (Fig. 15). At $T = 293 \div 363$ K the value b_m is independent on N_u , since nanocluster – loosely-packed matrix interactions are defined by their friction coefficient. Within the range of $T = 373 \div 413$ K intercomponent adhesion level enhancement (b_m reduction) at active sites number N_u growth is observed, as was to be expected. Thus, the data of both Figs. 16 and 15 correspond to Fig. 14 results.

With regard to the data of Figs. 15 and 16 two remarks should be made. Firstly, the transition from one reinforcement mechanism to another corresponds to loosely-packed matrix glass transition temperature, which is approximately equal to $T_g - 50$ K [11]. Secondly, the extrapolation of Fig. 16 plot to $b_m = 0$ gives the value $N_u \approx 71$, that corresponds approximately to polymer structure dimension $d_f = 2,86$.

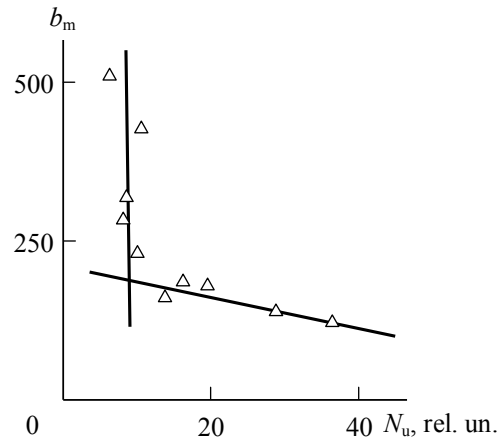


Fig. 16 - The dependence of parameter b_m on nano-cluster surface active ("nonscreened") sites number N_u for PC [43]

In this theme completion an interesting structural aspect of intercomponent adhesion in natural nanocomposites (polymers) should be noted. Despite the considered above different mechanisms of reinforcement and nanoclusters-loosely-packed matrix interaction realization the common dependence $b_m(\varphi_{cl})$ is obtained for the entire studied temperature range of 293÷413K, which is shown in Fig. 17. This dependence is linear, that allows to determine the limiting values $b_m \approx 970$ at $\varphi_{cl} = 1,0$ and $b_m = 0$ at $\varphi_{cl} = 0$. Besides, let us note, that the shown in Figs. 14÷16 structural transition is realized at $\varphi_{cl} \approx 0,26$ [43].

Hence, the stated above results have demonstrated, that intercomponent adhesion level in natural nanocomposites (polymers) has structural origin and is defined by nanoclusters relative fraction. In two temperature ranges two different reinforcement mechanisms are realized, which are due to large friction between nanoclusters and loosely-packed matrix and also perfect (by Kerner) adhesion between them. These mechanisms can be described successfully within the frameworks of fractal analysis.

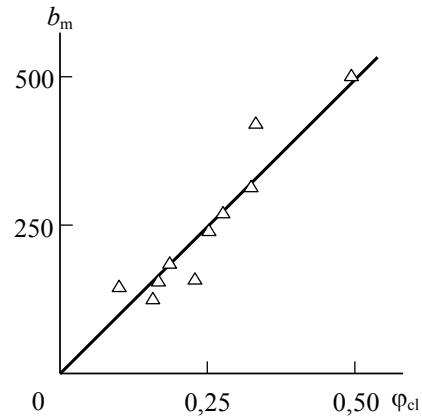


Fig. 17 - The dependence of parameter b_m on nano-clusters relative fraction φ_{cl} for PC [43]

The further study of intercomponent adhesion in natural nanocomposites was fulfilled in paper [50]. In Fig. 18 the dependence $b_m(T)$ for PC is shown, from which b_m reduction or intercomponent adhesion level enhancement at testing temperature growth follows. In the same figure the maximum value b_m for nanocompo-

sites polypropylene/Na⁺-montmorillonite [9] was shown by a horizontal shaded line. As one can see, b_m values for PC within the temperature range of $T = 373 \div 413$ K by absolute value are close to the corresponding parameter for the indicated nanocomposite, that indicates high enough intercomponent adhesion level for PC within this temperature range.

Let us note an important structural aspect of the dependence $b_m(T)$, shown in Fig. 18. According to the cluster model [4], the decay of instable nanoclusters occurs at temperature $T'_g \approx T_g - 50$ K, holding back loosely-packed matrix in glassy state, owing to which this structural component is devitrificated within the temperature range of $T'_g \div T_g$. Such effect results to rapid reduction of polymer mechanical properties within the indicated temperature range [51]. As it follows from the data of Fig. 18, precisely in this temperature range the highest intercomponent adhesion level is observed and its value approaches to the corresponding characteristic for nanocomposites polypropylene/Na⁺-montmorillonite.

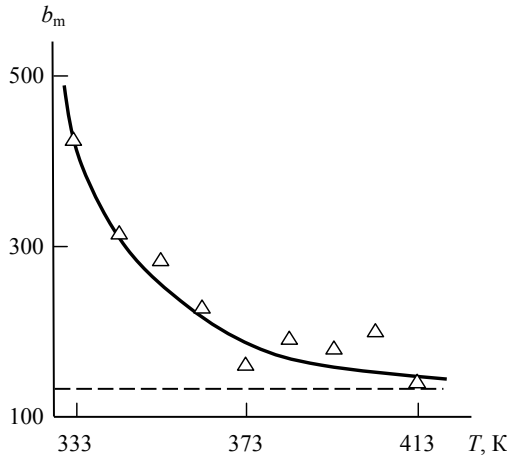


Fig. 18 - The dependence of parameter b_m on testing temperature T for PC. The horizontal shaded line shows the maximum value b_m for nanocomposites polypropylene/Na⁺-montmorillonite [50]

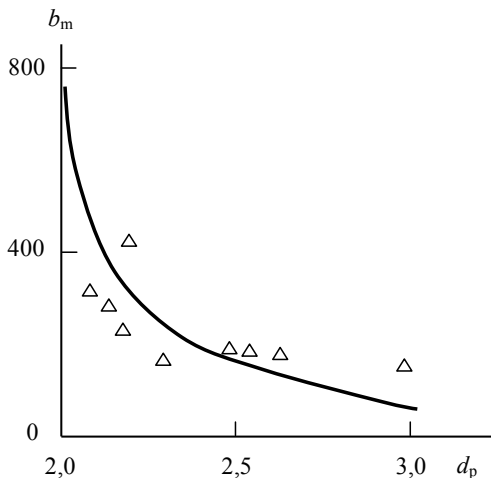


Fig. 19 - The dependence of parameter b_m on nanoclusters surface fractal dimension d_{surf} for PC [50]

It can be supposed with a high probability degree that adhesion level depends on the structure of

nanoclusters surface, coming into contact with loosely-packed matrix, which is characterized by the dimension d_{surf} . In Fig. 19 the dependence $b_m(d_{surf})$ for PC is adduced, from which rapid reduction b_m (or intercomponent adhesion level enhancement) follows at d_{surf} growth or, roughly speaking, at nanoclusters surface roughness enhancement.

The authors [48] showed that the interfacial adhesion level for composites polyhydroxyether/graphite was raised at the decrease of polymer matrix and filler particles surface fractal dimensions difference. The similar approach was used by the authors of paper [50], who calculated nanoclusters d_f^{cl} and loosely-packed matrix $d_f^{l.m.}$ fractal dimensions difference Δd_f :

$$\Delta d_f = d_f^{cl} - d_f^{l.m.}, \quad (28)$$

where d_f^{cl} is accepted equal to real solids maximum dimension ($d_f^{cl} = 2,95$ [40]) in virtue of their dense packing and the value $d_f^{l.m.}$ was calculated according to the mixtures rule (the equation from previous paper).

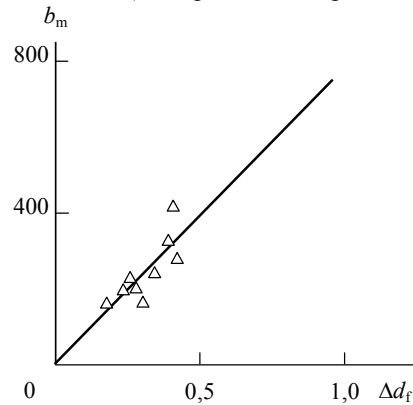


Fig. 20 - The dependence of parameter b_m on nano-clusters d_f^{cl} and loosely-packed matrix $d_f^{l.m.}$ structures fractal dimensions difference Δd_f for PC [50]

In Fig. 20 the dependence of b_m on the difference Δd_f is adduced, from which b_m decrease or intercomponent adhesion level enhancement at Δd_f reduction or values d_f^{cl} and $d_f^{l.m.}$ growing similarity follows. This dependence demonstrates, that the greatest intercomponent adhesion level, corresponding to $b_m = 0$, is reached at $\Delta d_f = 0,95$ and is equal to ~ 780 .

The data of Figs. 14 and 18 combination shows, that the value $b_m \approx 200$ corresponds to perfect adhesion by Kerner. In its turn, the Figs. 16 and 17 plots data demonstrated, that the value $b_m \approx 200$ could be obtained either at $d_{surf} > 2,5$ or at $\Delta d_f < 0,3$, accordingly. The obtained earlier results showed [24], that the condition $d_{surf} > 2,5$ was reached at $r_{cl} < 7,5 \text{ \AA}$ or $T > 373$ K, that again corresponded well to the stated above results.

And at last, the $\Delta d_f \approx 0,3$ or $d_f^{l.m.} \approx 2,65$ according to the equation (in previous paper) was also obtained at $T \approx 373 \text{ K}$.

Hence, at the indicated above conditions fulfilment within the temperature range of $T < T'_g$ for PC perfect intercomponent adhesion can be obtained, corresponding to Kerner equation, and then the value E_p estimation should be carried out according to the equation (15). At $T = 293$ K ($\varphi_{cl} = 0,56$, $E_m = 0,85$ GPa) the value E_p will be equal to 8,9 GPa, that approximately in 6 times larger, than the value E_p for serial industrial PC brands at the indicated temperature.

Let us note the practically important feature of the obtained above results. As it was shown, the perfect intercomponent adhesion corresponds to $b_m \approx 200$, but not $b_m = 0$. This means, that the real adhesion in natural nanocomposites can be higher than the perfect one by Kerner, that was shown experimentally on the example of particulate-filled polymer nanocomposites [17, 52]. This effect was named as nanoadhesion and its realization gives large possibilities for elasticity modulus increase of both natural and artificial nanocomposites. So, the introduction in aromatic polyamide (phenylene) of 0,3 mas.% aerosil only at nanoadhesion availability gives the same nanocomposite elasticity modulus enhancement effect, as the introduction of 3 mas. % of organoclay, which at present is assumed as one of the most effective nanofillers [9]. This assumes, that the value $E_p = 8,9$ GPa for PC is not a limiting one, at any rate, theoretically. Let us note in addition, that the indicated E_p values can be obtained at the natural nanocomposites nanofiller (nanoclusters) elasticity modulus magnitude $E_{cl} = 2,0$ GPa, i.e., at the condition $E_{cl} < E_p$. Such result possibility follows from the polymer composites structure fractal concept [53], namely, the model [44], in which the equations (15) ÷ (17) do not contain nanofiller elasticity modulus, and reinforcement percolation model [35].

The condition $d_{surf} < 2,5$, i.e., $r_{cl} < 7,5$ Å or $N_{cl} < 5$, in practice can be realized by the nanosystems mechanosynthesis principles using, the grounds of which are stated in paper [54]. However, another more simple and, hence, more technological method of desirable structure attainment realization is possible, one from which will be considered in subsequent section.

Hence, the stated above results demonstrated, that the adhesion level between natural nanocomposite structural components depended on nanoclusters and loosely-packed matrix structures closeness. This level change can result to polymer elasticity modulus significant increase. A number of this effect practical realization methods was considered [50].

The mentioned above dependence of intercomponent adhesion level on nanoclusters radius r_{cl} assumes more general dependence of parameter b_m on nanoclusters geometry. The authors [55] carried out calculation of accessible for contact sites of nanoclusters surface and loosely-packed matrix number N_u according to the relationship (23) for two cases. the nanocluster is simulated as a cylinder with diameter D_{cl} and length l_{st} , where l_{st} is statistical segment length, therefore, in the first case its butt-end is contacting with loosely-packed matrix nanocluster surface and then $L = D_{cl}$ and in the second case with its side (cylindrical) surface and then $L = l_{st}$. In Fig. 21 the dependences of parameter b_m on

value N_u , corresponding to the two considered above cases, are adduced. As one can see, in both cases, for the range of $T = 293 \div 363$ K l_{st} , where interactions nanoclusters – loosely-packed matrix are characterized by powerful friction between them, the value b_m does not depend on N_u , as it was expected. For the range of $T = 373 \div 413$ K, where between nanoclusters and loosely-packed matrix perfect adhesion is observed, the linear dependences $b_m(N_u)$ are obtained. However, at using value D_{cl} as Lb_m reduction or intercomponent adhesion level enhancement at N_u decreasing is obtained and at $N_u = 0$ b_m value reaches its minimum magnitude $b_m = 0$. In other words, in this case the minimum level of intercomponent adhesion is reached at intercomponent bonds formation sites (nodes) absence that is physically incorrect [48]. And on the contrary at the condition $L = l_{st}b_m$ the reduction (intercomponent adhesion level enhancement) at the increase of contacts number N_u between nanoclusters and loosely-packed matrix is observed, that is obvious from the physical point of view. Thus, the data of Fig. 21 indicate unequivocally, that the intercomponent adhesion is realized over side (cylindrical) nanoclusters surface and butt-end surfaces in this effect formation do not participate.

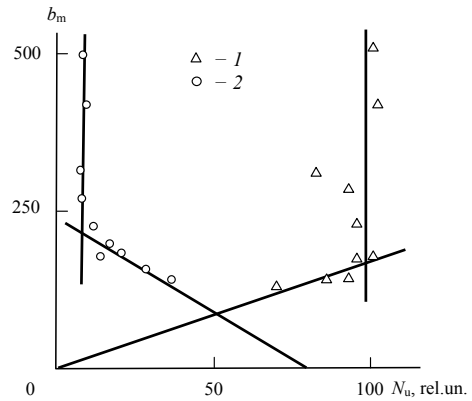


Fig. 21 - The dependences of parameter b_m on a number of accessible for intercomponent bonds formation sizes on nanocluster surface N_u at the condition $L = D_{cl}$ (1) and $L = l_{st}$ (2) for PC [55]

Let us consider geometrical aspects intercomponent interactions in natural nanocomposites. In Fig. 22 the dependence of nanoclusters butt-end S_b and side (cylindrical) S_c surfaces areas on testing temperature T for PC are adduced. As one can see, the following criterion corresponds to the transition from strong friction to perfect adhesion at $T = 373$ K [55]:

$$S_b \approx S_c, \quad (29)$$

Hence, the intercomponent interaction type transition from the large friction nanoclusters – loosely-packed matrix to the perfect adhesion between them is defined by nanoclusters geometry: at $S_b > S_c$ the interactions of the first type is realized and at $S_b < S_c$ – the second one. Proceeding from this, it is expected that intercomponent interactions level is defined by the ratio S_b/S_c . Actually, the adduced in Fig. 23 data demonstrate b_m reduction at the indicated ratio decrease, but at the criterion (29) realization or $S_b/S_c \approx 1$ S_b/S_c decreasing does not result to b_m reduction and at $S_b/S_c < 1$ intercomponent adhesion level remains maximum high and

constant [55].

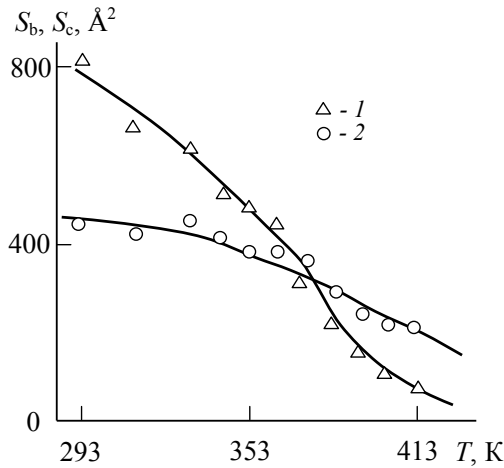


Fig. 22 - The dependences of nanoclusters butt-end $S_b(1)$ and cylindrical $S_c(2)$ surfaces areas on testing temperature T for PC [55]

Hence, the stated above results have demonstrated, that interactions nanoclusters-loosely-packed matrix type (large friction or perfect adhesion) is defined by nanoclusters butt-end and side (cylindrical) surfaces areas ratio or their geometry if the first from the mentioned areas is larger than the second one then a large friction nanoclusters-loosely-packed matrix is realized; if the second one exceeds the first one, then between the indicated structural components perfect adhesion is realized. In the second from the indicated cases intercomponent adhesion level does not depend on the mentioned areas ratio and remains maximum high and constant. In other words, the adhesion nanoclusters-loosely-packed matrix is realized by nanoclusters cylindrical surface.

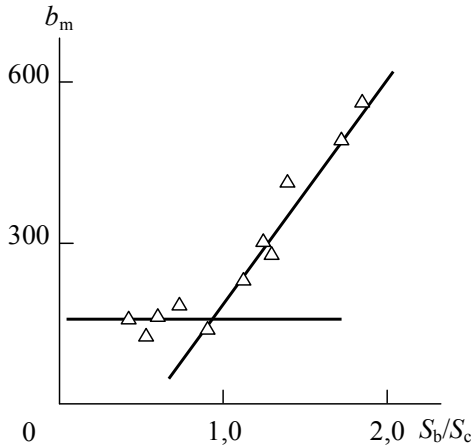


Fig. 23 - The dependence of parameter b_m on nanoclusters butt-end and cylindrical surfaces are ratio S_b/S_c value for PC [55]

The stated above results were experimentally confirmed by the EPR-spectroscopy method [56]. The equations (1) and (6) comparison shows, that dipole-dipole interaction energy ΔH_{dd} has structural origin, namely [56]:

$$\Delta H_{dd} \approx \left(\frac{v_{cl}}{n_{cl}} \right), \quad (30)$$

As estimations according to the equation (30)

showed, within the temperature range of $T = 293 \div 413$ K for PC ΔH_{dd} increasing from 0,118 up to 0,328 Erstedes was observed.

Let us consider dipole-dipole interaction energy ΔH_{dd} intercommunication with nanoclusters geometry. In Fig. 24 the dependence of ΔH_{dd} on the ratio S_c/S_b for PC is adduced. As one can see, the linear growth ΔH_{dd} at ratio S_c/S_b increasing is observed, i.e., either at S_c enhancement or at S_b reduction. Such character of the adduced in Fig. 24 dependence indicates unequivocally, that the contact nanoclusters-loosely-packed matrix is realized on nanocluster cylindrical surface. Such effect was to be expected, since emerging from the butt-end surface statistically distributed polymer chains complicated the indicated contact realization unlike relatively smooth cylindrical surfaces. It is natural to suppose, that dipole-dipole interactions intensification or ΔH_{dd} increasing results to natural nanocomposites elasticity modulus E_p enhancement. The second as natural supposition at PC consideration as nanocomposite is the influence on the value E_p of nanoclusters (nanofiller) relative fraction ϕ_{cl} , which is determined according to the percolation relationship (in previous paper).

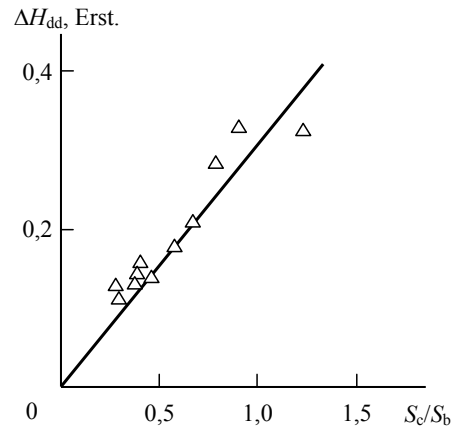


Fig. 24 - The dependence of dipole-dipole interaction energy ΔH_{dd} on nanoclusters cylindrical S_c and butt-end S_b surfaces areas ratio for PC [56]

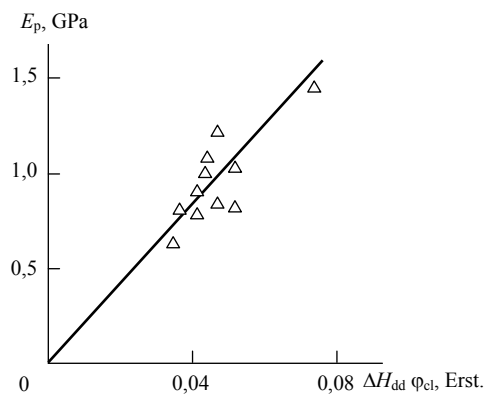


Fig. 25 - The dependence of elasticity modulus E_p on complex argument $(\Delta H_{dd} \phi_{cl})$ for PC [56]

In Fig. 25 the dependence of elasticity modulus E_p on complex argument $(\Delta H_{dd} \phi_{cl})$ for PC is presented. As one can see, this dependence is a linear one, passes through coordinates origin and is described analytically by the following empirical equation [56].

$$E_p = 21(\Delta H_{ad}(\varphi_{cl})), \text{ GPa}, \quad (31)$$

which with the appreciation of the equation (30) can be rewritten as follows [56]:

$$E_p = 21 \times 10^{-26} \left(\frac{\varphi_{cl} V_{cl}}{n_{cl}} \right), \text{ GPa}. \quad (32)$$

The equation (32) demonstrates clearly, that the value E_p and, hence polymer reinforcement degree is a function of its structural characteristics, described within the frameworks of the cluster model [3-5]. Let us note, that since parameters v_{cl} and φ_{cl} are a function of testing temperature, then the parameter n_{cl} is the most suitable factor for the value E_p regulation for practical purposes. In Fig. 26 the dependence $E_p(n_{cl})$ for PC at $T = 293 \text{ K}$ is adduced, calculated according to the equation (32), where the values v_{cl} and φ_{cl} were calculated according to the equations (in previous paper). As one can see, at small n_{cl} (<10) the sharp growth E_p is observed and at the smallest possible value $n_{cl} = 2$ the magnitude $E_p \approx 13,5 \text{ GPa}$. Since for PC $E_{l.m.} = 0,85 \text{ GPa}$, then it gives the greatest reinforcement degree $E_p/E_m \approx 15,9$. Let us note, that the greatest attainable reinforcement degree for artificial nanocomposites (polymers filled with inorganic nanofiller) cannot exceed 12 [9]. It is notable, that the shown in Fig. 26 dependence $E_p(n_{cl})$ for PC is identical completely by dependence shape to the dependence of elasticity modulus of nanofiller particles diameter for elastomeric nanocomposites [57].

Hence, the presented above results have shown that elasticity modulus of amorphous glassy polycarbonate, considered as natural nanocomposite, are defined completely by its suprasegmental structure state. This state can be described quantitatively within the frameworks of the cluster model of polymers amorphous state structure and characterized by local order level. Natural nanocomposites reinforcement degree can essentially exceed analogous parameter for artificial nanocomposites [56].

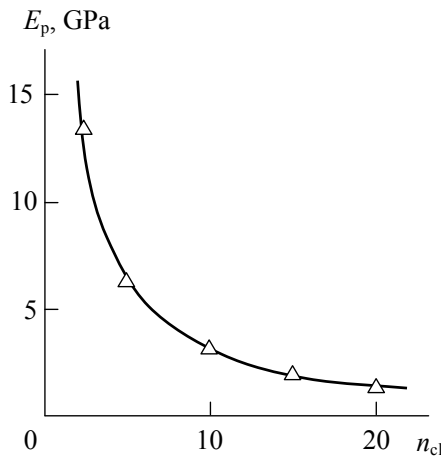


Fig. 26 - The dependence of elasticity modulus E_p on segments number n_{cl} per one nanocluster, calculated according to the equation (32) for PC at $T = 293 \text{ K}$ [56]

As it has been shown above (see the equations (7) and (15)), the nanocluster relative fraction increasing results to polymers elasticity modulus enhancement similarly to nanofiller contents enhancement in artificial

nanocomposites. Therefore the necessity of quantitative description and subsequent comparison of reinforcement degree for the two indicated above nanocomposites classes appears. The authors [58, 59] fulfilled the comparative analysis of reinforcement degree by nanoclusters and by layered silicate (organoclay) for polycarbonate and nanocomposite epoxy polymer/ Na^+ -montmorillonite [60], accordingly.

In Fig. 27 theoretical dependences of reinforcement degree E_n/E_m on nanofiller contents φ_n , calculated according to the equations (15) ÷ (17), are adduced. Besides, in the same figure the experimental values (E_n/E_m) for nanocomposites epoxy polymer Na^+ -montmorillonite (EP/MMT) at $T < T_g$ and $T > T_g$ (where T and T_g are testing and glass transition temperatures, respectively) are indicated by points. As one can see, for glassy epoxy matrix the experimental data correspond to the equation (16), i.e., zero adhesional strength at a large friction coefficient and for devitrified matrix – to the equation (15), i.e., the perfect adhesion between nanofiller and polymer matrix, described by Kerner equation. Let us note that the authors [17] explained the distinction indicated above by a much larger length of epoxy polymer segment in the second case.

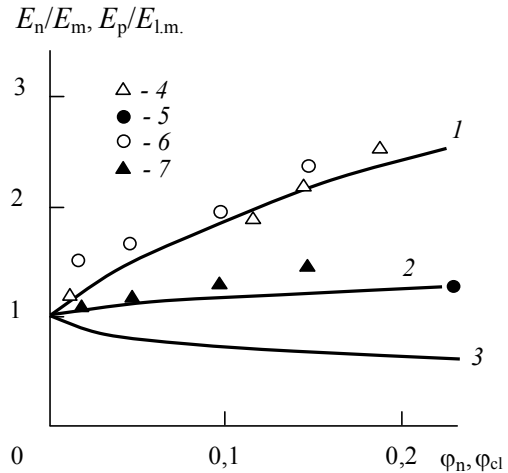


Fig. 27 - The dependences of reinforcement degree E_n/E_m and $E_p/E_{l.m.}$ on the contents of nanofiller φ_n and nanoclusters φ_{cl} , accordingly. 1÷3 – theoretical dependences (E_n/E_m) (φ_n), corresponding to the equations (15)÷(17); 4,5 – the experimental data ($E_p/E_{l.m.}$) for Par at $T = T_g' \div T_g$ (4) and $T < T_g'$ (5); 6, 7 – the experimental data (E_n/E_m) (φ_n) for EP/MMT at $T > T_g$ (6) and $T < T_g$ (7) [59]

To obtain the similar comparison for natural nanocomposite (polymer) is impossible, since at $T \geq T_g$ nanoclusters are disintegrated and polymer ceases to be quasi-two-phase system [5]. However, within the frameworks of two-stage glass transition concept [11] it has been shown, that at temperature T_g' , which is approximately equal to $T_g - 50 \text{ K}$, instable (small) nanoclusters decay occurs, that results to loosely-packed matrix devitrification at the indicated temperature [5]. Thus, within the range of temperature $T_g' \div T_g$ natural nanocomposite (polymer) is an analogue of nanocompo-

site with glassy matrix [58]. As one can see, for the temperatures within the range of $T = T'_g \div T_g$ ($\varphi_{cl} = 0,06 \div 0,19$) the value $E_p/E_{l.m.}$ corresponds to the equation (15), i.e., perfect adhesion nanoclusters-loosely-packed matrix and at $T < T'_g$ ($\varphi_{cl} > 0,24$) – to the equation (16), i.e., to zero adhesional strength at a large friction coefficient. Hence, the data of Fig. 27 demonstrated clearly the complete similarity, both qualitative and quantitative, of natural (Par) and artificial (EP/MMT) nanocomposites reinforcement degree behaviour. Another microcomposite model (for example, accounting for the layered silicate particles strong anisotropy) application can change the picture quantitatively only. The data of Fig. 27 qualitatively give the correspondence of reinforcement degree of nanocomposites indicated classes at the identical initial conditions.

Hence, the analogy in behaviour of reinforcement degree of polyarylate by nanoclusters and nanocomposite epoxy polymer/ Na^+ -montmorillonite by layered silicate gives another reason for the consideration of polymer as natural nanocomposite. Again strong influence of interfacial (intercomponent) adhesion level on nanocomposites of any class reinforcement degree is confirmed [17].

4. The Methods of Natural Nanocomposites Nanostructure Regulation

As it has been noted above, at present it is generally acknowledged [2], that macromolecular formations and polymer systems are always natural nanostructural systems in virtue of their structure features. In this connection the question of using this feature for polymeric materials properties and operating characteristics improvement arises. It is obvious enough that for structure-properties relationships receiving the quantitative nanostructural model of the indicated materials is necessary. It is also obvious that if the dependence of specific property on material structure state is unequivocal, then there will be quite sufficient modes to achieve this state. The cluster model of such state [3-5] is the most suitable for polymers amorphous state structure description. It has been shown, that this model basic structural element (cluster) is nanoparticles (nanocluster) (see section 15.1). The cluster model was used successfully for cross-linked polymers structure and properties description [61]. Therefore the authors [62] fulfilled nanostructures regulation modes and of the latter influence on rarely cross-linked epoxy polymer properties study within the frameworks of the indicated model.

In paper [62] the studied object was an epoxy polymer on the basis of resin UP5-181, cured by isomethyltetrahydrophthalic anhydride in the ratio by mass 1:0,56. Testing specimens were obtained by the hydrostatic extrusion method. The indicated method choice is due to the fact, that high hydrostatic pressure imposition in deformation process prevents the defects formation and growth, resulting to the material failure [64]. The extrusion strain ε_e was calculated and makes up 0,14, 0,25, 0,36, 0,43 and 0,52. The obtained by hydrostatic extrusion specimens were annealed at maximum tem-

perature 353 K during 15 min.

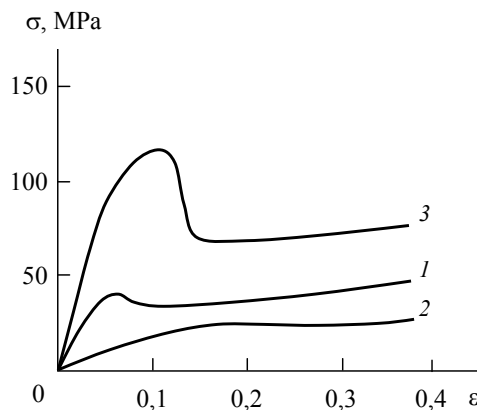


Fig. 28 - The stress – strain ($\sigma - \varepsilon$) diagrams for initial (1), extruded up to $\varepsilon_e = 0,52$ (2) and annealed (3) REP samples [62]

The hydrostatic extrusion and subsequent annealing of rarely cross-linked epoxy polymer (REP) result to very essential changes of its mechanical behaviour and properties, in addition unexpected ones enough. The qualitative changes of REP mechanical behaviour can be monitored according to the corresponding changes of the stress – strain ($\sigma - \varepsilon$) diagrams, shown in Fig. 28. The initial REP shows the expected enough behaviour and both its elasticity modulus E and yield stress σ_Y are typical for such polymers at testing temperature T being distant from glass transition temperature T_g on about 40 K [51]. The small (≈ 3 MPa) stress drop beyond yield stress is observed, that is also typical for amorphous polymers [61]. However, REP extrusion up to $\varepsilon_e = 0,52$ results to stress drop $\Delta\sigma_Y$ (“yield tooth”) disappearance and to the essential E and σ_Y reduction. Besides, the diagram $\sigma - \varepsilon$ itself is now more like the similar diagram for rubber, than for glassy polymer. This specimen annealing at maximum temperature $T_{an} = 353$ K gives no less strong, but diametrically opposite effect – yield stress and elasticity modulus increase sharply (the latter in about twice in comparison with the initial REP and more than one order in comparison with the extruded specimen). Besides, the strongly pronounced “yield tooth” appears. Let us note, that specimen shrinkage at annealing is small ($\approx 10\%$), that makes up about 20% of ε_e [62].

The common picture of parameters E and σ_Y change as a function of ε_e is presented in Fig. 29 and 30 accordingly. As one can see, both indicated parameters showed common tendencies at ε_e change: up to $\varepsilon_e \approx 0,36$ inclusive E and σ_Y weak increase at ε_e growth is observed, moreover their absolute values for extruded and annealed specimens are close, but at $\varepsilon_e > 0,36$ the strongly pronounced antibatness of these parameters for the indicated specimen types is displayed. The cluster model of polymers amorphous state structure and developed within its frameworks polymers yielding treatment allows to explain such behaviour of the studied samples [35, 65].

The cluster model supposes that polymers amorphous state structure represents the local order domains (nanoclusters), surrounded by loosely-packed matrix. Nanoclusters consist of several collinear

densely-packed statistical segments of different macromolecules and in virtue of this they offer the analog of crystallite with stretched chains.

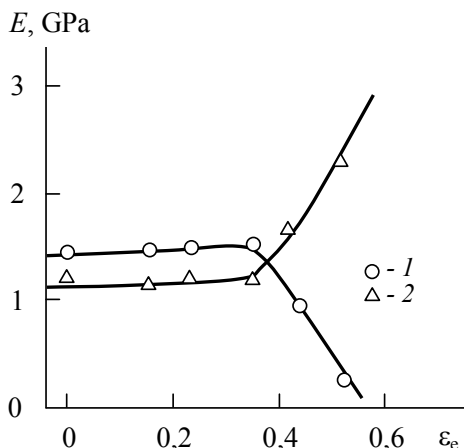


Fig. 29 - The dependences of elasticity modulus E_p on extrusion strain ϵ_e for extrudated (1) and annealed (2) REP [62]

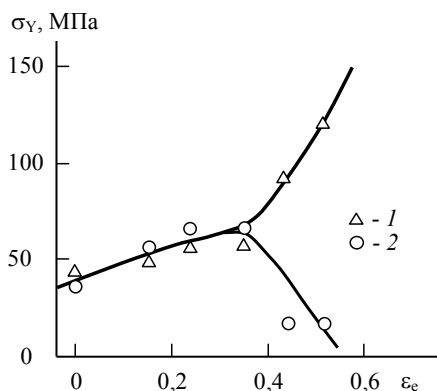


Fig. 30 - The dependences of yield stress σ_Y on extrusion strain ϵ_e for extrudated (1) and annealed (2) REP [62]

There are two types of nanoclusters – stable, consisting of a relatively large segments number, and instable, consisting of a less number of such segments [65]. At temperature increase or mechanical stress application the instable nanoclusters disintegrate in the first place, that results to the two well-known effects. The first from them is known as two-stage glass transition process [11] and it supposes that at $T'_g = T_g - 50$ K disintegration of instable nanoclusters, restraining loosely-packed matrix in glass state, occurs that defines devitrification of the latter [3, 5]. The well-known rapid polymers mechanical properties reduction at approaching to T_g [51] is the consequence of this. The second effect consists of instable nanoclusters decay at σ_Y under mechanical stress action, loosely-packed matrix mechanical devitrification and, as consequence, glassy polymers rubber-like behaviour on cold flow plateau [65]. The stress drop $\Delta\sigma_Y$ beyond yield stress is due to just instable nanoclusters decay and therefore $\Delta\sigma_Y$ value serves as characteristic of these nanoclusters fraction [5]. Proceeding from this brief description, the experimental results, adduced in Fig. 28 ÷ 30, can be interpreted.

The rarely cross-linked epoxy polymer on the

basis of resin UP5-181 has low glass transition temperature T_g , which can be estimated according to shrinkage measurements data as equal ≈ 333 K. This means, that the testing temperature $T = 293$ K and T'_g for it are

close, that is confirmed by small $\Delta\sigma_Y$ value for the initial REP. It assumes nanocluster (nanostructures) small relative fraction ϕ_{cl} [3-5] and, since these nanoclusters have arbitrary orientation, ϵ_e increase results rapidly enough to their decay, that induces loosely-packed matrix mechanical devitrification at $\epsilon_e > 0,36$. Devitrified loosely-packed matrix gives insignificant contribution to E_p [66, 67], equal practically to zero, that results to sharp (discrete) elasticity modulus decrease. Besides, at $T > T'_g$ ϕ_{cl} rapid decay is observed, i.e.,

segments number decrease in both stable and instable nanocluster [5]. Since just these parameters (E and ϕ_{cl}) check σ_Y value, then their decrease defines yield stress sharp lessening. Now extruded at $\epsilon_e > 0,36$ REP presents as matter of fact rubber with high cross-linking degree, that is reflected by its diagram $\sigma - \epsilon$ (Fig. 28, curve 2).

The polymer oriented chains shrinkage occurs at the extruded REP annealing at temperature higher than T_g . Since this process is realized within a narrow temperature range and during a small time interval, then a large number of instable nanoclusters is formed. This effect is intensified by available molecular orientation, i.e., by preliminary favourable segments arrangement, and it is reflected by $\Delta\sigma_Y$ strong increase (Fig. 28, curve 3).

The ϕ_{cl} enhancement results to E_p growth (Fig. 29) and ϕ_{cl} and E_p combined increase – to σ_Y considerable growth (Fig. 30).

The considered structural changes can be described quantitatively within the frameworks of the cluster model. The nanoclusters relative fraction ϕ_{cl} can be calculated according to the method, stated in paper [68].

The shown in Fig. 31 dependences $\phi_{cl}(\epsilon_e)$ have the character expected from the adduced above description and are its quantitative conformation. The adduced in Fig. 32 dependence of density ρ of REP extruded specimens on ϵ_e is similar to the dependence $\phi_{cl}(\epsilon_e)$, that was to be expected, since densely-packed segments fraction decrease must be reflected in ρ reduction.

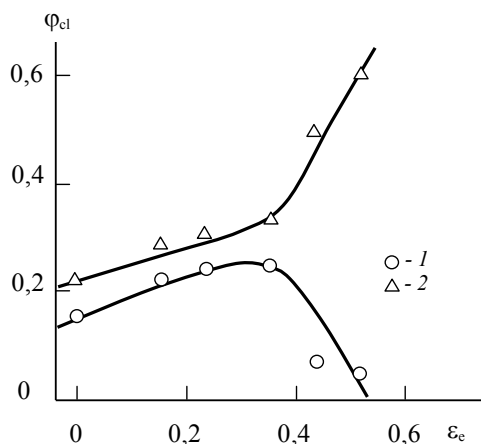


Fig. 31 - The dependences of nanoclusters relative fraction ϕ_{cl} on extrusion strain ϵ_e for extruded (1) and annealed (2) REP [62]

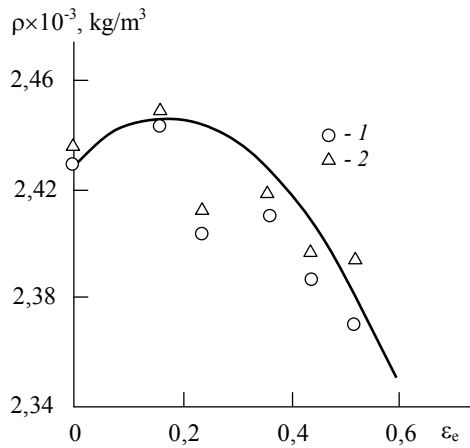


Fig. 32 - The dependence of specimens density ρ on extrusion strain ε_e for extruded (1) and annealed (2) REP [62]

In paper [69] the supposition was made that ρ change can be conditioned to microcracks network formation in specimen that results to ρ reduction at large ε_e (0,43 and 0,52), which are close to the limiting ones. The ρ relative change ($\Delta\rho$) can be estimated according to the equation:

$$\Delta\rho = \frac{\rho^{\max} - \rho^{\min}}{\rho^{\max}}, \quad (33)$$

where ρ^{\max} and ρ^{\min} are the greatest and the smallest density values. This estimation gives $\Delta\rho \approx 0,01$. This value can be reasonable for free volume increase, which is necessary for loosely-matrix devitrification (accounting for closeness of T and T'_g), but it is obviously small

if to assume as real microcracks formation. As the experiments have shown, REP extrusion at $\varepsilon_e > 0,52$ is impossible owing to specimen cracking during extrusion process. This allows to suppose that value $\varepsilon_e = 0,52$ is close to the critical one. Therefore the critical dilatation $\Delta\delta_{cr}$ value, which is necessary for microcracks cluster formation, can be estimated as follows [40]:

$$\Delta\delta_{cr} = \frac{2(1+\nu)(2-3\nu)}{11-19\nu}, \quad (34)$$

where ν is Poisson's ratio.

Accepting the average value $\nu \approx 0,35$, we obtain $\Delta\delta_{cr} = 0,60$, that is essentially higher than the estimation $\Delta\rho$ made earlier. These calculations assume that ρ decrease at $\varepsilon_e = 0,43$ and $0,52$ is due to instable nanoclusters decay and to corresponding REP structure loosening.

The stated above data give a clear example of large possibilities of polymer properties operation through its structure change. From the plots of Fig. 29 it follows that annealing of REP extruded up to $\varepsilon_e = 0,52$ results to elasticity modulus increase in more than 8 times and from the data of Fig. 30 yield stress increase in 6 times follows. From the practical point of view the extrusion and subsequent annealing of rarely cross-linked epoxy polymers allow to obtain materials, which are just as good by stiffness and strength as densely cross-linked epoxy polymers, but exceeding the latter by plasticity degree. Let us note, that besides extrusion and

annealing other modes of polymers nanostructure operation exist: plasticization [70], filling [26, 71], films obtaining from different solvents [72] and so on.

Hence, the stated above results demonstrated that neither cross-linking degree nor molecular orientation level defined cross-linked polymers final properties. The factor, controlling properties is a state of suprasegmental (nanocluster) structure, which, in its turn, can be goal-directly regulated by molecular orientation and thermal treatment application [62].

In the stated above treatment not only nanostructure integral characteristics (macromolecular entanglements cluster network density ν_{cl} or nanocluster relative fraction ϕ_{cl}), but also separate nanocluster parameters are important (see section 1). In this case of particulate-filled polymer nanocomposites (artificial nanocomposites) it is well-known, that their elasticity modulus sharply increases at nanofiller particles size decrease [17]. The similar effect was noted above for REP, subjected to different kinds of processing (see Fig. 28). Therefore the authors [73] carried out the study of the dependence of elasticity modulus E on nanoclusters size for REP.

It has been shown earlier on the example of PC, that the value E_p is defined completely by natural nanocomposite (polymer) structure according to the equation (32) (see Fig. 26)

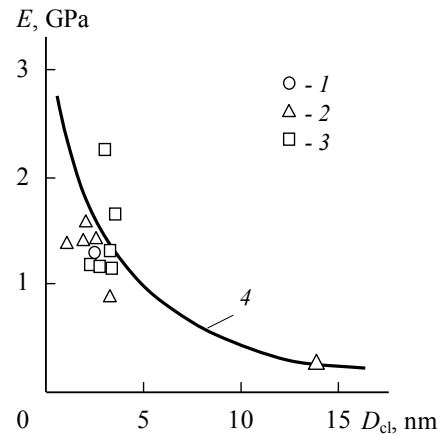


Fig. 33 - The dependence of elasticity modulus E_p on nanoclusters diameter D_{cl} for initial (1), extruded (2) and annealed (3) REP. 4 - calculation according to the equation (32) [73]

In Fig. 33 the dependence of E_p on nanoclusters diameter D_{cl} , determined according to the equation (in previous paper), for REP subjected to the indicated processing kinds at ε_e values within the range of $0,16 \div 0,52$ is added. As one can see, like in the case of artificial nanocomposites, for REP strong (approximately of order of magnitude) growth is observed at nanoclusters size decrease from 3 up to 0,9 nm. This fact confirms again, that REP elasticity modulus is defined by neither cross-linking degree nor molecular orientation level, but it depends only on epoxy polymer nanocluster structure state, simulated as natural nanocomposite [73].

Another method of the theoretical dependence $E_p(D_{cl})$ calculation for natural nanocomposites (polymers) is given in paper [74]. The authors [75] have

shown, that the elasticity modulus E value for fractal objects, which are polymers [4], is given by the following percolation relationship:

$$K_T, G \sim (p - p_c)^\eta, \quad (35)$$

where K_T is bulk modulus, G is shear modulus, p is solid-state component volume fraction, p_c is percolation threshold, η is exponent.

The following equation for the exponent η was obtained at a fractal structure simulation as Serpinsky carpet [75]:

$$\frac{\eta}{v_p} = d - 1, \quad (36)$$

where v_p is correlation length index in percolation theory, d is dimension of Euclidean space, in which a fractal is considered.

As it is known [4], the polymers nanocluster structure represents itself the percolation system, for which $p = \varphi_{cl}$, $p_c = 0,34$ [35] and further it can be written:

$$\frac{R_{cl}}{l_{st}} \sim (\varphi_{cl} - 0,34)^{v_p} \quad (37)$$

where R_{cl} is the distance between nanoclusters, determined according to the equation (4.63), l_{st} is statistical segment length, v_p is correlation length index, accepted equal to 0,8 [77].

Since in the considered case the change E_p at n_{cl} variation is interesting first of all, then the authors [74] accepted $v_{cl} = \text{const} = 2,5 \times 10^{27} \text{ m}^{-3}$, $l_{st} = \text{const} = 0,434 \text{ nm}$. The value E_p calculation according to the equations (35) and (37) allows to determine this parameter according to the formula [74]:

$$E_p = 28,9(\varphi_{cl} - 0,34)^{(d-1)v_p}, \text{ GPa}. \quad (38)$$

In Fig. 34 the theoretical dependence (a solid line) of E_p on nanoclusters size (diameter) D_{cl} , calculated according to the equation (38) is adduced. As one can see, the strong growth E_p at D_{cl} decreasing is observed, which is identical to the shown one in Fig. 33. The adduced in Fig. 34 experimental data for REP, subjected to hydrostatic extrusion and subsequent annealing, correspond well enough to calculation according to the equation (38). The decrease D_{cl} from 3,2 up to 0,7 nm results again to E_p growth on order of magnitude [74].

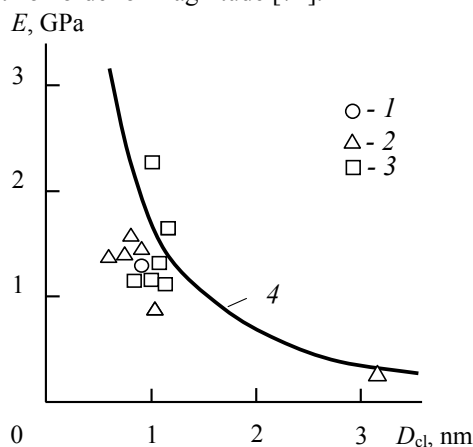


Fig. 34 - The dependence of elasticity modulus E_p on nanoclusters diameter D_{cl} for initial (1), extruded (2) and annealed (3) REP. 4 – calculation according to the equation (38) [74]

The similar effect can be obtained for linear amorphous polycarbonate (PC) as well. Calculation according to the equation (38) shows, n_{cl} reduction from 16 (the experimental value n_{cl} at $T = 293\text{K}$ for PC [5]) up to 2 results to E_p growth from 1,5 up to 5,8 GPa and making of structureless ($n_{cl} = 1$) PC will allow to obtain $E_p \approx 9,2 \text{ GPa}$, i.e., comparable with obtained one for composites on the basis of PC.

Hence, the stated in the present chapter results give purely practical aspect of such theoretical concepts as the cluster model of polymers amorphous state structure and fractal analysis application for the description of structure and properties of polymers, treated as natural nanocomposites. The necessary nanostructure goal-directed making will allow to obtain polymers, not yielding (and even exceeding) by their properties to the composites, produced on their basis. Structureless (defect-free) polymers are imagined the most perspective in this respect. Such polymers can be natural replacement for a large number of elaborated at present polymer nanocomposites. The application of structureless polymers as artificial nanocomposites polymer matrix can give much larger effect. Such approach allows to obtain polymeric materials, comparable by their characteristics with metals (for example, with aluminium).

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