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EVOLUTION OF DISSIPATIVE STRUCTURES IN THE FLOW PROCESS OF CROSS-LINKED POLYMERS

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The behavior of a deformable solid body under mechanical action is determined by the processes of formation and evolution of dissipative structures (DS), which ensure optimum conditions for the dissipation of energy coming from outside [1, 2]. For metals, this approach is generally recognized, although there is no consensus on the mechanism of structural reorganization [3]. For polymers, this problem has not been studied, although the presence of DS in them has been discussed [4]. At the same time, its solution will make it possible to approach polymer deformation from the viewpoint of the fundamental physical principles of nonequilibrium thermodynamics [5]. These principles can be applied if a quantitative structural model is available. For cross-linked polymers, such a model could be the cluster model of their amorphous state in [6, 7], which identifies quantitatively a local order whose regions are DS. This paper deals with the evolution of DS (cluster structure) in the flow process using, as an example, epoxy polymers as a typical representative of this class of materials.

We studied two series of samples obtained by hardening of ÉD-22 epoxy oligomer by means of isomethyltetrahydrophthalic anhydride with a varied hardener–oligomer ratio K_{st} in moles (equivalents). The samples of the first series (ÉP-1) were tested immediately after preparation, and those of the second (ÉP-2), after their natural aging under atmospheric conditions for 3 years. The conditions of preparation of samples and test methods are described in [8]. The structural parameters were calculated according to [6, 7].

The model of [6, 7] assumes that the structure of amorphous polymers consists of regions of local order (clusters) surrounded by a loosely packed matrix. Each cluster consists of several collinear segments of different macromolecules whose length is assumed to be equal to that of a statistical segment l_s. Thus, the cluster is an analog of a crystallite with elongated chains (CEC). At the same time, each cluster is regarded as a multifunction node of a fluctuation grid of macromolecular entanglements with density V_{h}. With this interpretation, the quantity V_{h} has another physical meaning: the number of segments in the clusters per polymer unit volume, i.e., it can serve as an indicator of the degree of local order.

Figure 1 presents the dependences of the cluster grid density in the undeformed state V_{h} (points 1 and 2) and after flow V_{h}^{f} (points 3 and 4) on the hardener–oligomer ratio K_{st} for the compositions ÉP-1 (points 1 and 3) and ÉP-2 (points 2 and 4). In Figs. 1–4, curves are used to approximate dependences obtained as sets of the corresponding points. From the data in Fig. 1 it follows that aging leads to an increase in V_{h}. This agrees well with the concept of the aging process as the transition to a more stable state with closer molecular packing [9]. The maximum increase in V_{h} is observed in compositions that are the most different from stoichiometry, which makes it possible to consider their structure the farthest from equilibrium.

The flow process in amorphous linear polymers has been shown [10] to occur when the effective Poisson ratio $\mu_{\text{f}} \simeq 0.41$. Assuming that this conclusion is valid for the polymers discussed and using the relationship between μ and V_{h} obtained in [11], we calculated V_{h}^{f} for the flow limit σ_{f}. The obtained values are given in Fig. 1. The values of V_{h}^{f} are independent of K_{st} and practically coincide for ÉP-1 and ÉP-2, and this is due to the initial choice of μ_{f}. At the same time, they are markedly lower than those of V_{h}. This means that decay of a certain number of DS clusters is required to realize flow in cross-linked polymers. This situation is diametrically opposite to metal deformation processes, in which, on the contrary, formation of DS of

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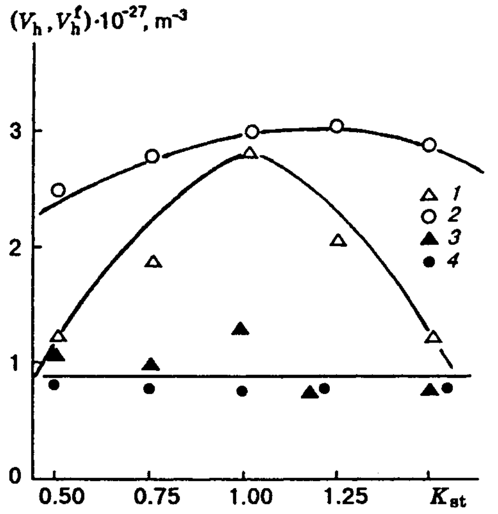

Fig. 1

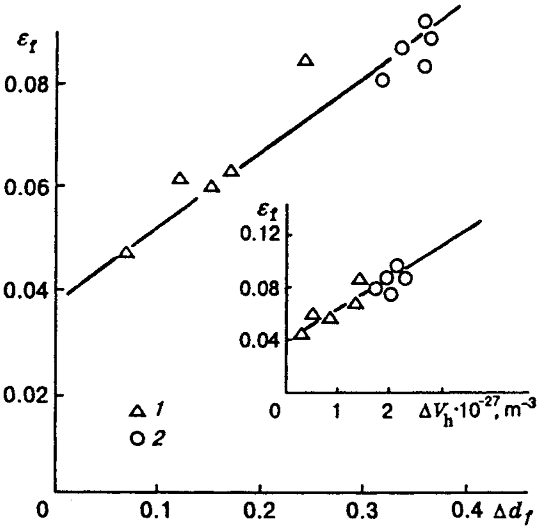

Fig. 2

dislocation substructures [2, 5] is observed. This difference is fundamental and due to different concepts of ideal (defectless) structures of the materials compared [12].

It should be expected that the above structural changes will determine the parameters characterizing flow in cross-linked polymers. We consider it, taking, as an example, the flow deformation ε_f. It is natural to assume that the greater the number of DS that decay in flow, the larger the value of ε_f. This number of DS can be determined as the difference between the cluster grid densities before flow V_h and after it V_h^f, i.e., $\Delta V_h = V_h - V_h^f$, which can be readily found from the graphs in Fig. 1. The inset in Fig. 2 gives the correlation $\varepsilon_f(\Delta V_h)$, which confirms the assumption made.

Polymer structure can be represented as a fractal with dimension d_f [2, 10]:

$$d_f = (d-1)(1+\mu). \tag{1}$$

Here, d is the dimension of Euclidean space in which the fractal is imbedded (for the case in question, obviously, $d = 3$); μ is Poisson's ratio, which is found from the results of mechanical tests using the relation [13]

$$\sigma_f/E = (1-2\mu)/6(1+\mu), \tag{2}$$

where σ_f is the flow limit and E is the modulus of elasticity.

Figure 2 shows the dependence of ε_f on the difference Δd_f between fractal dimensions for ÉP-1 and ÉP-2 (points 1 and 2) prior to and after the flow, which is calculated by formulas (1) and (2). The observed linear correlation $\varepsilon_f(\Delta d_f)$ again indicates that the value of ε_f is determined by the evolution of DS in the flow process.

The stability of a solid body against shear deformation is a fundamental property and can be expressed in terms of the indices m and n of the well-known Mie equation as $1/mn$ [2]. In turn [13],

$$1/mn = (1-2\mu)/6(1+\mu). \tag{3}$$

The relationship between ε_f and the parameter $1/mn$ calculated from Eq. (3) for ÉP-1 and ÉP-2 (points 1 and 3) is linear and is extrapolated to the coordinate origin (Fig. 3); hence the flow process is the loss of stability of the polymer as a system [2].

The cluster model [6, 7] implies that the structure of an amorphous polymer contains two types of clusters (DS): stable clusters, which consist of a large number of segments, and unstable clusters, which contain a small number of segments and retain the loosely packed matrix in the glassy state. The number of segments

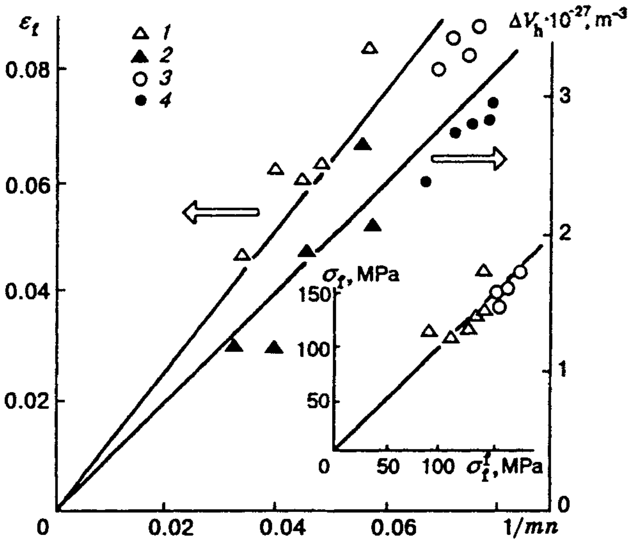

Fig. 3

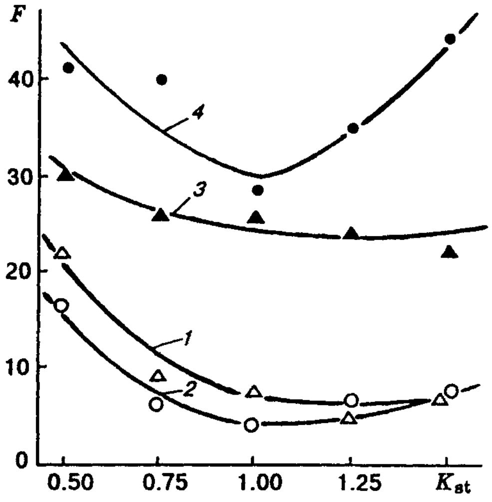

Fig. 4

in a cluster can be estimated by means of its functionality F, which is equal to the number of chains emerging from the cluster. Since the latter is an analog of a CEC [6], it is obvious that the number of segments in one cluster is equal to $F/2$.

A characteristic feature of DS is the existence of a hierarchy of spatial scales [3]. Their relationship for adjacent structural levels can be described by the expression [3]

$$L_{i+1}/L_i = \Lambda_i = 2(1-\mu)/(1-2\mu). \tag{4}$$

Here L_i and L_{i+1} are the linear scales of the DS of the ith and $(i+1)$th level; and Λ_i is the self-similarity coefficient. One can use l_s as L_i, and the distance between the clusters, as L_{i+1} [14]

$$R_{cl} = 1.8 \cdot 10^{-9}(2V_h/F)^{-1/3}, \text{ m}. \tag{5}$$

Then

$$\Lambda_i = R_{cl}/l_s. \tag{6}$$

Equations (4)–(6) allow one to determine values of F before and after flow. Figure 4 presents the curves of $F(K_{st})$ that correspond to the undeformed state (points 1 and 2) and to the state after flow (points 3 and 4) for ÉP-1 (points 1 and 3) and ÉP-2 (points 2 and 4). The most characteristic difference between the relationships compared is a considerable increase in F on attainment of the flow limit. The simultaneous decrease in V_h and increase in F during polymer deformation up to the flow limit (Figs. 1 and 4) indicates decay of unstable clusters with a small value of F; as a result, for σ_f, only stable clusters with a large value of F remain. The decay of unstable clusters causes mechanical devitrification of the loosely packed matrix, which explains the rubber-like behavior of polymers on a forced high-elasticity plateau (cold flow) [15].

Let us estimate, within the framework of the suggested model, the consumption of energy related to the decay of clusters under the action of an external load. The energy U_d required for association (dissociation) of a pair of segments in a cluster can be calculated using dislocation analogies [16]. Then the total energy required for flow deformation has the form

$$U = U_d \Delta V_h, \tag{7}$$

where ΔV_h is the number of dissociating pairs of segments. On the other hand, the value of U can be determined from the stress–strain diagram assuming that it is approximately triangular up to the flow limit:

$$U = (1/2)\,\varepsilon_f \sigma_f. \tag{8}$$

Equating (7) and (8), we find a theoretical value of the flow limit σ_f^f and compare it with the experimental value σ_f (inset in Fig. 3). A good agreement between σ_f^f and σ_f means that the flow limit is actually determined by the energy of decay of unstable clusters.

In conclusion, we again turn to the stability of a polymer under shear deformations, which is characterized by the quantity $1/mn$. Figure 3 shows this quantity versus V_h, i.e., the degree of local order [6], for ÉP-1 and ÉP-2 (points 2 and 4). The presence of a one-to-one correspondence between $1/mn$ and V_h makes it possible to consider V_h a fundamental characteristic of an amorphous polymer, as is $1/mn$ for a solid body.

Thus, the flow process of cross-linked polymers is described within the framework of the synergy of a deformed body, i.e., by the evolution of dissipative structures. Quantitative representation of the latter can be realized using the cluster model for the polymer structure in the amorphous state.

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