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DIMENSION OF THE LOCAL-PLASTICITY ZONE AS A CORRELATION LENGTH OF THE STRUCTURE OF POLYMERS UNDER INELASTIC DEFORMATION

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The structural meaning of the dimension r_{pl} of the zone of local plastic deformation in polymers is determined. In simulating the polymer structure as a percolation cluster, the quantity r_{pl} is the correlation length of the structure of the polymer deformed until inelastic deformations appear. This rule holds for both amorphous glassy polymers and amorphous-crystalline polymers and for various types of the indicated zones (crazing or shear).

The zone of local plastic deformation (the craze or the zone of shear yield) is the most important element of a deformed polymer at quasibrittle (quasiductile) failure. The type of local-plasticity zone determines the type of failure: if a craze is formed at the vertex of the defect, the failure of the polymer is quasibrittle, whereas if a zone of local shear yield is formed, the failure of the polymer is quasiductile [1]. A change in the deformation mechanism from crazing to shear yield is usually considered as a brittle-ductile transition [2]. An increase in the dimension of both the craze [3] and the shear-yield zone [4] leads, as a rule, to an increase in the ductility in polymer failure, which is characterized by the quantity K_{Ic} or G_{Ic}. In essence, the only theoretical method for evaluating the dimension of the local-plasticity zone $r_{\rm pl}$ is the Dugdale–Barenblatt equation [1]

$$r_{\rm pl} = \frac{\pi}{8} \frac{K_{Ic}^2}{\sigma_{\rm y}^2} . \tag{1}$$

Although Eq. (1) gives good agreement with experiment for both crazes [3] and zones of local shear [5], it does not relate the parameter $r_{\rm pl}$ to any structural characteristics of the polymer. It is obvious that this situation inhibits prediction of the quantity $r_{\rm pl}$ and accordingly of the parameters of quasibrittle (quasiductile) failure of polymers. Therefore, the present work seeks to obtain the interrelationship between $r_{\rm pl}$ and the structural characteristics of polymers within the framework of percolation theory using as an example two polymers, namely, polyethylene of high density (PEHD) and polystyrene (PS). We selected these polymers because they belong to different classes (amorphous-crystalline and amorphous-glassy, respectively) and are deformed by different mechanisms (shear yield and crazing, respectively). Therefore, obtaining identical results for these polymers presupposes a high degree of generality of the concept suggested.

Gas-phase PEHD of commercial production (grade 276) with a weighted-mean molecular weight $\overline{M}_{\rm w} \cong 1.5 \cdot 10^5$ and a degree of crystallinity of 0.67 is used. Specimens for impact tests according to All-Union State Standard 4647-80 (size II) are obtained by the injection-molding method. Polystyrene of PSM grade with a molecular weight $\overline{M}_{\rm w} \cong 2.5 \cdot 10^5$ in the form of granules is also used. PS specimens of the same size as the PEHD ones are produced by high-pressure molding under the following conditions: temperature 443 K and pressure 5.5 MPa.

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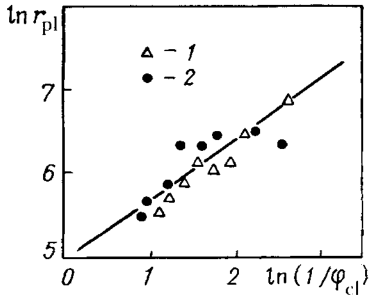

Fig. 1. Relation between the length of the local-plasticity zone r_{pl} and the relative fraction of the clusters φ_{cl} in double logarithmic coordinates that corresponds to relation (3) for PEHD (1) and PS (2).

We made cuts with the blade of a sharp razor. The length of the cut a was controlled by a support in a special device and was varied within the limits of 0.5–1.5 mm in the case of PEHD. For PS, the quantity a was constant and equal to 0.2 mm.

Impact tests of PS specimens by Sharpy's procedure are carried out in the range of temperatures from193 to 333 K, and of PEHD specimens, at a temperature of 293 K. There are a number of polymers, including PEHD and PS, whose zones of local plasticity can easily be identified on the surface of failure. Here the shear-yield zones ("shear jaws") and crazes differ in both appearance and position on the surface of failure. The shear-yield zones have a dull white color and are located perpendicular to the base of the cut. The craze has a brilliant silvery color and is located parallel to the base of the cut. This makes it possible to determine the dimension r_{pl} of these local-plasticity zones on the surface of failure of the specimens by means of a Zeiss optical microscope (the accuracy is ± 10 μm).

The cluster model for the structure of the amorphous state of polymers [4] suggests that the above structure consists of two components: regions of local order (clusters) and a loosely packed matrix, the sum of whose relative fractions is equal to 1. The relative fraction of the clusters φ_{cl} for PEHD is taken according to the data of [6], while for PS it is calculated from the following relation [7]:

$$\varphi_{cl} \cong 0.03\,(T_{gl.tr} - T)^{0.55}\,. \tag{2}$$

The theory of occurrence (percolation) [8] presupposes formation, near the percolation threshold, of an infinite cluster that constricts the system. The polymer structure itself can be considered as a percolation system at rather high molecular weights, since precisely formation of a grid of linkages over the entire extent of the polymer specimen imparts deformability and strength to it [2]. The formation of this percolation cluster when the temperature decreases to $T_{gl.tr}$ was shown in [7, 9] using the cluster model for the structure of the amorphous state of polymers [10]. Within the framework of this model, the percolation skeleton is considered as a grid of macromolecular linkages, whose nodes are regions of local order (clusters) immersed in a loosely packed matrix. In this case, the probability that a particle (a statistical segment) belongs to an infinite percolation cluster is equal to the relative fraction of the clusters φ_{cl}. If we assume the quantity r_{pl} to be the correlation length of this percolation system, we can write [8]

$$r_{pl} \sim (\varphi_{cl} - \varphi_{cl}^{th})^{-\nu}\,. \tag{3}$$

As was shown previously [7, 9], the glass-transition temperature (the melting point) is the percolation threshold for the polymer structure on a temperature scale. On approaching this temperature, the quantity φ_{cl} decreases and can be as small as desired. Therefore, in a first approximation we take $\varphi_{cl}^{th} = 0$. Figure 1 presents the dependence $r_{pl}(1/\varphi_{cl})$ in double logarithmic coordinates for PEHD and PS that corresponds to Eq. (3). As can be seen, the data for both investigated polymers fall on one linear dependence, thus making it possible to determine ν, equal to ~ 0.80 [8].

Let us consider the physical meaning of the critical index ν. It was shown in [11] that a percolation cluster is a fractal object with the dimensionality d_f, for which the following relation is fulfilled:

$$\nu = \frac{2}{d_f}. \tag{4}$$

Thus, the index ν acquires a clear physical meaning. Evaluation of d_f by Eq. (4) yields a value of ~2.63, which is in agreement with the values of d_f obtained by other methods [12].

We note that the index ν characterizes the part of the percolation system that surrounds the percolation skeleton [11]. As was noted above, as applied to polymers this means that the index ν characterizes the loosely packed matrix, in which the entire fluctuational free volume of the polymer is concentrated [13]. Consequently, the formation of the plasticity zone, as would be expected, is associated with the loosely packed component of the structure of the polymer and its free volume. This conclusion follows directly from the absolute value of the critical index ν, since for the other structural component (the cluster grid) the index $\beta = 0.4$ for the indicated value of d_f, which differs from the obtained value 0.8.

It should also be noted that the combination of Eqs. (3) and (4) demonstrates a typical example of the necessity of using at least two parameters of the order to describe the structure and properties of polymers. In the case considered, these parameters are φ_{cl} and d_f.

Thus, the structural meaning of the length of the local-plasticity zone in polymers is elucidated for the first time. The application of percolation theory shows that independently of the class of the polymer or the type of zone of local plasticity its length is the correlation length of the structure of the polymer deformed until inelastic deformations appear. This approach makes it possible to predict r_{pl} within the framework of the model suggested and, consequently, to predict the properties of polymers at quasibrittle (quasiductile) failure.

NOTATION

K_{Ic}, critical coefficient of stress intensity (resistance to cracks); G_{Ic}, critical rate of deformation-energy release; r_{pl}, dimension of the local-plasticity zone; σ_y, yield stress ; $\overline{M}_w$, weighted-mean molecular weight; a, length of the cut; φ_{cl}, relative fraction of the regions of local order (clusters); $T_{gl.tr}$, glass-transition temperature, equal to ~368 K for PS [14]; T, test temperature; φ_{cl}^{th}, percolation threshold; d_f, fractal (Hausdorff) dimensionality. Superscripts and subscripts: I, opening or extension of the crack; c, critical; pl, plasticity; y, yield; w, weighted-mean; cl, cluster; gl.tr, glass transition; ν, critical index of percolation theory; f, fractal.

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