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A. T. Sanzharovsky, G. A. Grinyute, T. V. Likhtman

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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A. T. Sanzharovsky, G. A. Grinyute, T. V. Likhtman

INVESTIGATION OF THE INFLUENCE OF LOADING DURATION AND TEMPERATURE ON THE STRENGTH OF THREE-DIMENSIONAL POLYMERS

(Presented by Academician P. A. Rebinder, 21 III 1964)

In the present work, the long-term strength of polymer films made from melamine-formaldehyde (MFS) and polyester (PS) resin and its dependence on temperature were investigated. It was established that over a wide temperature range the long-term strength of these films (Figs. 1, 2) obeys the well-known (^{1}) equation:

$$\tau = Ae^{-\alpha\sigma}, \tag{1}$$

where τ is the time to failure of the specimen under the action of stress σ; A and α are constants.

Fig. 1. Change in the long-term strength of melamine-formaldehyde films at temperatures −23° (1), 0° (2), 20° (3), 30° (4), 50° (5), 60° (6), and 70° (7)

However, the relative arrangement of the dependences $\tau = f(\sigma)$, obtained at different temperatures, turned out to be completely different from that established in works (^{1},^{2}) and others. The dependences $\tau = f(\sigma)$ for MFS films formed two families of straight lines (Fig. 1). The first family, 1, 2, 3—the straight lines obtained at temperatures 20 and −23°—intersect at $\tau_0 \approx 10^{-13}$ sec. The straight lines 5, 6, and 7, obtained at temperatures 50, 60, and 70°, formed the second family, which converges at the point $\tau_0 = 10^{5.5}$ sec. Line 4 occupied an intermediate position.

The straight lines $\tau = f(\sigma)$ for films made from PS (Fig. 2), obtained at temperatures 23, 50, and 70° (lines 1, 2, 3), converge at a point at $\tau = 10^{5.6}$

Fig. 2

Figure 2: Fig. 2

sec. Lines 4 and 5, taken at temperatures 80 and 90°, as well as lines 6 and 7 (Fig. 2), obtained at temperatures 10 and 0°, proved to be parallel.

From the data of Figs. 1 and 2, temperature dependences of long-term strength were constructed in the coordinates $\lg \tau – 1/T$.

The temperature dependences of the long-term strength of MFS films, $\tau = f(1/T)$, likewise gave two distinct families of straight lines. Family I, converging at $\tau = 10^{-13}$ sec, and family II, at $\tau = 10^{5.5}$ sec. The same dependences for PS films gave a more complex picture. Lines 1, 2, 3 (Fig. 2), corresponding to temperatures 23, 50, and 70°, formed a family of straight lines I, converging at the point $\tau = 10^{6.5}$ sec. The dependences $\tau = f\left(\frac{1}{T}\right)$ for temperatures 80 and 90° formed a family of parallel straight lines II, and for temperatures 10 and 0°, a family of parallel straight lines III, with a larger angle of inclination to the abscissa axis.

Within the range of temperatures used by us, the dependences $\lg \tau = f\left(\frac{1}{T}\right)$ are expressed by straight lines, which are described by the equation:

$$\tau = Ae^{U/RT}, \tag{2}$$

where U is the activation energy of the fracture process.

Using equation (2), the activation energies U of the films studied were calculated at various stresses σ (Fig. 3).

The activation energy U of MFS films, calculated for family I, from the dependences $\lg \tau = f\left(\frac{1}{T}\right)$, increases as the breaking stresses σ decrease (straight lines 1 and 2), while for family II it decreases (straight lines 3-4). The value of U for PS films, calculated for family I, decreases as σ decreases (straight lines 5-6), whereas U, calculated from the parallel straight lines of family II, proved to be independent of the stress and equal to 22 kcal/mole (straight lines 7-8).

Fig. 2. Change in the long-term strength of polyester films at temperatures −23° (1), 50° (2), 70° (3), 80° (4), 90° (5), 10° (6), and 0° (7)

Analysis of the dependences of the activation energy of the fracture process of the films studied on stress shows that the fracture mechanism of the polymers investigated is different in different temperature intervals. In this connection, the transition points of the polymers studied were determined. It turned out that MFS films at temperatures below 20° are in the glassy state, and above this temperature, in a high-elastic state with long relaxation times.

Fig. 3. Change in the activation energy U of fracture of melamine-formaldehyde (1, 2, 4) and polyester (5, 6, 7) films as a function of stress

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

σ

Fig. 4. Change in the activation energy U of fracture of a three-dimensional polymer in the glassy state (1, 2), in the high-elastic state with long relaxation times (2, 3), and with short relaxation times (3, 4) as a function of stress σ

PS films at temperatures below 20° are in the glassy state; in the temperature interval 20–70°, in a high-elastic state with long relaxation times; and above 70°, with short relaxation times.

It follows from this that, with the transition of a polymer from one state to another, the character of the dependence of long-term strength on stress and temperature, and of activation energy on stress, changes fundamentally. Thus, in the region of the glassy state the long-term strength of MFS films obeys Zhurkov’ s equation (1). There is no doubt that an analogous picture will also be obtained for polyester films in the glassy state.

In accordance with the activation theory of fracture of solids (1-3), the activation energy U increases with decreasing σ and, at $\sigma = 0$, is 62 kcal/mole for MF .

The fracture of the films investigated in the highly elastic state with long relaxation periods is characterized by a different type of dependence of long-term strength on stress and temperature (see Fig. 1). The activation energy of fracture of the polymer in this state decreases sharply with decreasing σ.

The time and temperature dependences of the long-term strength of the polymer in the highly elastic state with short relaxation periods were studied on PS films at temperatures of 80 and 90° (straight lines 5, 4, Fig. 2). The activation energy of fracture of the polymer in this state does not depend on stress and is close in magnitude to the energy of intermolecular interaction (Fig. 3). This last result was obtained earlier by G. M. Bartenev and L. S. Bryukhanova (4) in studying the activation energy of fracture of rubbers in the region of positive temperatures.

On the basis of the data obtained, it is possible to construct a generalized dependence of the activation energy U of polymer fracture on stress σ over a broad temperature range encompassing all three states of the polymer. In Fig. 4 the solid heavy line shows the actual change in activation energy, while the dashed lines show fictitious sections which are probably obtained as a result of an unjustified extrapolation.

The results of our experiments allow us to formulate the following mechanism of fracture of polymeric materials. In the glassy state of a polymer, intermolecular interactions are substantial and relaxation processes are strongly hindered. When the polymer is loaded, the load is borne by chemical bonds, since they have no possibility of being unloaded as a result of relaxation processes, and fracture proceeds along these chemical bonds. In these cases, fracture of the polymer occurs in accordance with the fluctuation mechanism ([1],[3]). The activation energy increases with decreasing σ (section 1—2, Fig. 4), and at $\sigma = 0$ is equal to the energy of the bonds being broken.

The process of polymer fracture in the highly elastic state with long relaxation periods is determined by chemical and intermolecular bonds. In this case their role in the fracture process changes as the rate of fracture changes. When the polymer is loaded in this state, the chemical bonds, as a result of relaxation, can be unloaded to a greater or lesser extent, and the load is borne by intermolecular bonds. Therefore the activation energy of such fracture is significantly lower than in the first case. The more slowly the process of polymer fracture develops, the greater the role in the fracture process played by the comparatively weak intermolecular bonds. This leads to a decrease in the activation energy with decreasing breaking stresses, since the rate of polymer fracture decreases with decreasing σ (section 2—3, Fig. 4).

When a polymer is loaded in the highly elastic state with short relaxation periods, the chemical and intermolecular bonds are stressed uniformly as a result of rapid relaxation. In this state of the polymer, the nucleation of fracture cracks along intermolecular bonds becomes most probable. The kinetics of the development of fracture cracks under these conditions is controlled by intermolecular bonds, and the activation energy is close in magnitude to the energy of the intermolecular bonds and does not depend on σ (section 3—4, Fig. 4).

Institute of Physical Chemistry
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.