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INVESTIGATION OF THE SPONTANEOUS CONTRACTION OF POLYMERS WITH A DEVELOPED SPATIAL STRUCTURE DURING THEIR RUPTURE

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One of the distinctive features of polymer rupture is a substantial change in the structure of the material during its deformation and destruction. In this process changes occur in the relaxation properties of the material, which until now it has not been possible to evaluate during rupture.

In the present work an attempt has been made to evaluate the relaxation properties of a rupturing specimen from the rate of spontaneous contraction.

By means of high-speed cinematography, the spontaneous contraction of specimens of unfilled vulcanizates of butadiene–nitrile rubbers SKN-18, SKN-26, and SKN-40, having different contents of nitrile groups but the same degree of cross-linking, was investigated.

In carrying out the investigation, specimens of two types were used. Specimen No. 1 was a plate of vulcanizate measuring 60 × 50 × 1 mm. A notch 2.5 and 1 mm in size was made in the middle of the longer edge. Specimen No. 2 was a narrow strip of vulcanizate 60 × 10 × 1 mm. The specimens were deformed along the larger dimension. To determine the rate of spontaneous contraction, the length of the contracting specimens shown in the individual frames was measured.

The filming was carried out with an SKS-1 motion-picture camera. When specimen No. 1 was stretched at a definite deformation rate, the notch gradually grew during loading. After the rupture had passed, the specimen at the site of the preceding failure began to contract.

Fig. 1. Dependence of the rate of spontaneous contraction on time for SKN-18 vulcanizates at a deformation rate of 100 mm/min.
a –specimen No. 1, with a 1 mm notch; *b* –specimen No. 2.

Figure 1

Figure 1: Figure 1

Fig. 2

Figure 2: Fig. 2

At the final moment before failure, the specimen had only a narrow unbroken part, which then failed and began to contract. The rate of contraction of this narrow part of the specimen was studied in the present work. The method of investigation by means of high-speed cinematography and the appearance of the failing specimens were described earlier ([1]). Spontaneous co-

shortening of type 2 specimens occurred after the specimens were cut in the lower clamp upon their reaching a specified elongation. In this case the rate of spontaneous contraction was determined as the rate of motion of the lower boundary of the entire narrow strip of the specimen.

Using this method, data were obtained on the rates of spontaneous contraction corresponding to particular moments of time. From these data, plots were constructed of the dependence of the rate of spontaneous contraction of the end of the specimen on the time from the beginning of contraction t (Fig. 1).

Fig. 2. Dependence of the rate of spontaneous contraction at the initial instant (v_0): *a*—on the deformation rate, *b*—on the deformation time for SKN-18 vulcanizates. Specimen No. 1.
The numbers on the graph indicate the size of the notch in mm.

By graphically extrapolating the values of the rate of spontaneous contraction ($v_{\text{s.c.}}$) to the zero instant of time, values of the initial rate of spontaneous contraction v_0 were obtained; these were used to characterize the relaxation properties of the material at the moment of rupture. The possibility of extrapolation was determined by the fact that the first 4–5 points lay well on a straight line in the coordinates $\lg v_{\text{s.c.}}$—t.

From consideration of the curves shown in Fig. 1, it is seen that, depending on the type of specimen, $v_{\text{s.c.}}$ decreases in different ways.

In specimens No. 2 the curve of the change in rate has the form of damped oscillations, which is associated with the manifestation of the previously established ([2]) wave character of spontaneous contraction. In specimen No. 1 the manifestation of the wave character of spontaneous contraction is hindered, since the unloading wave is dispersed in the wide and already significantly contracted part of the specimen. In specimen No. 2 the propagation of the unloading wave along the specimen was observed in the form of a thickening. In specimens No. 1 the dependence of v_0 on the deformation rate and on the deformation time up to rupture was studied. Such data for SKN-18 rubber are presented in Fig. 2.

Fig. 3

Figure 3: Fig. 3

From consideration of Fig. 2 it is seen that, first, with increasing deformation rate the rate of spontaneous contraction increases, but the higher the deformation rates reached, the smaller this increase; second, the shorter the time the specimen remains in the deformed state, the higher the contraction rate. Similar dependences are characteristic of materials possessing relaxation properties.

Figure 3 shows the dependences of v_0 on elongation, studied on specimens No. 1 and No. 2.

It should be noted that for both specimens the magnitude of elongation was determined from the distance between the clamps at the moment of rupture and before the beginning of deformation. In the case of testing specimens No. 2, the dependence of v_0 on elongation is represented by a straight line passing through the origin, with

in this case the line corresponding to the lower deformation rate lies lower, which is in good agreement with the considerations given above.

However, as can be seen from Fig. 3, the presence of a notch leads to more rapid rupture of specimen No. 1 and changes the course of the dependence. These straight lines no longer pass through the origin; they are located higher than the straight lines for specimens No. 2. With increasing notch size, the angle of inclination of these curves to the abscissa axis increases. This is explained by the fact that the overstress developing by the moment of rupture in the remaining narrow part of specimen No. 1 is the greater, the larger the size of the preliminary notch. For large notches, an increase in deformation will be accompanied by larger increases in stresses at the notch tip and, consequently, by greater additional deformation and a higher rate of spontaneous contraction.

Fig. 3. Dependence of the rate of spontaneous contraction at the initial moment on elongation for SKN-18 vulcanizate. *a* –specimen No. 2, deformation rate 100 mm/min; *b* –specimen No. 2, deformation rate 1000 mm/min; *v* –specimen No. 1, with a 1 mm notch; *g* –specimen No. 1, with a 2.5 mm notch.

The initial rate of contraction of the ends of the narrow part of specimen No. 1 is considerably greater than the initial rate of contraction of the edge of specimen No. 2 at the same value of the total deformation of the specimen. On this basis, a method was developed for estimating the magnitude of the additional orientation of the material at the tip of a growing notch at the moment of rupture, which, possibly, permits estimation of the overstress.

Table 1

Dependences of v_0 and γ on deformation rate and notch size for vulcanizates from nitrile rubbers

Rubber specimen	$v_0 \cdot 10^{-3}$ (cm/sec), specimen No. 1 at $v_{def} =$ 500 mm/min, a	$v_0 \cdot 10^{-3}$ (cm/sec), specimen No. 1 at $v_{def} =$ 500 mm/min, b	$v_0 \cdot 10^{-3}$ (cm/sec), specimen No. 1 at $t_{def} =$ 0.2 min, a	$v_0 \cdot 10^{-3}$ (cm/sec), specimen No. 1 at $t_{def} =$ 0.2 min, b	$v_0 \cdot 10^{-3}$ (cm/sec), specimen No. 1 at $\varepsilon =$ 50%, a	$v_0 \cdot 10^{-3}$ (cm/sec), specimen No. 1 at $\varepsilon =$ 50%, b	$v_0 \cdot 10^{-3}$ (cm/sec), specimen No. 2 at $\varepsilon =$ 100%	γ, a	γ, b
SKN-18	16	15.3	7.5	5.8	9	12.7	11.7	2.8	2.8
SKN-26	18.7	17.7	11.0	9.5	9.5	15.3	12.7	1.9	2.65
SKN-40	19.5	17.9	14.7	10.5	10.0	13.3	13.0	1.76	2.25

Note: a —notch 1 mm; b —notch 2.5 mm.

Knowing the elongation of specimen No. 1 at the moment of rupture and the corresponding value of v_0, we find, using the graph $v_0 = f(\varepsilon)$ (Fig. 3) for specimens No. 2, the value of the elongation at which the edge of the strip of specimen No. 2 has the same rate of spontaneous contraction as the rupturing specimen. The value obtained represents the true elongation that develops at the tip of the rupturing specimen No. 1. The course of such a determination is shown by the line with arrows in Fig. 3.

If the elongation ε_p determined in this way is divided by the total elongation of the specimen at rupture, then we obtain the value of the additional orientation of the material at the crack tip (1), $\gamma = \varepsilon_p/\varepsilon$, in relative units. Since the dependences of v_0 on ε are expressed by straight lines, it is clear,

that the degree of additional orientation of the material does not depend on elongation, but depends on the size of the cut. Curves similar to those shown in Figs. 1, 2, and 3 were also obtained for SKN-26 and SKN-40 vulcanizates. These data fully confirm the general character of the dependences obtained.

To determine the effect of the polarity of vulcanizates, Table 1 gives the values of v_0 and γ for SKN vulcanizates with an equal degree of crosslinking.

From consideration of Table 1 it follows that, with increasing polarity of the vulcanizates, the rate of spontaneous contraction increases, all other conditions being equal. At the same time, with an increase in the number of nitrile groups, the degree of additional orientation decreases. This is a consequence of the decreasing flexibility of the chain molecules.

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