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## Abstract

## Full Text

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## THE INFLUENCE OF THE DEGREE OF DEFORMATION ON OZONE CRACKING OF RUBBERS

*(Presented by Academician P. A. Rebinder on 6 VI 1957)*

It is known from the literature that there exists a so-called critical deformation at which the most severe destruction of rubbers in ozone is observed. However, the data on this question are rather contradictory.

According to a number of assertions, critical deformation is observed in vulcanizates of natural rubber, but different authors give different values for it—from 5 to 50% (1-4). For synthetic rubbers that are unstable to ozone, some authors find a critical deformation (1), while others consider that it does not exist (5, 6). It is believed that critical deformation does not exist for polychloroprene and butyl rubber (1, 7). All these data, however, cannot be regarded as reliable, since in most cases ozone cracking was characterized by conventional methods, mainly according to the "degree of cracking," expressed in points.

**Fig. 1.** Influence of the magnitude of deformation on the time to the appearance of cracks: **1** –NR, ozone concentration 0.0033%; **2** –SKS-30, ozone concentration 0.0027%; **3** –nairite, ozone concentration 0.010%

We carried out a detailed investigation of the influence of the degree of deformation on ozone cracking of rubbers, the rate of crack growth being determined by an objective method (8), from the effective crack depth calculated from the decrease in the force in a stress-relaxed specimen during its ozonation. Rubbers based on NR, SKS, nairite, SKN, SKB (standard formulations), gutta-percha (elastic vulcanizate), and butyl rubber* were investigated at the optimum with respect to true strength.

The investigation showed:

Fig. 2

Figure 2: Fig. 2

1. For all rubbers there is observed a qualitatively identical dependence of the time to the appearance of cracks on the magnitude of deformation: with increasing deformation, the time to the appearance of cracks gradually decreases to zero (Fig. 1).

* Composition of rubbers: gutta-percha 100, captax 0.8, sulfur 5; butyl rubber 100, stearin 3, captax 0.65, thiuram 1.3, zinc oxide 5, sulfur 2.

2. The rate of crack growth, determined on the stationary segment of the kinetic curve, initially increases with increasing deformation and passes through a maximum in the region of small deformations ( “critical elongation” ), and subsequently, up to 500% deformation, decreases (Fig. 2a).

3. For all rubbers, irrespective of their properties, the time to rupture as deformation is varied passes through a minimum in the region of the critical deformation $\varepsilon_{\min}$ and through a maximum in the region of large deformations (Fig. 2b).

Fig. 2. Dependence of the crack-growth rate (a) and the time to rupture (b) on the magnitude of deformation:
1 –NR, ozone concentration 0.003%; 2 –SKS-30, ozone concentration 0.002%; 3 –nairite, ozone concentration 0.01% (in the region of small deformations) and 0.02% (in the region of large deformations)

Undoubtedly the most interesting result is the establishment, by an objective method, for all the rubbers studied, of the strengthening effect of deformation, as a result of which the crack-growth rate for deformations greater than $\varepsilon_{\min}$ decreases, while the time to rupture increases.

From the point of view of the existing ideas about ozone cracking of rubbers as a process determined by the chemical interaction of rubber with ozone, one would have expected deformation to have an activating effect on the destruction of rubber in ozone, but in no way the reverse effect.

We expressed the supposition (9) that this phenomenon, despite the sharp increase in the rate of the process, is analogous to static fatigue. Direct experiments also showed an immediate connection between the strength of rubbers and their resistance to ozone cracking. The greater the true tensile strength of rubbers made from non-crystallizing caoutchoucs, the greater their resistance to ozone cracking, namely:

| Rubber from SKB, stress 2 kg/cm$^2$, $C_{O3} = 2.2 \cdot 10^{-3}\%$ | | | | | |
|---|---|---|---|---|---|
| True tensile strength, kg/cm$^2$ | 8.6 | 247 | 516 | 758 | 830 |
| Time to rupture, min | 25 | 54 | 86 | 105 | 116 |

| Rubber from SKS-30, stress 2.5 kg/cm$^2$, $C_{O3} = 2.5 \cdot 10^{-3}\%$ | | | | |
|---|---|---|---|---|
| True tensile strength, kg/cm$^2$ | 346 | 401 | 430 | 757 |
| Time to rupture, min | 15 | 17 | 19 | 23 |

In rubbers made from crystallizing caoutchoucs, in the region of large deformations, a pronounced anisotropy of strength is observed: along the stretching axis the strength is lower, while transverse to it it is higher. In ozone, in this case, not transverse cracks, as usual, but longitudinal cracks are observed to develop, i.e., in the direction of the lowest strength (Fig. 3).

Testing the resistance to ozone cracking of rubber made from NR, previously subjected to repeated deformations of 110% for 4 hours, showed that the breaking strength thereby decreased by approximately 25%, and the time to rupture in ozone by 25–30%.

The influence of the mechanical strength of rubbers on ozone cracking can be understood if one imagines that this process proceeds in two stages.

1. Interaction of ozone with the polymer at the site of a double bond. Naturally, since double bonds are not arranged one after another, this interaction and, consequently, the "chemical" growth of a crack quickly ceases. 2. At the mouth of the crack that has formed, an overstress arises, under the influence of which further "mechanical" growth of the crack occurs without the participation of ozone. The rate of this process depends on mechanical strength. These stages, continuously alternating, lead to the successive deepening of cracks and rupture of the specimen. The two-stage character of ozone cracking is well confirmed by the microscopic picture of the formation of "longitudinal" cracks in rubbers from crystallizing rubbers (NR, nairite) at large deformations (300%) (Fig. 3): they are secondary formations: splitting of the rubber along the fibers between the initially formed transverse cracks.

**Table 1**

**Values of $\varepsilon_{\text{min}}$ for various rubbers**

| Rubber | $\varepsilon_{\text{min}}$ | Modulus*, kg/cm$^2$ |
|---|---:|---:|
| Natural rubber | 16 | 12 |
| Elastic gutta vulcanizate | 28 | 10.4 |
| Butyl rubber | (70) | 17 |
| Nairite | 65 | 19.5 |
| SKS-30, vulcanization time 30 min | 16 | 7.2 |
| SKS-30, vulcanization time 40 min | 20 | 9.7 |
| SKS-30, vulcanization time 60 min | 33 | 10.2 |

* The value of the static modulus was determined 1 hour after loading, i.e., at the moment when ozonation of the rubbers began.

The existence of a direct connection between the mechanical strength of rubber and its resistance to the chemical action of ozone makes understandable the influence of deformation on this process. The appearance of a strength minimum for rubbers in ozone is a consequence of the dual influence of deformation: on the one hand, an increase in deformation increases the stress in the rubber, which accelerates destruction*; on the other hand, with increasing deformation the degree of orientation and the strength increase, which slows destruction ([11]). It is interesting that in noncrystallizing rubbers, in the region of small deformations**, orientation processes appear, whose positive influence on the strength of rubbers in ozone, already from nominal deformations of 15–20%***, begins to predominate over the influence of stress for most rubbers. The position of $\varepsilon_{\text{min}}$ will be determined by the relative influence of deformation on the degree of orientation of the polymer and its influence on the magnitude of stress. With the same influence of deformation on the degree of orientation of two rubbers, $\varepsilon_{\text{min}}$ will be smaller for the specimen with the larger modulus***.

Figure 4: Effect of deformation magnitude on the dynamic strength of rubbers.

Figure 3: Figure 4: Effect of deformation magnitude on the dynamic strength of rubbers.

In rubbers with identical moduli, $\varepsilon_{\text{min}}$ will be larger in the case where the influence of deformation on the degree of orientation is greater (Table 1). The considerably smaller influence of deformation on orientation in butyl-rubber vulcanizate than in NR**** leads to a shift of $\varepsilon_{\text{min}}$ for butyl rubber toward larger deformations*****. The growth of intermolecular interaction (which reduces the influence of deformation on the degree of orientation) in gutta and nairite in comparison with NR, and also with an increase in vulcanization time for SKS-30,* leads to a shift of $\varepsilon_{\text{min}}$ toward higher values.

The appearance of a maximum in the strength of rubbers in ozone is not connected with a change in the rate of crack growth in this deformation range, since with increasing deformation there is a monotonic decrease in the rate of crack growth (Fig. 2). The presence of a strength maximum is explained by a sharp increase in the role of mechanical rupture in the process of ozone cracking, owing to the fact that the rubbers are in the region of large deformations.

Orientational processes occurring in rubbers when the deformation is changed also appear in other cases. In particular, we investigated the influence of the magnitude of static deformation on the dynamic fatigue of punctured specimens. The test regime was $\Delta L = \text{const}$, i.e., with a change in the magnitude of the static deformation, the total deformation increases so that the magnitude of the dynamic deformation remains constant (for NR 120%, for nairite 100%, butyl rubber and SKS-30 80%, and SKB 60%).

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* At present it has been established that strength should be characterized not only by the value of the stress at break ($\sigma$), but also by the time to break ($t$). The normal character of the dependence will be a decrease in $t$ with increasing $\sigma$ (10).

** At the mouths of cracks the deformation is greater than the nominal deformation of the specimen.

*** Under the condition of identical resistance to static fatigue.

**** This is evident from the fact that crystallization of butyl rubber begins at significantly larger deformations than crystallization of NR.

***** The time to break in ozone at comparatively small deformations (approximately up to 50–60%) in butyl-rubber vulcanizates depends sharply on the magnitude of deformation, and at larger deformations only weakly. As a result, $\varepsilon_{\text{min}}$ for butyl rubber is not very clearly expressed, and sometimes it cannot be detected at all.

Fig. 4. Effect of the magnitude of deformation on the dynamic strength of rubbers: 1 –NR, 2 –SKS-30, 3 –nairite, 4 –SKB, 5 –butyl rubber

The results obtained show (Fig. 4) that the strength of rubbers under repeated deformations obeys the same regularity as in ozone cracking. For all rubbers a strength minimum is likewise observed, and the value of $\varepsilon_{\text{min}}$ increases in the series NR –polychloroprene –butyl rubber.

On the basis of the results obtained, the following conclusions may be drawn.

1. The destruction (cracking) of deformed rubbers as a result of their chemical interaction with ozone is analogous to the process of static fatigue, despite the difference in the rates of these processes by many orders of magnitude. From this follows the fundamental possibility of accelerated investigation of the static fatigue of rubbers, in particular in the region of small deformations, by means of ozone cracking.
2. Very small nominal deformations (of the order of 10%) cause in rubber, at the mouths of cracks, a change in the degree of orientation of its structural units. A sensitive indicator of these changes is the resistance of rubbers to destruction in ozone. This phenomenon can in principle be used as the basis for a method of studying the orientation of rubbers.

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* Vulcanized with an oxidation-reduction system.

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