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The Mechanism of Crack Formation in Rubbers under the Effect of Ozone

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The formation and growth of cracks under an effect of ozone were investigated in different types of rubbers, such as NR, PBR, BMSR, SBR† and in composite materials based on these rubbers. The study was carried out by the reflection-light optical microscopy method with using the MMP-4 microscope. In the presence of microinhomogeneities in a surface structure the crack formation is shown to start from those defects. In the absence of inhomogeneities the cracks are formed uniformly over the whole surface of a specimen. It is found that even insignificant quantities of low-modulus rubber in the PBR-based composite material may result in changing the shape of a crack during its growth. An attempt is undertaken to describe the shape of formed cracks quantitatively. The calculational and experimental data are presented.

The influence of deformation on the number of cracks per surface unit, on their shape, geometrical size, cracking degree is studied for example of natural rubber specimen.

Key words Rubbers, crack formation, ozone.

When the stressed rubbers and their products are influenced by atmospheric ozone during their usage process, the cracks are formed in these materials. Though the aging of rubbers has been extensively studied this process still remains to be of great interest because of its practical importance.

The paper presents the results of studying the crack formation under an effect of ozone in rubber specimens of various chemical compositions and in rubber-based composite materials. The quantitative data of the effect of deformation on

† NR—natural rubber, PBR—polybutadiene-based rubber, BMSR—butadiene- α -methylstyrene-based rubber, SBR—butyl-styrene-based rubber.

crack parameters under ozone aging conditions are presented. The studies have been carried out by the reflected-light optical spectroscopy method using the metallographic MMP-4 microscope. The system of replaceable objectives allowed to vary the magnification within the range of $\times 50$ to $\times 600$. A special microscope attachment allowed to expose specimens to ozone directly under the microscope objective, thus providing the deformation required. The microscope design made it possible to take photographs of the specimen surface under study. The influence of deformation on crack parameters has been studied by the technique described in paper¹ for a natural-rubber-based vulcanisate. This technique allowed to specify deformation within the range of 0 to 90% for a single specimen.

Figure 1 shows initial surface photographs for specimens of complicated composition. It is seen that the structure of surface may drastically differ depending on the nature of rubber and on composition ingredients. The crystalline formations on the specimen surface are components which exuded from the volume, and can be easily removed by wiping the specimen surface with organic solvents (ether, for instance). In further studies the exuded components have not been removed from the surface.

Figure 2 presents the data on kinetics of variation of the number cracks vs. exposure time for a butadiene rubber-based specimen. The number of cracks is seen to pass through a maximum, the decrease of their number being caused by their coalescence, which is distinctly observed via the microscope objective. Use of short exposure times (of the order of some minutes), allowed observation of the appearance and growth of individual cracks.

In studying the cracks in unfilled specimens (Figures 3, 4) it was found, that at the polyisoprene rubber surface (Figure 3) the cracks are first formed at the boundaries of surface microinhomogeneities and then grow unhampered either by coalescence of neighbouring cracks, or by their normal natural growth. In this case the initial shape of cracks is close to being oval. As the crack size increases, their tips became acute, and the cracks acquire elongated shape. In the case of unfilled natural rubber (Figure 4) the specimen surface did not possess any visible microinhomogeneities, and the cracks have formed uniformly throughout the specimen surface. These cracks were oval-shaped, as a rule. Figure 4 also shows that near side faces in many cracks one can clearly see that "unstressed" regions of surface, which are not observed near crack tips.

The most interesting crack shape was observed in polybutadiene-based specimens of unfilled rubbers, (Figure 5) and in butadiene-styrene copolymer-based rubber specimens (Figure 6). The isolated cracks have a shape that differs from the shape of cracks in natural and polyisoprene-based rubber specimens. At the moment of formation the shape of these cracks was close to rectangular. During the crack growth process, however, the shape of cracks changed for a butadiene-styrene copolymer but, remained unchanged—for a polybutadiene-based rubber. The rectangular shape of cracks has also been observed for specimens made of butadiene- α -methylstyrene rubber composition (Figure 7).

The introduction of some small quantities of polyisoprene rubber into the polybutadiene-based rubber composition markedly changes the crack develop-

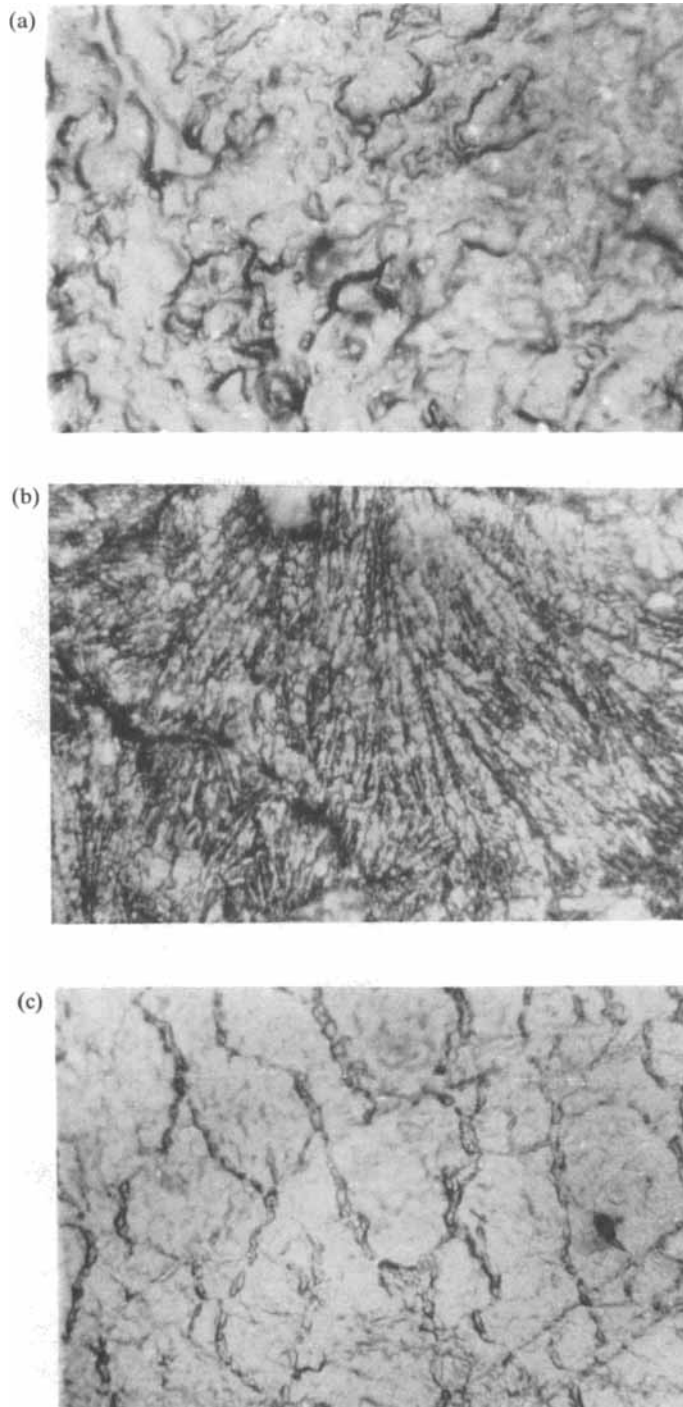


FIGURE 1 View of the initial surface of the samples: a—BMSR, b—NR, c—PBR.

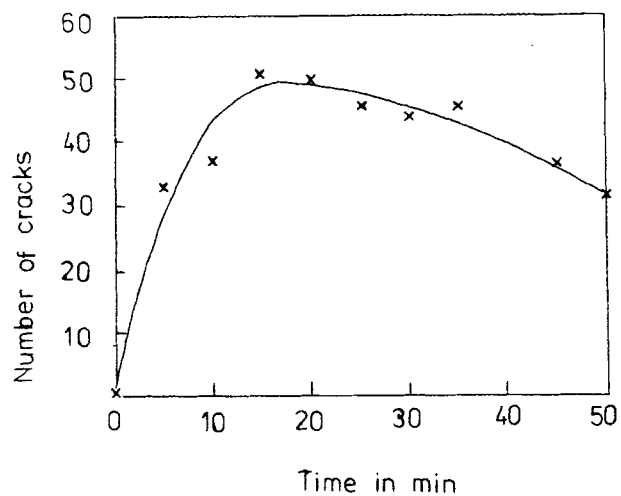


FIGURE 2 Dependence on cracks growth vs. time.

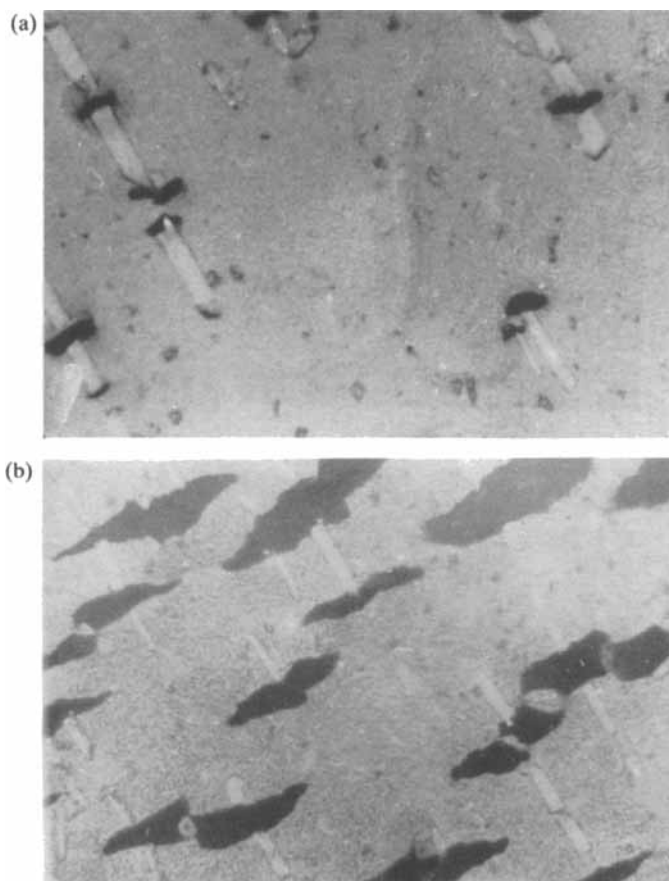


FIGURE 3 Surface view of ozonized vulcanized sample of 1,4-cis-polyisoprene rubber without ingredients.

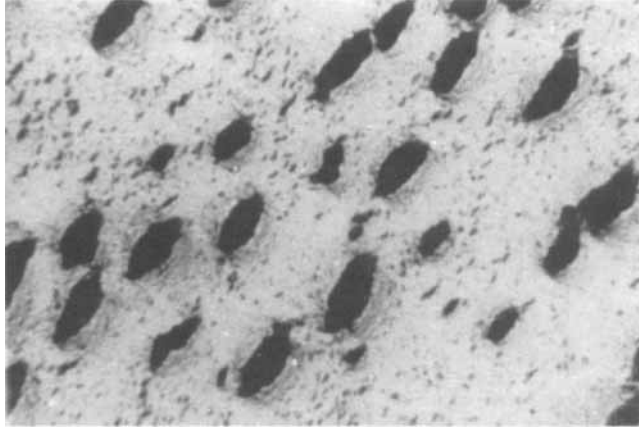


FIGURE 4 View of the ozonized surface of vulkanized sample of NR rubber without inients.

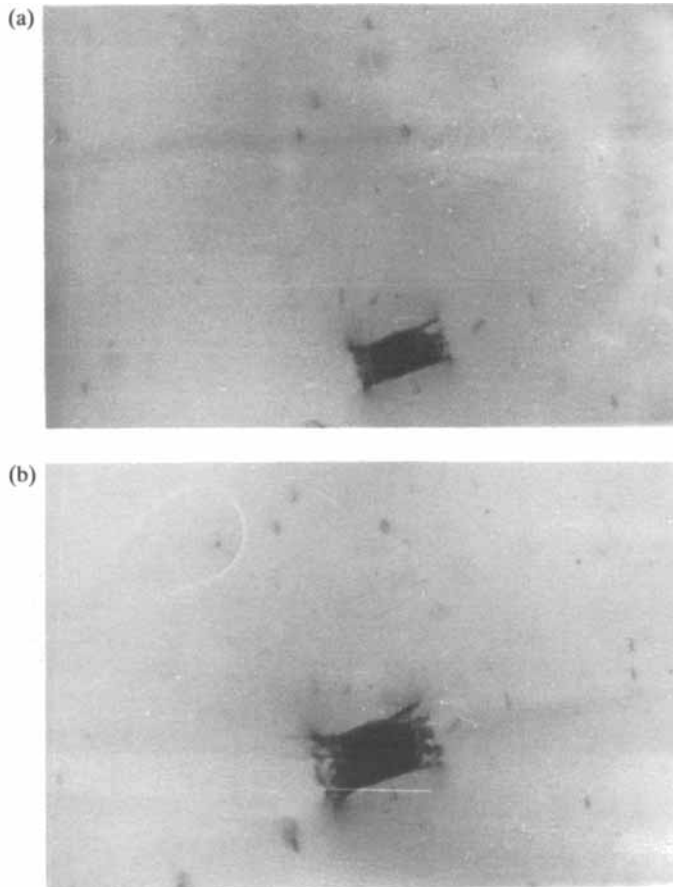


FIGURE 5 View of the ozonized surface of vulkanized sample of PBR rubber without ingredients.

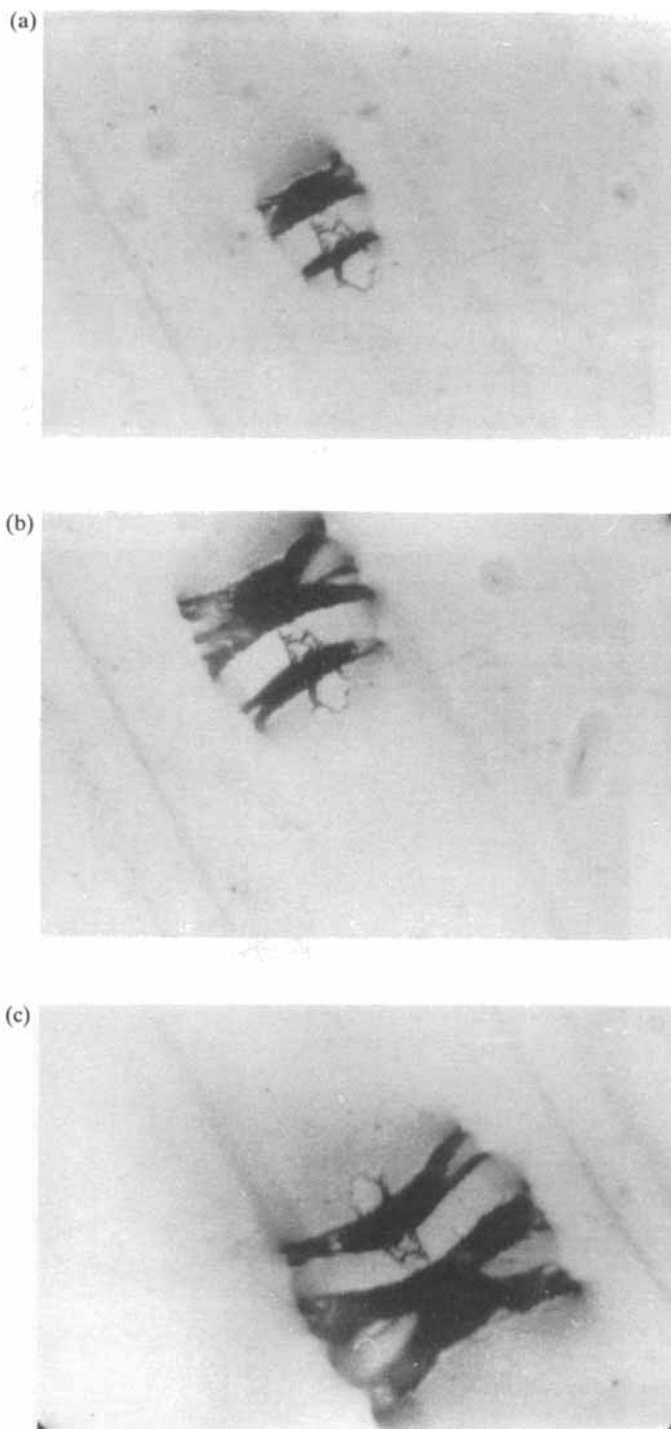


FIGURE 6 View of the ozonized surface of vulkanized sample of SBR rubber without ingredients.



FIGURE 7 Shape of cracks. Ozonized BMSR rubber surface.

ment process (Figure 8a, b). Whereas at the moment of formation the cracks are rectangular, they acquire an oval shape during the growth process. In this case one could observe the formation of links between the faces—this phenomenon was absent for an unfilled rubber based on the same material. These links are formed, apparently, by introducing polyisoprene into the composition. This observation allows to conclude that even very small quantities of rubber, possessing high molecular segmental mobility segments, can drastically change the shape of cracks during their growth and, apparently, they can change the general specimen cracking pattern under the influence of ozone.

Figure 9 shows the crack shape for a specimen made of natural-rubber-based composition. It is seen that the introduction of ingredients does not practically change the shape of cracks. This picture clearly shows that the crack edges are elevated over the specimen surface. This fact is rather surprising, since the crack contour was earlier assumed to be within the specimen plane.

To describe the observed differences in crack shape quantitatively, the crack size data have been processed by using the equations of two planar geometrical shapes: the rectangle whose area is

$$S = a \cdot b \quad (1)$$

and the ellipse whose area is given by

$$S = \frac{\pi}{4} \cdot a \cdot b \quad (2)$$

where a and b are crack length and width, respectively. The area (S_{exp}) of cracks recorded photographically was determined by the weight method. The measure of correspondence to any crack shape idea was the relationship: $S_{\text{exp}}/S_{\text{theor.}}$, where $S_{\text{theor.}}$ is the area calculated by relation (1) or (2), which must be equal to 1 in the case of complete agreement.

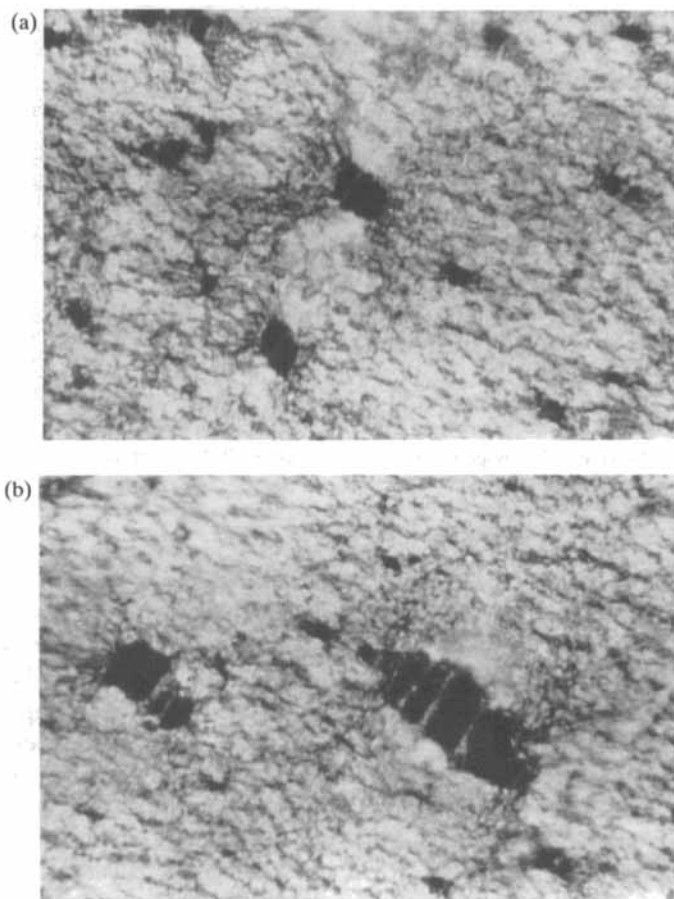


FIGURE 8 Shape of cracks of PBR/PI blends: a—on time of appearance; b—during ozonation.

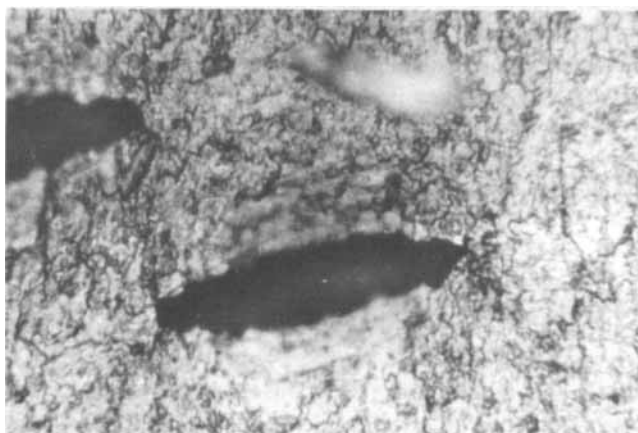


FIGURE 9 Shape of cracks on the surface of NR compositions.

TABLE I

No.	Type of rubber	S_{exp}	S_{el}	S_{rect}	S_{exp}/S_{el}	S_{exp}/S_{rect}
1	PB + CPI-3	13.2	13.7	17.4	0.97	0.75
		1.3	1.6	1.4	0.82	0.95
2	PB (without filling)	1.7	1.4	1.8	1.20	0.96
3	NR	10.9	11.8	16.3	0.92	0.67
4	BMSR-10	9.1	8.8	11.1	1.03	0.82

Table I presents calculation results (S is in cm^2). As the table shows, in the case of polybutadiene-based rubber specimens without filling (specimen 2) the crack area is well described by Eq. (1). This conclusion is also true for a polybutadiene + polyisoprene rubber composition in the case, when the cracks are small in size. In all remaining cases the crack area can be described by Eq. (2) for all ellipse area.

Figure 10 presents the dependence of number of cracks per surface unit area for natural rubber-based specimen on applied deformation. The number of cracks is seen to increase according to some complicated law as the deformation grows and reaches its maximum value at 82% deformation. The same figure (curve 2) gives the values of a total area of cracks observed at surface unit (the area of a unit crack was calculated by Eq. 2). As the plot shows, the area of cracks varies inversely to their number. Figure 11 shows the dependence of crack depth on the

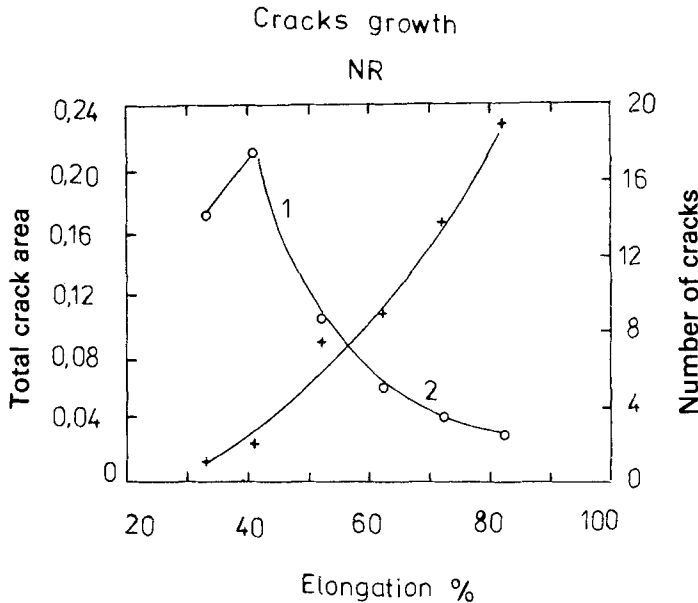


FIGURE 10 Dependence on number of cracks on unit surface (1) and surface of cracks (2) vs. elongation. NR.

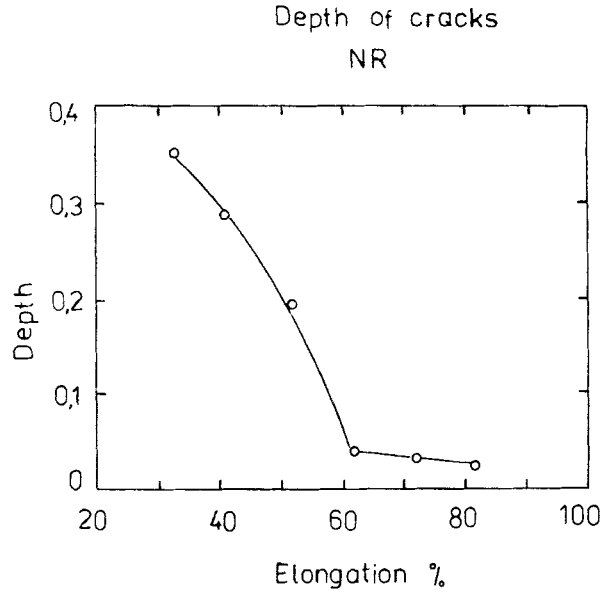


FIGURE 11 Dependence on depth of cracks vs. elongation. NR.

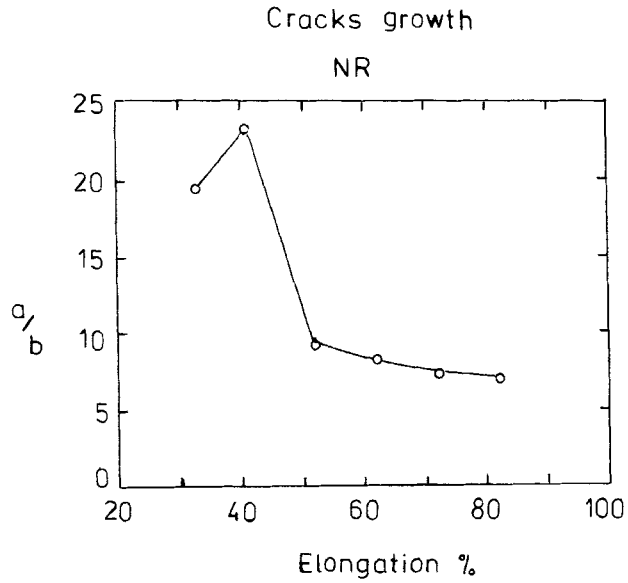


FIGURE 12 Dependence on relation a/b vs. elongation. NR.

deformation, which also decreases as the deformation grows. The plots suggest that within the investigated deformation range the largest depth of cracks and their maximum total area (and, hence, the most severe damage of a specimen) takes place at low deformations. The obtained quantitative data are in a good agreement with observed dependences of specimens longevity on the strain (deformation) applied.

It is noted in the literature² that, as the deformation grows, the shape of cracks changes along with growing of their number and decreasing of their size. Figure 12 presents the dependence of a crack length (a) to thickness (b) ratio on the deformation applied. It is seen that up to deformation value of 41% the crack length grows faster than its width, and then the situation changes. This means that, with the increasing deformation the cracks area decreases while their shape becomes more and more oval. By further increasing the strain on the specimen, the crack walls re-arrange ever more, and the crack shape becomes more and more round. At the limits of deformations which greatly exceed the range reported in present study, one the cracks oriented parallel to the extension direction are observed. These observations do not, however, mean that the distribution of stresses is also reversed, because with such reversed cracks the side sections remain to be most highly loaded. We believe that the crack capability to change its shape under load is closely related to the flexibility and mobility of elastomer segments. Note that similar dependences of crack morphology on strain is not observed with more rigid polybutadiene and nitril elastomers. Under the same conditions these specimens failed catastrophically after being exposed for a short time to the zone environment.

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