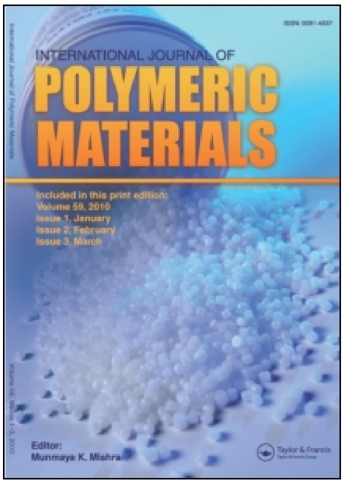

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Physico-Chemical Principles Governing the Ageing of Elastomers Under the Action of Atmospheric Ozone

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Physico-Chemical Principles Governing the Ageing of Elastomers Under the Action of Atmospheric Ozone

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Complex process of ozone degradation of elastomers have been considered as phisico-chemical system. It was shown that reaction of ozone with double bonds in macromolecules was a limiting stage of process. Sensitive methods studying of cracks formation and growth were used in combination with ozone absorption control. It was given basic dependences of cracks growth and stress relaxation upon time and ozone concentration.

KEYWORDS: *Ozone, degradation, elastomers, formation of crack, mechanism, molecular mobility, prognosis*

One of the main types of ageing of elastomers in service under natural conditions is surface cracking of articles caused by atmospheric ozone.[1]

Ozone in the atmosphere is usually formed as a result of natural photochemical processes; its concentrations are extremely low, ranging from 20 to 2000 pphm. However, even such minor quantities are sufficient for covering the surface of articles made of ozone-sensitive materials with a dense network of visible cracks within a period of 1–1.5 months of exposure in the air, thus rendering the articles unfit for further service. Figure 1 presents typical pictures of cracking of elastomers.

The highest sensitivity to ozone is manifested by materials and articles made of cured polyisoprene and polybutadiene and their copolymers. Unfortunately, this group includes the most widely used types of elastomers, viz. vulcanizates of natural rubber and synthetic polyisoprenes, copolymers of butadiene with acrylonitrile and styrene, and many other polymers.

Named among ozone-resistant elastomers can be polychloroprenes, butyl rubber and most of elastic materials whose macromolecules do not contain C=C bonds in the backbone.

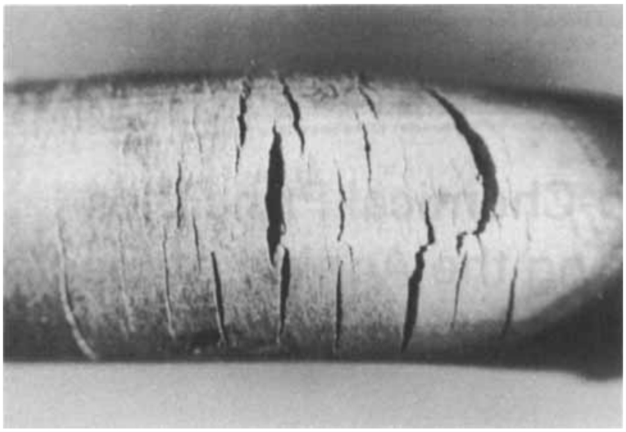


FIGURE 1 The appearance of specimen of rubber tube after contact with ozonated air.

GENERAL DESCRIPTION OF THE OZONE AGEING PROCESS

The detectable manifestations of ozone ageing are stress relaxation and the formation of a large number of cracks on the surface of an article; the cracks grow normally to the stretching direction; thorough removal of ozone from the atmospheric air contacting the specimen stops the ageing process and terminates crack formation and growth and stress relaxation; it becomes possible using IR spectroscopy to detect in the material of the specimen the emergence of new functional groups having the nature of ozonides, aldehydes and acids upon a very long exposure to ozone atmosphere. Figure 2 depicts schematically the events occurring in the specimen exposed to ozone. It can be seen that by the end of the test the specimen becomes covered with a rather dense network of cracks: 40–150 in 1 mm^2. Shown on the butt of the specimen is the graph of changes in the concentration of functional groups with the distance from the surface of the specimen. The shape of the dependence is indicative of the surface nature of the reaction.

The time dependences of S and σ_τ/σ_0 characterize the dynamics of ageing. It is evident that its rate increases with ozone concentration and depends non-linearly on time which points to a complex nature of the process.

The processes of relaxation, crack formation and growth indicated above occur only in the cases where the specimens under test are deformed mechanically (tension). The necessary combination of the effect of ozone and mechanical loads is well illustrated by Figure 3 presenting the dependence of the life time (τ) of cured polybutadiene on load at various ozone concentrations.[2] The upper curve refers to the dependence of life time on the magnitude of the load applied in the absence of ozone. It characterizes the ultimate parameters of the material determined by the structure and conformation of specimen's macromolecules. Small amounts of ozone reduce noticeably the life time of the specimen; as the

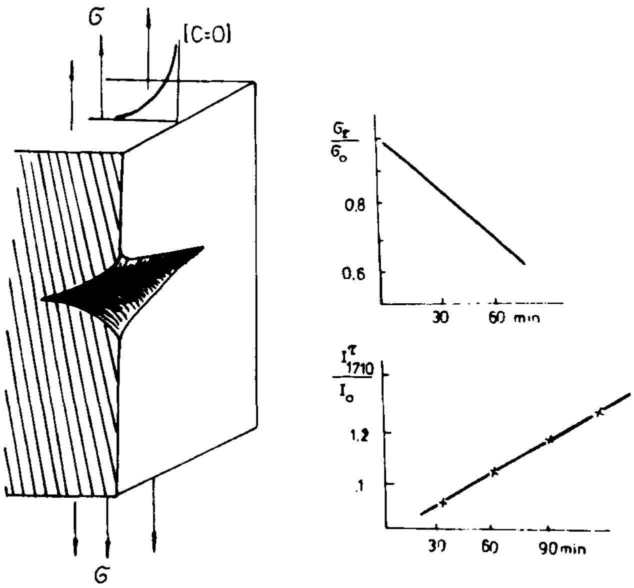


FIGURE 2 Major changes in a specimen exposed to ozone: crack formation and growth, stress decay (a), and the kinetics of accumulation of functional groups in the subsurface layer (b).

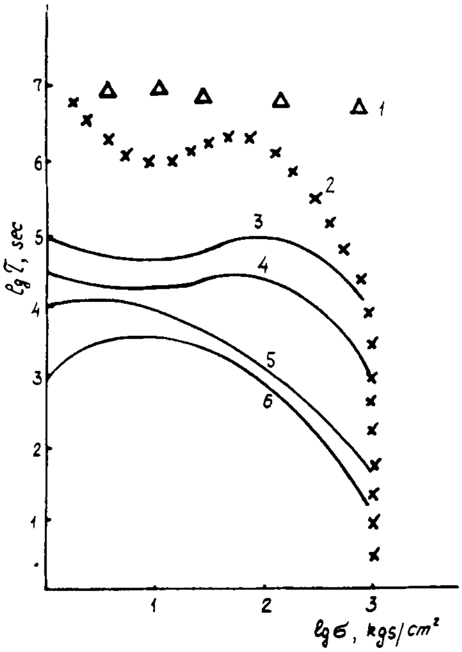


FIGURE 3 Life time (τ) of polybutadiene vulcanizates in ozonated air at different stresses in the specimens (σ).

concentration grows, life time decreases dramatically, by several orders of magnitude. The $\tau = f(\sigma)$ curve can be divided into three zones in the context of the effect of ozone on the shape of the curve. In the region of maximum loads the specimen breaks down rather rapidly. In this case the influence of ozone usually plays no essential part. The second zone features a weak dependence of life time on the load. Such conditions are rather frequently encountered in practice, the harmful effect of ozone manifesting itself most distinctly. In the region of very low loads the effect of ozone rapidly loses its intensity and in the full absence of loads the formation of cracks and stress relaxation stop.

PHYSICAL AND CHEMICAL CRACK GROWTH THEORIES

An analysis of the ageing kinetics in the region of low loads makes it possible to put forward two alternative hypotheses on the causes of crack formation and growth. The first hypothesis is based on the prerequisite that ozone, through damaging macromolecules on the sites of stress concentration in the material, triggers the mechanism of physical crack growth. This hypothesis, in an explicit or implicit form, underlies most of earlier discussions dedicated to the cracking mechanism.[3,4] The authors of the papers cited employed many concepts of the mechanism of failure of solids such as those put forward by Griffith[5] and other authors. The magnitudes of the surface energy of growing cracks and the sources where this energy could be drawn from were estimated. Regardless of a sound mathematical apparatus used, the results of application of this hypothesis proved to be unsatisfactory because it did not fit the real ageing process. Figure 4 displays

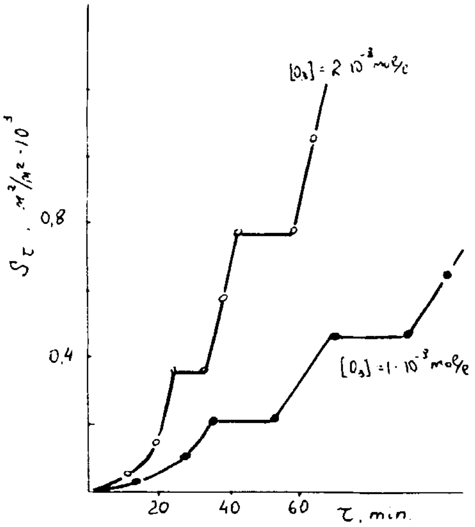


FIGURE 4 The dependence of the surface area of the cracks (S, cm^2/cm^2) on time (τ) upon cyclic exposure of polyisoprence specimens to ozone.

the results of studies of crack formation and growth kinetics on a polyisoprene specimen exposed periodically to ozone. It can be seen that in intervals between the periods of contact with ozone crack growth on the specimen stops till the beginning of next contact. This experiment indicates that under the conditions of ozone ageing chemical, rather than physical, processes of crack formation and growth prevail because of the influence of ozone. These findings enable the second hypothesis of the causes of crack formation and growth to be formulated: the growth and propagation of cracks on the surface of an elastomer exposed to ozone under tension are due to the effect of mechanical factors on the rate and direction of competing chemical reactions in a stretched specimen, as distinct from an unstretched one.

The second hypothesis has not found yet as many supporters as the first one but it is backed by considerable experimental evidence. It fits well the data given in Figures 3 and 4. The large plateau on curve 1 (Figure 3) shows that deformation by itself is not the cause of the crack growth and specimen failure. It can be rather considered as a sort of "developer" of a latent process accompanied by deterioration of mechanical properties. In the presence of ozone (curves 2–6) the plateaus turn into inclined segments whose slope grows with ozone concentration. This fact testifies to the emergence of a new constituent of the specimen failure process caused by the effect of ozone.

The absence of cracks on the surface of an unstretched specimen indicates that even in this case stretching plays the part of a "developer" or of a similar factor.

In order to better understand the role of the tensile load, its effect on the kinetics and mechanism of ozone reaction with the surface of the elastomer should be considered. Figure 5 exhibits the data on the kinetics of ozone

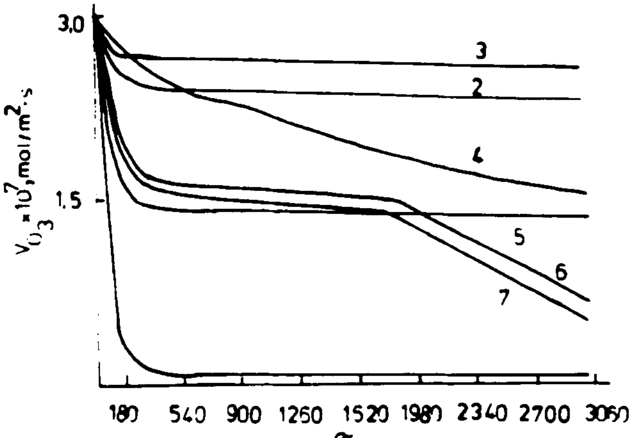


FIGURE 5 The dependence of the rate of ozone addition (V_{O_3}) on the time of exposure to ozone. Vulcanizates: 1, 4—polyisoprene; 2, 5—butadiene-styrene copolymer; 3, 6—polychloroprene; 1, 2, 3—undeformed specimens; 4, 5, 6—specimens extended by 20%.

absorption by specimens of various rubbers.[6] Curves 1–3 depict the change of the rate of ozone absorption by 1 cm^2 of the surface of unstretched specimens with time. The curves demonstrate that the rate rather distinctly depends on the material of the specimen since it changes in going from polyisoprene to polychloroprene. This is understandable since under the conditions of the experiment ozone adds to C=C bonds in the macromolecules whose reactivity changes in this series. However, the rate of ozone absorption decreases to a much lower extent than reactivity. This fact is due to diffusion resistance of the gas phase levelling off the difference in the rates of the process.

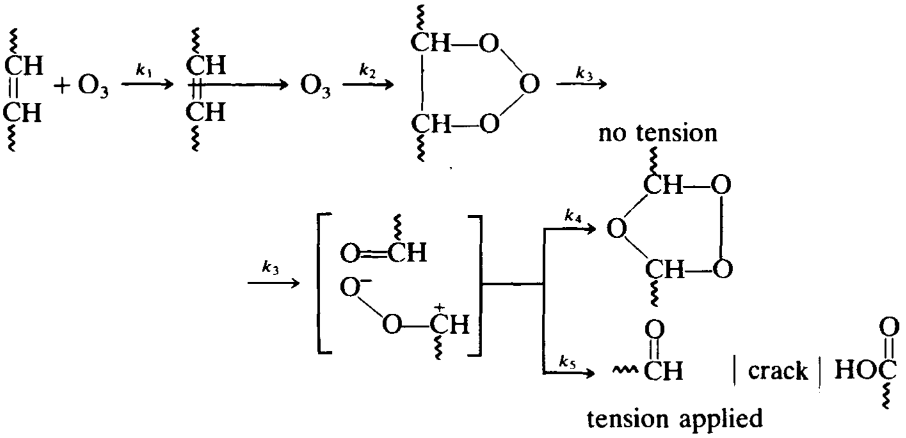
After absorption of 1–2 equivalents of ozone on a C=C bond basis (in the surface layer of the material) the rate of ozone absorption drops drastically. The process enters into a region controlled by the rate of ozone diffusion into the elastomer which is by 5–6 orders of magnitude lower than in the gas phase. This is one of the causes of slow ageing of unstretched specimens.

The kinetics of ozone addition to a stretched specimen differs substantially from the kinetics of the process described above. The rate of ozone absorption by the specimen remains unchanged over a long period of time even after absorption of 1, 2, 5, 15 and more ozone equivalents (curves 4, 5, Figure 5). In terms of normal kinetics this means that throughout the whole observation period the concentration of the surface C=C bonds is maintained constant, i.e. the application of tensile force to the specimen triggers a certain mechanism of the replacement of the C=C bonds which have reacted with ozone in the surface layer by new bonds accessible for the attack of ozone from the gas phase to the same extent.

The observed difference in the character of ozone absorption by the stretched and unstretched specimens can be most simply explained by the assumption that the depletion of C=C bonds in the surface layer is made up for by the growth of the surface through crack formation and growth. This assumption can be easily verified by exposing a stretched specimen to ozone for a sufficiently long period of time, releasing the load, and measuring the rate of ozone addition under the conditions of closure of the cracks as a result of specimen contraction. This experiment is depicted by curve 4 in Figure 5. After the release of tension the rate of absorption and the amount of ozone added to the unit area of the surface virtually coincide with the same parameters determined for a fresh undeformed specimen. This simple experiment is evidence of an interesting and unexpected phenomenon, the renewal of the surface of the elastomer in the course of its interaction with ozone. As it will be clear from the discussion that follows, the renewal of the surface strongly affects the kinetics of crack growth, stress relaxation, and other macrokinetics characteristics of the ozone ageing process.

It is obvious from the said above that tension applied to the specimen changes substantially not only the dynamics of alteration of physical properties of the specimen but also the kinetics of the chemical reaction of ozone with C=C bonds of macromolecules in the surface layer.

Owing to the efforts of many researchers [1, 7, 8], the mechanism of the reaction of ozone with C=C bonds of macromolecules appears to be rather well established. Its main features are presented in Scheme 1:



SCHEME 1

The first step of the reaction is the formation of a labile π complex which further on is converted into a similarly unstable trioxalane or, as it is more often named, primary ozonide. The primary ozonide decomposes to give two fragments one of which—the aldehyde—is stable and the second one is unstable and very active. The latter has an unclassical structure; there were many attempts to characterize it as an aldehyde oxide (carbonyl oxide) or a bipolar ion (amphion). The aldehyde and the amphion are able to combine again very rapidly even in the cage to furnish a relatively stable "isoozonide"; also, they can leave the cage (the microspace where they have been formed), and the amphion undergoes isomerization into an acid with a high degree of probability. This act brings about breakdown of the macromolecule.

Tension applied to the specimen raises the rate of exit of the fragments from the cage. In the ultimate cases the formation of isoozonides by reaction 4 stops and all the split fragments are withdrawn from the cage. This even manifests itself in the experiment as a plateau on the graphs of the dependence of the crack growth rate on the load or strain. Figure 6 displays characteristic dependences of the crack growth rate on the surface of vulcanized natural rubber on load under cyclic deformation conditions.[9] The increment of the average crack length after 10^6 loading cycles (*dl*/*dn*, cm) was taken as the measure of the crack growth rate. The results of two sets of experiments at two different ozone concentrations show that in the region of low loads applied to the specimen the crack growth rate rises with the load until it reaches a certain constant value. It seems that in this region the proportion of split fragments leaving the cage increases. The region where the crack growth rate is independent of the applied load (or strain since these parameters are usually interrelated) embraces a broad range of stresses, from 10^{-4} to 10^{-2} kg/cm^2. It can be thus believed that in this stress range all the split fragments are withdrawn from the cage and hence the load change does not affect the crack growth rate. The latter depends only on the rate of ozone addition to the surface. Comparison of curves 1 and 2 in Figure 6 indicates that the crack growth rate is proportional to the concentration of ozone in the gas medium

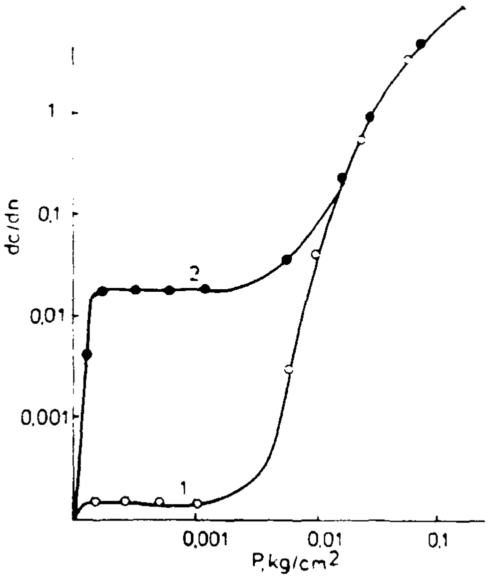


FIGURE 6 The dependence of the rate of growth of the average length of cracks relative to 10^6 loading cycles (*dl/dn*, cm/10^6 cycles) on the applied tensile force (*P*, kg/cm^2). [O_3]: 1—1.12 × 10^{-10} mol/l; 2—10 × 10^{-10} mol/l. Natural rubber vulcanizate.

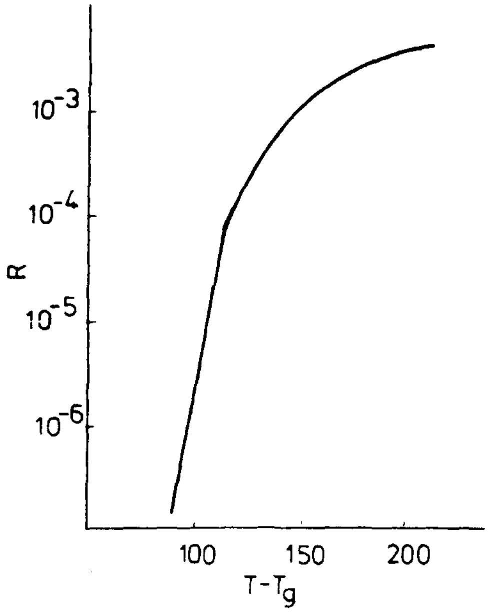


FIGURE 7 The dependence of the rate of growth of an individual notch (R_1, cm/s) on temperature (*T*, *K*). Butyl rubber. T_g—glass transition temperature.

where the specimen is placed. Under the conditions of the tests ozone is usually fed into the reaction at a constant rate and is absorbed almost completely. That is why the crack growth rates prove to be constant in a broad range of loads.

MOLECULAR MOBILITY AND CRACK GROWTH

Apart from stress, temperature also affects crack growth in the ozone ageing process. At lower temperatures the life time of the elastomer increases by several orders of magnitude. The crack growth rate is retarded particularly strongly at temperatures approaching the glass transition temperature (T_g). Shown in Figure 7 is the dependence of the growth rate of a single notch at the edge of a butyl rubber specimen.[10] In the region not very distant from T_g this dependence follows the exponential law. At sufficiently high temperatures (~100°C) the rate of growth of the notch (R) reaches its maximum (10^{-3} cm/s per mg O_3) and undergoes almost no changes at higher temperatures. This phenomenon is also due to the fact that the breakdown of chains occurs in all reaction events whose number is limited by the rate of ozone addition.

The dynamics of R is on good agreement with the changes of the frequency of segmental motions. The activation energy of the crack growth process in the vicinity of T_g is ~200 kJ/mol and does not differ much from E_{ac} of segmental mobility. The role of molecular mobility in the course of crack growth can be clearly seen in comparing the $R = f(T)$ dependences for butadiene-styrene copolymers containing various amounts of styrene (Figure 8).[10] As the concentration of styrene in the copolymer grows, the rigidity of the chain increases and, accordingly, the crack growth rate drops.

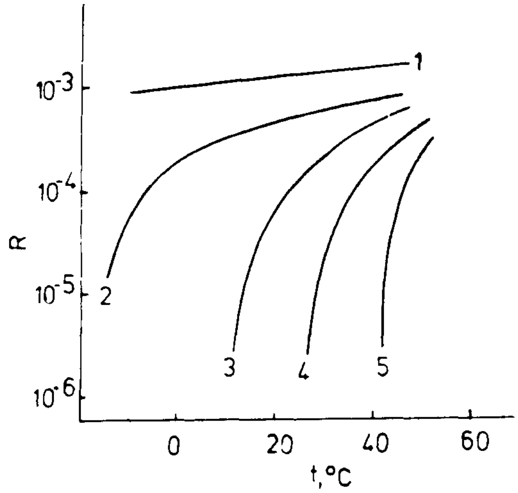


FIGURE 8 The dependence of the rate of growth of the average length of cracks (R, cm/s) on temperature (t, °C) for vulcanized butaniene-styrene copolymers. Styrene concentration, %: 1—0; 2—25; 3—56; 4—67; 6—80.

THE EFFECT OF THE NATURE OF THE ELASTOMER OR THE CRACKING RATE

It is common knowledge that the structure of the molecules of the elastomer greatly affects the ozone resistance of articles prepared from it. Very sensitive to ozone are cross-linked polyisoproprenes; polybutadienes are more resistant. In the family of polydienes particularly resistant to the effect of atmospheric ozone are polychloroprene vulcanizates. High ozone resistance is featured by copolymers of isobutylene with dienes (butyl rubbers).

Figure 9 shows the dependence of the time of specimen fracture (τ_α) on its elongation at load for vulcanizates of different types (λ).[11] In these experiments the concentration of ozone during tests was chosen in such a manner as to place the experimental curves on one chart. In spite of a certain difficulty in matching the results, it can be seen that atmospheric ozone-resistant vulcanizates of isobutylene-isoprene copolymers (butyl rubber) and polychloroprene are more long-lived than BR vulcanizates although the former were exposed to ozone concentrations one order of magnitude higher.

In discussing the nature of the difference in ozone resistance two different explanations can be put forward. The first explanation is based on the difference in molecular mobility and the second one on the dissimilarity in the rates of the reaction of ozone with C=C bonds. The point is that ozone-resistant elastomers contain low amounts of double bonds (butyl rubber) or C=C bonds in them are surrounded by electronegative substituents reducing their reactivity (polychloroprene). Studies of the ozone ageing process including the measurement of ozone absorption showed that the absorption rates change only slightly in going from one elastomer to another while the rates of crack formation and growth differ by several orders of magnitude. Table I lists the values of time to the

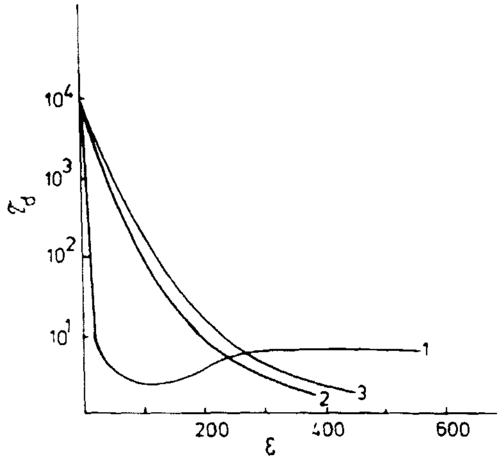


FIGURE 9 The dependence of time to rupture (τ_α) of specimens of rubber of different types on the elongation ratio (ε, %): 1—NR, [O_3] = 0.2%; 2—polychloroprene, [O_3] = 2%; 3—butyl rubber, [O_3] = 6%.

TABLE I

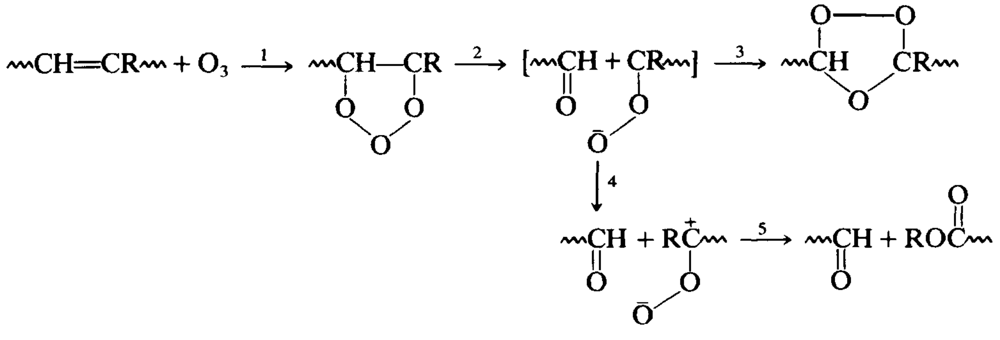
The amounts of ozone added to elastomers of different nature by the instant of appearance of visible cracks

Elastomer type	[C=C] × 10^5, mol/m^2	Time to the appearance of cracks, $\tau_\varepsilon \times 10^{-2}$ s	$\Delta Q \times 10^5$ mmol/m^2
Natural rubber (NR)	6.6	3.9	7.9
cis-Polyisoprene (SKI-3)	6.6	3.0	5.2
Butadiene-styrene copolymer (SKS-30 ARKP)	6.1	4.5	5.9
cis-Polybutadiene (SKD)	7.8	13.5	30.7
Isobutylene-isoprene copolymer (BK)	0.5	30.0	38.1
Polychloroprene	6.8	60.0	385.5

emergence of visible cracks (τ_c) and of the amount of ozone absorbed by this instant (ΔQ).

It follows from the Table that vulcanizates of polyisoprene and a butadiene-styrene copolymer absorb, by the instant of the emergence of visible cracks, the lowest amounts of ozone comparable with the quantities of C=C bonds on the surface. In such ozone-resistant elastomers as butyl rubber and polychloroprene C=C bonds are consumed at a depth of about 60 monolayers from the surface.

If the addition rate and the amounts of added ozone are not related to the crack growth rate, then different levels of molecular mobility of segments determines the dissimilarity in ozone resistance. The most natural explanation of the effect of molecular mobility on the rate of crack formation consists in the alteration of the proportion between two competing processes 3 and 4: exit from the cage and recombination of the fragments in the cage (Scheme 2).



SCHEME 2

The formation of cracks is a consequence of many events of breakdown of macromolecules occurring as a result of competition of processes 3 and 4. The

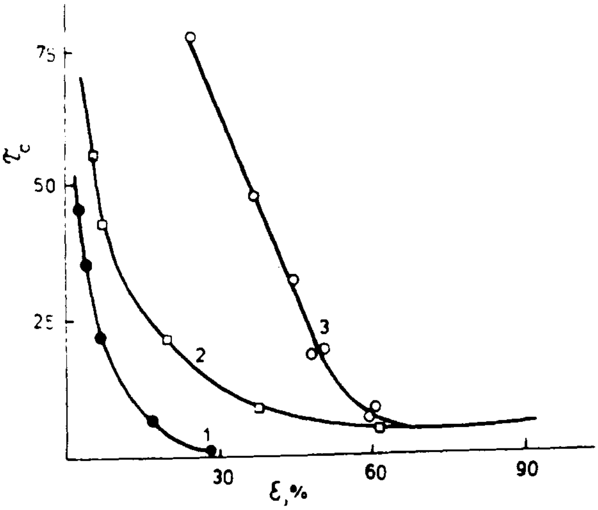


FIGURE 10 The effect of the elongation ratio (ε, %) on time to the emergence of cracks (τ_c, min) for elastomers of different types: 1—NR, $[O_3] = 1.5 \times 10^{-6}$ mol/l; 2—SKS—30, $[O_3] = 1.3 \times 10^{-6}$ mol/l; 3—polychloroprene, $[O_3] = 4.5 \times 10^{-6}$ mol/l.

proportion between reactions 3 and 4 governs the mobility of the fragments. If it is sufficient, a large number of fragments have time to leave the cage and the cracks grow rapidly. If the mobility is low, the conditions develop which favour recombination of fragments and the formation and growth of cracks are slowed down.

The truth of the said above lends itself to additional experimental verification. Above we compared crack growth rates for different elastomers at one and the same elongation ratio (20%); in other words, an attempt was made to create more or less similar conditions for competition of reactions 3 and 4. Having found that in polychloroprene the k_3/k_4 ratio is larger than in SKI-3, we can alter the conditions, e.g. raise the extension strain, thus increasing the rate of exit from the cage and lowering the k_3/k_4 ratio. In this case the rate of growth of cracks on the surface of polychloroprene should grow. Figure 10 shows the dependence of the time to the emergence of visible cracks (τ) on the strain of the speciments made of different elastomers. As it will be clear from the further discussion, τ_c is related to the crack growth rate by an affine dependence and therefore a decrease of τ_c characterizes the growth of the crack formation rate. The data given in Figure 10 give a good reason in favour of the explanation presented above.

High ozone resistance of butyl rubber can also be caused by the structural features of its macromolecules in which double C═C bonds are located at large distances from one another. Saturated fragments covering the bottom of the growing crack hinder its growth and most of ozone is consumed in the bulk of the polymer rather than on the surface of the crack.

CRACK GROWTH KINETICS

The number and shape of growing cracks are a function of the stress applied. Figure 11 displays the dependences of the time to rupture (τ_d) and of the shape

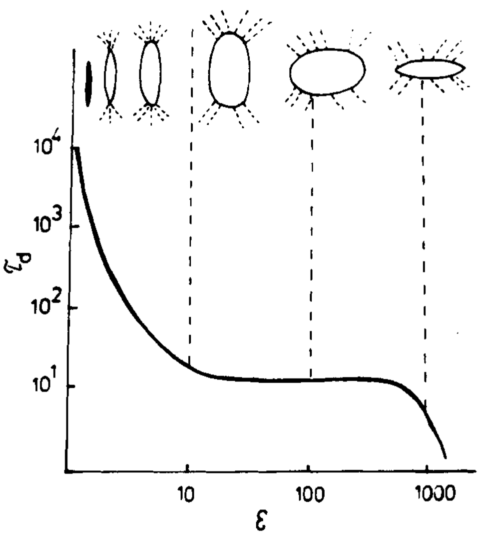


FIGURE 11 The dependence of the shape of cracks and of time to rupture of the specimen (τ_d) on elongation (ε, %). Dots mark the stress concentration areas. Natural rubber; $[O_3] = 0.2\%$.

of visible cracks on the elongation ratio of a natural rubber specimen.[11] The dependence of the time to rupture on the elongation ratio correlates well with the dependence of the crack growth rate on tension (Figure 6). The initial region (0–10%) features the increase of the crack growth rate and the shortening of the time to rupture. This region is followed by a relatively broad plateau where τ_d is independent of the elongation ratio. It can be believed that in this region all fragments leave the cage, and the rate of the process is limited by the rate of ozone supply to the surface of the elastomer.

In the region of large deformations and loads the contribution of mechanical breakdown becomes noticeable.

Concurrently with elongation of the specimen, the shape of the cracks changes. In the initial period the cracks have a typical extended shape and are oriented normally to the stretching direction. As strain increases, the walls undergo progressive realignment, the cracks acquire a rounded shape, and in the limit a crack oriented along the stretching direction can be observed. It seems proper to indicate here that full reversal of the crack's shape is only possible because of high flexibility of NR molecules. However, this does not mean that the distribution of stresses has also reversed. In such a reversed crack the lateral sections remain most intensely loaded. The ability of cracks to change their shape under the action of a load is closely related to the flexibility and mobility of the segments of the elastomer. The elongation ratio being identical (20%), the cracks on more rigid polybutadiene and butadiene-styrene copolymers feature a more pointed wedge-like shape. The cracks on polychloroprene vulcanizates have a more uneven relief than on the elastomers mentioned above.

The simplest dependences in experiments involving measurements of the crack growth rate as a function of time were obtained in studying the kinetics of growth of an isolated notch made on the edge of the specimen with the help of a razor blade. The length of the notch increased in proportion to the time of exposure to ozone; the growth rate did not depend on the thickness of the specimen, decreased at higher densities of the vulcanization network, and was independent of the nature of bonds in the network (sulphur or peroxide type). The rate of growth of the notch was proportional to ozone concentration and strongly depended on the nature of the polymer. Under comparable conditions the crack growth rate on different vulcanizates changed in the following order: butadiene-styrene copolymer (30% of styrene)—0.22 mm/min; butadiene-acrylonitrile copolymer (18% of acrylonitrile)—0.22 mm/min; synthetic polyisoprene—0.25 mm/min; natural rubber (cis-polyisoprene)—0.22 mm/min; gutta-percha (trans-polyisoprene)—0 mm/min; butyl rubber—0.02 mm/min; polychloroprene—less than 0.01 mm/min. This series characterizes well the relative resistance of elastomers of different structure to ozone ageing.

The process can be evaluated more fully by observing the kinetics of formation and growth of cracks arising spontaneously on the surface of a specimen placed in a gas medium containing ozone. It is expedient to use a microscope in order to detect the smallest cracks at the possibly earliest ageing stages. The results of such studies carried out on polyisoprene specimens are presented in Figure 12 displaying the dependences of the specific area of growing cracks (S_τ, m^2/m^2) on time at different ozone concentrations [13]. In general, these dependences resemble those obtained for the growth of an individual notch. The ascending branches of the $S_\tau = f(\tau)$ curves in Figure 12 are fairly well described by a linear function. The main difference from the notch growth features consists in the fact that the cracks start growing not immediately but after a certain induction period

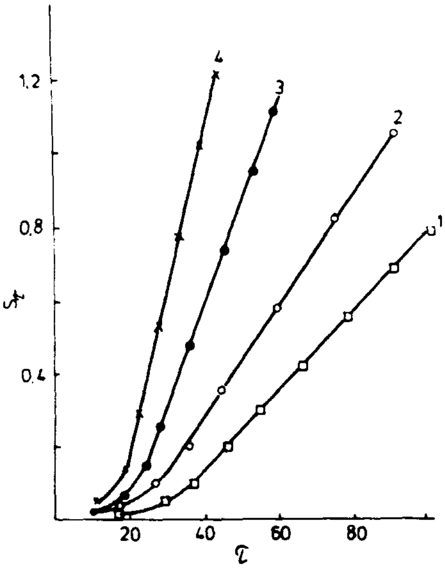


FIGURE 12 The dependence of the surface area of cracks (S_τ, m^2/m^2 × 10^3) on the time of exposure to ozone (τ, min) at different ozone concentrations, mol/l: [O_3]; 1—1.8 × 10^{-8} mol/l; 2—3.7 × 10^{-8} mol/l; 3—5.5 × 10^{-8} mol/l; 4—7.7 · 10^{-8} mol/l.

during which the growth rate of a crack is low and not constant. The experimental data in Figure 12 are well described by the equation for a line shifted from the origin:

$$S_\tau = a + b(\tau - \tau_i) \tag{1}$$

where S_τ is the surface area of the growing cracks, a and b are empirical parameters, τ is the full time of the experiment, and τ_i is the duration of the pseudoinduction period.

The data shown in Figure 12 and Eq. (1) interpret in quantitative terms the intuitive views rather frequently found among researchers.

Evidence accumulated recently makes it possible to express some ideas concerning the physical sense of the terms in Eq. (1). It seems that τ_i is the period of time within which C=C bonds on the surface are consumed to a substantial extent. A comparison of the τ_i values with the amounts of ozone absorbed (Figure 5) shows that within the τ_i time the surface absorbs an almost constant amount of ozone which is 10–15 equivalents in relation to the C=C bonds on the surface of the specimen. Such a large consumption of ozone becomes possible as a result of renewal of the surface. Denoting the surface renewal factor as γ, it is possible to connect its value to τ_i as follows:

$$\tau_i = \frac{\gamma[\mathrm{C{=}C}]}{V_g([\mathrm{O_3}]_0 - [\mathrm{O_3}]_g)}$$

where [C=C] is the concentration of C=C bonds in the surface layer, V_g is the rate of supply of an ozone-containing gas mixture to the ozone chamber, $[\mathrm{O_3}]_0$ and $[\mathrm{O_3}]_g$ are ozone concentrations in the gas flow at the chamber inlet and outlet.

Term a characterizes the surface of cracks at the point of inflection ($\tau - \tau_i = 0$). Under the experimental conditions (Figure 12) the values of a coincided for different curves although it cannot be excluded that this is an accidental situation.

Term b takes into account the effect of the concentration of ozone on the rate of growth of the surface area of cracks in the region where it becomes linear; therefore, it is more reasonable to express it as

$$b = d[\mathrm{O_3}]^m$$

The above analysis of the nature of terms a and b makes it possible to relate the kinetics of growth of the specific area of cracks to the time of exposure to ozone and its concentration in an explicit form:

$$S_\tau = a + d[\mathrm{O_3}]^m \left\{ \tau - \frac{\gamma[\mathrm{C{=}C}]}{V_g([\mathrm{O_3}]_0 - [\mathrm{O_3}]_g)} \right\} \tag{2}$$

Equation (2) is in a good agreement not only with the data given in Figure 11 but also with the specific features of growth of an individual notch discussed above. This equation is also convenient for the reason that it relates physical (crack growth) to chemical kinetics (the rate of ozone interaction with C=C bonds), i.e. describes two aspects of one process analysed separately in earlier studies.

The two-stage nature of the crack growth process and the existence of the slow and rapid stages are due to the fact that the rate of the process on the whole is limited by the diffusion resistance of the gas layer adjacent to the specimen. During the initial period when the concentration of C=C bonds is at maximum the concentrations of ozone on the surface and in the volume of the subsurface layer are relatively low. As the surface C=C bonds are consumed, the concentrations of ozone grow and the crack growth rate rises. Strictly speaking, the crack growth kinetics should follow the pattern of changes of ozone concentration at the surface of the specimen without being necessarily described by Eqs (1) and (2). On the contrary, the fulfilment of these relationships should rather be regarded as a kind of a particular case under the conditions of renewal of the surface.

An analysis of the experimental data demonstrates that the major amount of ozone approaching the surface (>90%) is absorbed by the uncracked zones of the surface. The kinetic data also indicate that the walls of the growing crack do not participate in the crack growth process and that ozone seems to absorb slowly. Figure 13 illustrates this statement. The bottom of the growing crack (marked in Figure 13) is the active growth zone where the material is continuously renewed and stresses are concentrated. If the whole surface of the crack interacted with ozone and participated in its growth, the temporal dependence of S_τ would follow the parabolic law, $s_\tau = k\tau^2$. Since the linear dependence, $S_\tau = k\tau$, is observed in the experiment, it can be thought that the area of the "growth spot" at the mouth of the crack changes slightly in time regardless of the increase of its geometric dimensions. The inertness of the major portion of the surface of the growing crack appears to be due to the fact that stresses in it have relaxed completely, the surface is broken down, and there is no renewal of the surface under these conditions. C=C bonds accessible to ozone have interacted with equivalent

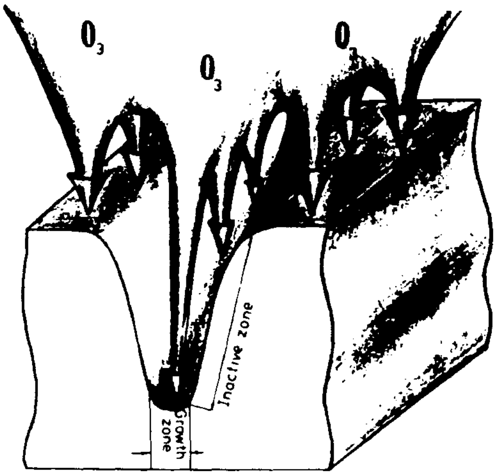


FIGURE 13 The scheme of distribution of the amounts of interacting ozone in the profile of a growing crack.

amounts of ozone and the reaction has been inhibited. On this basis one can calculate the quantity of ozone consumed by 1 cm^2 of the surface of the cracks—$\sim 8 \times 10^{-10}$ mol. In terms of the amount of ozone absorbed by the whole specimen this quantity accounts for a small proportion (0.2–0.6%).

A direct examination of stress distribution in growing cracks by photoelasticity technique[11] gives the results which agree well with the kinetic findings indicating the absence of stresses in the walls of the crack and the maximum of stress concentrations in the bottom and side sections.

It was said that the methods of assessment of ozone resistance by the time to the appearance of visible cracks (τ_t) or to complete rupture of the specimen have become the commonest practice. Eqs. (1) and (2) allow these indicators to be related to the parameters of the experiment. Substituting τ_t or τ_p for τ in Eq. (2) and solving Eq. (2) for them, it is not difficult to find this relationship in an explicit form, e.g.

$$\tau_t = \frac{\gamma[\mathrm{C{=}C}]}{V_g([\mathrm{O_3}]_0 - [\mathrm{O_3}]_g)} + \frac{S'_\tau - a}{d[\mathrm{O_3}]^m} \qquad (3)$$

Here S'_τ is the area of the cracks formed by the instant when they become detectable by the naked eye.

STRESS RELAXATION KINETICS

The second macroscopic manifestation of the effect of ozone on stressed elastomers is stress relaxation in them. It exhibits itself in a gradual elongation of a specimen with a weight attached to it, in creep, in irreversible shape change, etc.

Creep and stress relaxation are not infrequently observed in use of articles made of polymer materials, in fatigue, and in oxidative ageing. Both phenomena are caused by the breakdown of macromolecules passing through the cross-section of a specimen and hence by the decrease of this number of active chains bearing the load. Equilibrium stress in an extended specimen with an ideal network (σ) depends on the magnitude of strain (λ):

$$\sigma = NkT(\lambda^2 - \lambda^{-1})$$

where N is the number of active chains in unit volume, k is the Boltzmann constant, T is absolute temperature.

The relationship between stress and strain in real vulcanizates with network defects is best described by the expression

$$\sigma = \left(NkT + \frac{C}{\lambda}\right)(\lambda^2 - \lambda^{-1})$$

where C is an empirical constant. It follows from these equations that stress relaxation in the course of an experiment should be described by the expression

$$\frac{\sigma_\tau}{\sigma_0} = \frac{N_\tau kT + \dfrac{C^\tau}{\lambda}}{N_0 kT + \dfrac{C_0}{\lambda}}$$

where index τ refers to current values at any instant of the experiment.

Studies of thermal-oxidative destruction showed that chains, rather than cross-links, undergo splitting and that the alteration of N_τ is accompanied by an equivalent change of C^τ, the relationship

$$\frac{\sigma_\tau}{\sigma_0} = \frac{N_\tau}{N_0} \tag{4}$$

being satisfied with good accuracy. This relationship also seems to hold in the case of ozone degradation of elastomers since it relates stress relaxation (through the number of split chains) to the number of the events of ozone reaction with C=C bonds in the macromolecules (see Scheme 5.1).

Stress relaxation and crack formation are usually associated processes. They develop actively in polyisoprene vulcanizates and are only slightly noticeable in polychloroprene. Figure 14 demonstrates typical dependences of the relative force decay (P_τ/P_0) on the time of exposure of the specimen to ozone. An unloaded specimen does not change its mechanical properties in contact with ozone. At small strains there exists a rather narrow region where the stress relaxation rate increases; after that it remains unchanged, thus following the dependences peculiar to crack growth Figure 15. However, an essential difference is observed: the cracks begin to form and grow not immediately after

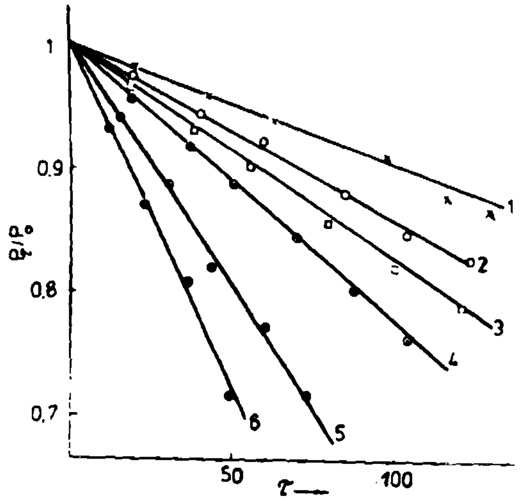


FIGURE 14 The dependence of force decay (P_τ/P_0) on the time of exposure of specimens of cured polyisoprene to ozonated air. $[O_3] \times 10^8$ mol/l: 1—1.02; 2—3.65; 3—4.48; 4—5, 6; 5—7, 5; 6—9, 5.

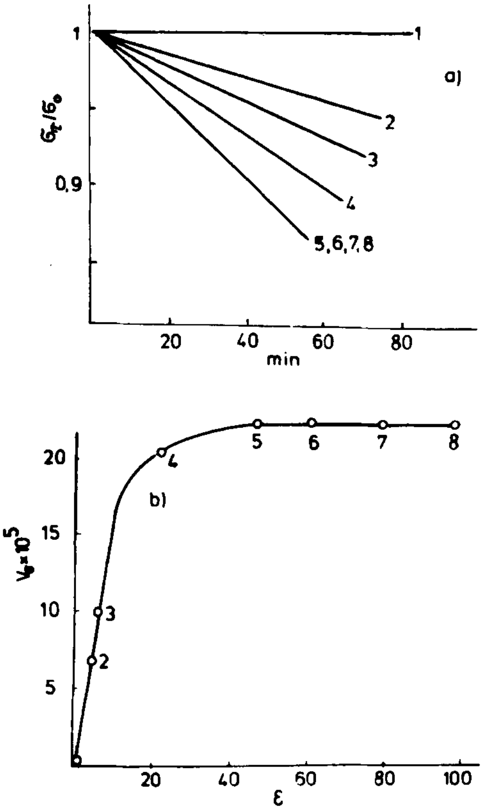


FIGURE 15 Stress relaxation (σ_τ/σ_0) in polyisoprene vulcanizates as a function of time and the dependence of relaxation rate on the elongation λ, %(b): 1—0; 2—5; 3—10; 4—20; 5—50; 6—60; 7—80; 8—100.

placing the specimen into the ozone atmosphere whereas stress relaxation is observed from the very commencement of exposure to ozone. This fact makes it possible to regard relaxation and cracking as two different processes having a common nature but described in terms which do not fully coincide.

Judging from the data given in Figure 15, the dependence of stress relaxation on time follows a linear law which agrees well with the reaction mechanism. A comparison of Eq. (4) with Scheme 1 gives

$$\frac{d\sigma}{d\tau} = \rho V_{O_3}$$

where τ is the ozone action time, V_{O_3} is the rate of ozone absorption, ρ is proportionality factor. The dependence of the relative force decay on time at $V_{O_3} = \text{const}$ is expressed as

$$\frac{\sigma_\tau}{\sigma_0} = 1 - \rho[O_3]\tau$$

which is the equation of a straight line. At sufficiently advanced stages of ozone ageing the contribution of the reduction of the cross-section of the specimen by local cracks and of the growth of the surface concentration of ozone becomes substantial. Inflections appear on the $\sigma_\tau/\sigma_0 = f(\tau)$ dependences appear; sometimes these dependences lose their linearity. This fact seems to account for the disagreement about the form of the real dependence existing in the literature.

It appears advisable to separate the stress relaxation processes into two constituents, volume and local. Volume relaxation includes stress relaxation processes taking place in the subsurface layers in areas free of cracks. Local relaxation is concerned with the decrease of the cross-section of the specimen as a result of crack growth.

At early stages of the process, presumably up to the emergence of visible cracks, the volume constituent is the major factor of stress relaxation. This is also evidenced by the following reasoning: each ozone molecule splits one chain in the elastomer network, no matter whether the chain is present in the mouth of the crack or away from it, on the surface. The shares of these processes should be proportional to the ozone addition rates. The distribution of ozone flows was made above (0.2–0.6% in cracks and the rest is absorbed by the surface between them). In this time interval the area of the growing cracks increases more than by one order of magnitude while the rate of force decay characterized by the slopes of the $(P_\tau/P_0) = f(\tau)$ dependences remains constant, as indicated by Figure 16. The absence of the relationship between the force decay and the dimensions of the growing cracks shows that the contribution of the cracks to the relaxation process at this stage is small. At advanced stages, particularly in the vicinity of the point of rupture of the specimen, the contribution of crack formation becomes decisive. Therefore, discussions of the ozone ageing process should take into account the dual character of stress relaxation processes.

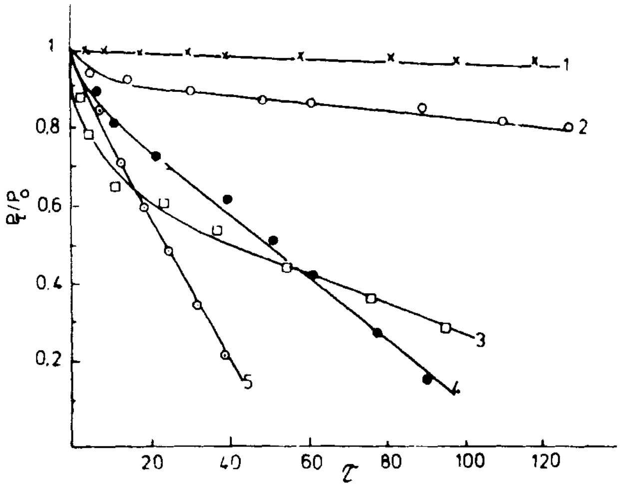


FIGURE 16 The dependence of force decay (P_τ/P_0) on time (τ, min) for vulcanized elastomers of different types: 1—polychloroprene; 2—butyl rubber; 3—natural rubber; 4—synthetic polyisoprene; 5—butadiene-styrene copolymer.

Stress relaxation kinetics, along with the crack growth rate, is highly sensitive to the nature of the elastomer. Figure 16 presents the curves of force decay for rubbers of different nature; the data were obtained in one series of experiments. It can be seen that the dependences for all elastomers are of a similar kind but ozone sensitivity or the effective number of split chains per ozone molecule decreases in going from polyisoprenes to butyl rubber and polychloroprene.

It appears that the influence of the nature of the elastomers on stress relaxation noted above is due to the same competition of the processes of exit from the cage and of association of intermediate products which was discussed here in analysing the processes of crack formation.

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