V. V. Podmasteryev, S. D. Razumovsky, G. E. Zaikov,
O. V. Stoyanov, S. Kubica

THE REGULARITY OF CRACKS FORMATION ON VULCANIZED ELASTOMERS UNDER OZONE ACTION. POLYISOPRENE

Keywords: ozone, polyisoprene, cracks, vulcanized elastomer.

The regularity of cracks formation had been concluded from precise experimental data. The mean value of crack surface was used as a measure of cracking degree. It was shown that the rate of cracks surface growth consists from two stages: a relative slow one at beginning of test and a faster one on the second stage. It was running with constant rate. A probable explanation of experimental observation and kinetic law of process was given. It was counted of the amount of ozone consumed per 1 cm^2 of forming cracks surface, which was found to be ~8 x 10^{-10} mol/cm^2, what is about 1% of the total amount of ozone absorbed by the sample.

Ключевые слова: озон, полиизопрен, трещины, вулканизованный эластомер.

По экспериментальным данным было сделано заключение о закономерности образования трещин. Среднее значение количества трещин было принято в качестве степени растрескивания. Было показано, что скорость роста трещин состоит из двух частей: относительно медленная в начале испытания и высокая на втором этапе. Работа выполнялась при постоянной скорости. Было дано объяснение экспериментальных данных и кинетического закона процесса. Было рассчитано количество озона необходимое на формирование трещин площадью 1см^2, обнаружено, что это количество равно ≈8·10^{-10}мол/см^2, что составляет около 1% от общего количества поглощенного озона.

Introduction

Crosslinked unsaturated elastomers are very sensitive to atmospheric ozone action [1, 2]. Ozone react with surfaces of elastomers goods forming cracks what leads to a loss in performance characteristics and ultimately to the failure of articles made from them. It's possible to find in literature many empirical papers presenting experimental data on elastomers aging in ozone atmosphere [1, 4-5]. Although of great practical importance, the intimae mechanism of crack formation and kinetic it growth has been poorly studied up to the present [4,5]. The kinetics of crack growth has been investigated in terms of stress decreasing in a stretched specimen [6] and increasing in the length of a single crack.[7]. The results of these studies stand in disagreement with one another (Fig. 1).
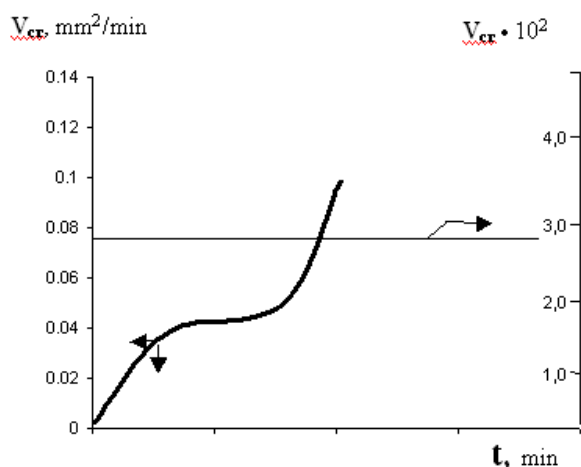
While a single crack grows at a constant rate, the growth rate of a total area of crack surface, determined from the fall of stress, is complex. It was published some attempt to use automatic system with computer treatment of experimental data and forecasting of real stability of a new elastomers to ozone aging [4]. Such attempts need in more advanced kinetic modeling of ozone aging process. The present paper gives an analysis of the kinetics of the growth of cracks on most sensitive elastomer to ozone action – vulcanized synthetic poliisoprene (SKI-3.).

Experimental

Polyisoprene (SKI-3) unfilled rubbers vulcanized by sulphur were used. The composition of the initial mixture have had 100 parts by weight of rubber, two parts of zinc oxide, two parts of zinc diethyldithiocarbamate and two parts of sulphur. The mixture was rolled at 50-70°C for 12 min, then placed in the press and vulcanized at 143°C for 30 min for the preparation of specimens in the form of 100 x 100 x 0-4 mm plates. The plate was cuted into 30 x 5 mm bands. Specimens stretched by 20% were placed in an inert medium for 3-10 h to complete the processes of physical relaxation, fixed in a revolving clamp and introduced into the ozone chamber.
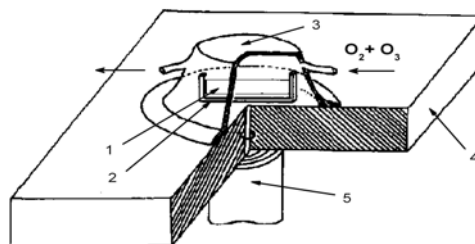

Fig. 1 - Crack growth rate (Vcr) versus time according to the data published in references 4 and 5

Fig. 2 - The ozone chamber

The ozone chamber, shown in Fig. 2, had a glass cell, about 7 cm^3 in volume, provided with a removable cover, and with an inlet and outlet for the gas flow.

Ozone was generated by passingoxygen through narrow gap between two electrodes selected glass dielectric supplied by approximately 8-kV discharge, ozone concentrations in the gas flow at the cell inlet and outlet being measured spectrophotometrically at λ= 254 nm. Ozone concentration varied between 1,8 x 10^{-8} and 7,3 x 10^{-8} mol/l by regulating electrode voltage.

The gas flow rate (100 ml/min) and the chamber temperature (200°C) were maintained at constant levels. During passage through the ozone chamber, more than 70% of the ozone in the gas flow was absorbed. The kinetics of crack growth was studied in transmitted light by means of optical microscopy using a microscope MIN-8 with x100 magnification. Area 1 x 3 mm was chosen in the center of each sample under study, in which the length, width and depth of all cracks formed were measured. Minimal sizes of these cracks were 00075 x 0015 x 001 mm.

Results

Crack dimensions as a function of time are presented in Table 1. These data show that the length, width and length-width product are not suitable as measures of sample cracking. Alternatively, the average value of crack surface has been assumed to be a measure of the degree of cracking, which is determined as an arithmetical mean of the total crack surface per cubic millimeter of a chosen area of a specimen. The crack has been considered to be a pyramid with a rhombus as its base, whose diagonals correspond to the length and width of the crack, its height being the crack depth.

Table 1 - Parameters of Cracks

τ, min	$l_1 \times 10^{-2}$	l_2	$(l_1 \times l_2) \times 10^{-3}$	$S \times 10^{-3}$
	μm		μm^2	
15	0,40	5,03	0,20	1,48
30	0,70	12,38	0,87	4,51
45	1,06	18,60	1,98	6,91
60	1,39	22,00	3,07	11,63
75	2,08	26,41	5,50	23,79
90	2,43	30,08	7,32	28,06
105	3,20	33,12	10,59	33,97
120	3,26	35,33	11,58	44,65
135	3,400	35,9	12,26	48,99

Note: l1 and l2 are, respectively, the width and length of a crack; $[O_3]$ = 1,83x10^{-8} mol/l.

Figure 3 shows the dependence of crack surface on time of exposure to ozone at various concentrations. Evidently, the experimental data can be described either by the parabolic equation

$$S_t = a\tau^n \qquad (1)$$

or by the equation of a straight line:

$$S_\tau = a + b(\tau - \tau_i) \qquad (2)$$

where S is the crack surface at time τ, and a and b is the proportionality coefficients; τ_i is the period of slow growth of cracks. Under a parabolic law (1) experimental data Fig.2 became straight lines in logs - log plot coordinates and formed the family of straight lines (shown in Fig. 3). The index "n" (eqn (1)) was obtained from the slope lines. The values of "n" lay within the range 1,2-1,7. The model underlying a parabolic dependence assumes that the growth of cracks is accelerated due to the expansion of fresh surface with increasing crack size and a value of "n" must to be = 2. Described above data stand in contradiction with model. The lower values of "n" and it change with ozone concentration make it impossible to describe the process in terms of parabolic dependency.
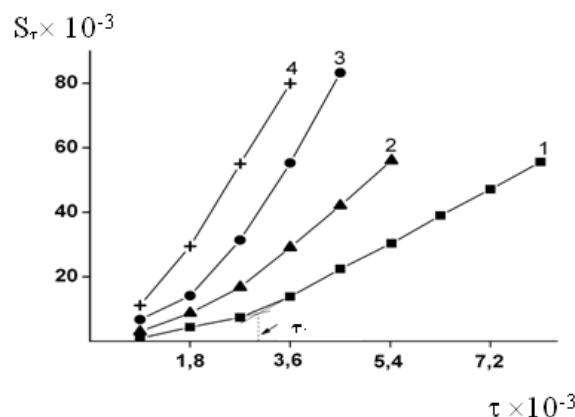

Fig. 3 - Time dependance of S . Here and on the Fig. 4 and 5 $[O_3]_0 \times 10^8$ = 1•83(1); 3•65 (2); 5•48 (30; 7•30 mol/l (4)

If dependence (2) holds, all experimental data must fall on a straight line described by the equation

$$(S - a)/ b = \tau - \tau i \qquad (3)$$

Fig.4 data shows that experimental data stand in good agreement with equation 3. Table 2 lists the numerical values of the coefficients i, a and b of this equation, calculated from the data of Fig. 3. The calculation procedure is described below. From Fig. 5 it follows that the experimental data fall satisfactorily on a one straight line and, consequently, eqn (2) describes correctly the dependence of the value of crack surface on the time of exposure to ozone. Values of i, given in Table 2 were determined by plotting the intersections of tangents A and C on the abscissa (Fig. 4). It is characteristic that i decrease with increasing ozone concentration. Comparison of i values with the amount of consumed ozone has indicated that nearly the same amount of ozone, 20-30 equivalents per double bond on the surface, is absorbed by the surface at various $[O_3]_0$ during the period i Such a high consumption of ozone is due to the renovation of the surface layer during the course of its reaction with ozone [6]. It follows that

$$\tau = \delta[C=C]/ v_g([O_3]_0 - [O_3]_g)$$

here [C=C] is the concentration of C=C bonds in a surface layer, δ is the renovation coefficient which is equal to 20-30 for SKI-3, vg - the rate of gas supply to the ozone reactor, and $[O_3]_0$ and $[O_3]_g$ are the ozone concentrations at the reactor inlet and outlet, respectively.
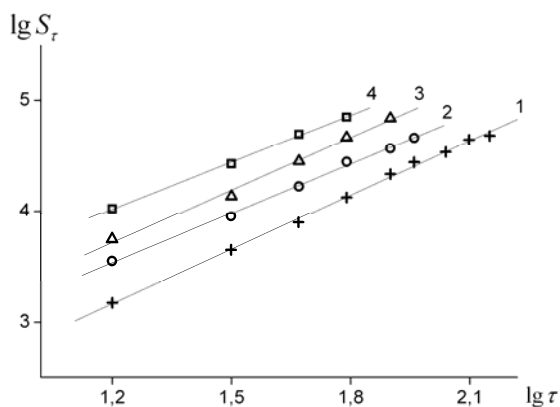
Fig. 4 - log Sτ versus logτ. Ozone concentrations as in Fig.3

Table 2 - Numerical Values of the Coefficient of Eqn (3)

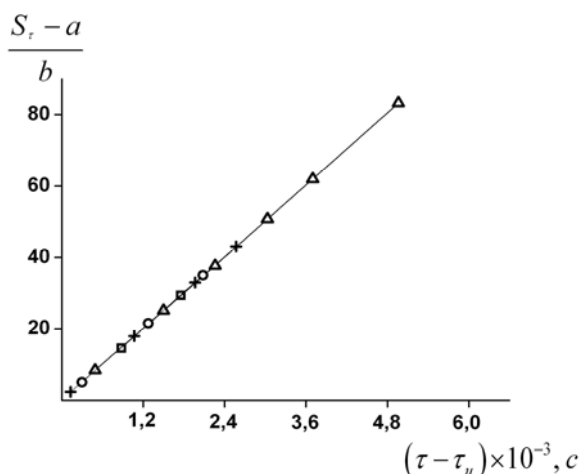| $[O_3]_0 \times 10^8$, mol/l	τ_i, min	$b \times 10^{-3}$, μm^2/min	$a \cdot 10^{-4}$, μm^2	$[O_3]_0 \times 10^8$ mol/l	τ_i, min	$b \times 10^{-3}$, μm^2/min	$a \cdot 10^{-4}$, μm^2
1,83	52	0,51	0,84	5,48	40	1,54	2,14
3,65	43	0,75	1,35	7,30	30	1,48	2,76

Fig. 5 - Experimental data in the coordinates of eqn.(3)

The coefficient a is characteristic of crack surface size in a bending area. Under experimental conditions a values were dependent upon the ozone concentration (Fig. 6).

The coefficient b is introduced for the region where the rate of crack surface growth obeys a linear law. This coefficient allows us to count the effect of the ozone concentration on the rate of crack surface growth. Values of b given in Table 2 are determined from the slopes of straight lines in Fig. 6. Since the coefficient b depends upon the ozone concentration

$$B = C[O_3]_0 m \qquad (4)$$

a certain b value corresponds to each experimental curve.

The data presented in Fig. 6 and Table 2 permit the determination of the values of C and m in eqn (4),

which are $4,81 \times 10^8$ and $0,77$, respectively. The exponent of m is less than 1. Obviously, this is due to the fact that the process occurs under diffusion-kinetic conditions and the ozone concentration on the sample surface increases more slowly than in the volume of the gaseous phase. Similar phenomena have already been observed on studying the kinetics of ozone absorption by elastomers of various nature [7].
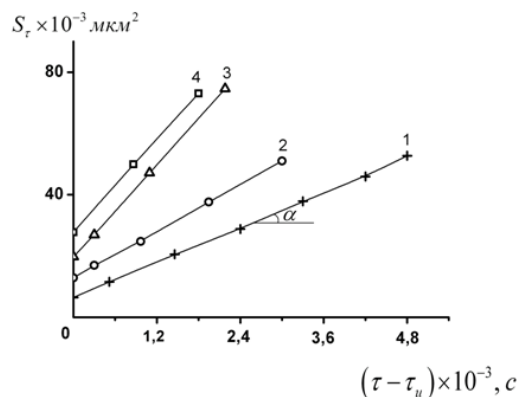

Fig. 6 - Sτ versus (τ-τl). Ozone concentrations as in Fig. 3

In general, the dependence of crack surface on the time of action of ozone and its concentration in the gaseous phase is described by the equation (5):

$$S_\tau = a + g \cdot [O_3]^m \left[\tau - \frac{\delta [C=C]_s}{V_g \cdot \left([O_3]_o - [O_3]_g \right)} \right] \qquad (5)$$

The validity of eqns (2) and (5) indicates that the growth of crack surface occurs in two stages, a relatively slow one at the beginning of the process and a faster one which proceeds at a constant rate. The slow stage may be caused by the decrease in the ozone concentration near the surface due to the physical adsorption and quick consumption. Experiments on saturated polymers have shown that the equilibrium concentration of the adsorbed ozone is about 100 times greater than that of the dissolved ozone [6]. After exhausting of the double bonds in the surface layer, the rate of the adsorbed ozone consumption go down, its concentration in the near-the-surface layer increases, and the higher rate of crack growth being observed.

The constancy of the rate of crack growth in the second stage indicates that the whole crack surface is not active towards ozone. Obviously, the growth of cracks proceeds near the apexes of cracks in very small sites, the size of which does not change significantly in the course of the experiment. Otherwise, the rate of surface growth would be related to the surface value, the experimental data being described by a parabolic law:

DS/dτ = nτ.

The low activity of the surface of a growing crack is obviously explained by the fact that all C=C bonds on its surface have reacted with ozone earlier. The surface of a growing crack can be assumed to be in the unstrained state, all the load being concentrated at its apex. Under this condition no renovation of the crack surface takes place, while ozone reacts only with two surface layers of the elastomer [6] This permits to count

110

of the amount of ozone consumed per 1 cm2 of forming cracks surface, which was found to be ~8 x 10-10 mol/cm^2, what is about 1% of the total amount of ozone absorbed by the sample.

References

1. Cataldo F. The action of ozone on polymers having unconjugated and cross- or linearly conyugation: chemistry and technological aspects. Polym. Degrad. and Stab., 2001,v.73, p. 511-520.
2. Podmasterjev V. Kinetic Regularities Cracking of Elastomers under Influence of Ozone. Diss… PhD degree. Inst. Biochemical Physics, Moscow. 2008 (russ).
3. Huang D., La Count B.J., Castro J.M., Ignatz-Haver F. Development of a service simulating, accelerated method for exterior tire rubber compounds. Polym. Degrad. and Stab., 2001,v.74, p. 353-362.
4. Tuzhikov O., Mednikov S., Sichev N., Suvorina S., Olschanskii O., Zheltobryuchova V., The influence of respturno-technological factors on vulcanized rubbers. Trudi Internat. Conference. "Rezinovaja Promishlennost. Sirje. Materials. Technologii" . Moscow. 21-25.05.2012., p. 154. (russ).
5. KruzlakJ., Hudec I., Dosoudil R. Influence of Polym. Degrad. and Stab., 2001,v.73, p. 511-520. thermo-oxidative and ozone aging on the properties of elastomeric magnetic composites. Polym. Degrad. and Stab., 2012, v.97, p. 921-928.
6. S.D.Razumovsky, V.V.Podmasteriyev and G.Ye.Zaikov, Dokl.Akad.nauk SSSR, 268 (1), 129 (1983).
7. S.D.Razumovsky, V.V.Podmasteriyev and G.Ye.Zaikov, Vysokomol.Soed., A, 25 (8), 1173 (1983).

© **V. V. Podmasteryev** - - Institute of Biochemical Physics, Russia; **S. D. Razumovsky** - Institute of Biochemical Physics, Russia; **G. E. Zaikov** - N.M.Emanuel Institute of Biochemical Physics, Russian academy of sciences, chembio@sky.chph.ras.ru; **O. V. Stoyanov** - Kazan National Research Technological University; **S. Kubica** - Institute for Engineering of Polymer Materials and Dyes, Torun, Poland.