

Resistance to Ozone Cracking in Elastomer Blends

E. H. ANDREWS, *Science of Materials Section, Department of
Mechanical Engineering, Queen Mary College, London, England*

Synopsis

The phenomenon of ozone cracking has been investigated for elastomer blends containing an ozone-reactive phase (natural rubber) and an ozone-inert phase (ethylene-propylene rubber). Electron microscopical studies reveal phase separation in the blend and the locus of ozone attack. Ozone cracks traverse the reactive phase and occasionally jump across inert particles without severing them. This mechanism provides the basis of a theory which correctly predicts the dependence of both the critical stored energy for ozone cracking and the crack density upon the blend composition.

INTRODUCTION

The phenomenon of ozone cracking in unsaturated polymers held under strain has been widely studied.¹⁻³ By observing the growth of single cracks in natural rubber, Braden and Gent⁴ were able to show that the process is governed by a critical energy criterion, and later it was established that this critical energy, of the order of 50 ergs/cm.² of newly created interface, could be identified with the surface energy of an ozone-degraded layer and that the Griffith theory of crack propagation therefore provided a full account of the effect.⁵ Using the same techniques, Braden and Gent⁶ went on to examine the influence of various chemical additives (the "anti-ozonants") which are known to diminish the extent or rate of ozone attack. They found that these fell into two distinct classes, namely, those that raised the critical energy required for rupture propagation and those that only lowered the rate at which cracks grew. An explanation of these effects was advanced by Andrews and Braden⁷ on the basis of electron microscopical studies of the surfaces of chemically protected rubbers. There are, however, other ways of increasing the resistance of polymers to ozone cracking which are physical rather than chemical in nature. One obvious way is to coat the rubber surface with some unreactive protective layer, and this is often done by the incorporation of wax, which "blooms" to the surface of a molded specimen. A further method is to blend the reactive rubber with a second polymer which is not susceptible to ozone attack. The blending of nitrile rubber with poly(vinyl chloride) is particularly effective, and blends of natural rubber with ethylene propylene (EPR) or chlorobutyl rubbers are also more resistant to ozone than the

natural rubber itself. The purpose of the work now reported was to study the nature of the ozone resistance obtained when an inert polymer is blended with a reactive rubber and to suggest what physical mechanism is responsible for this resistance. The present studies were carried out on blends of natural rubber with EPR.

EXPERIMENTAL

Materials

Natural rubber (*cis*-polyisoprene) (NR) and an ethylene-propylene copolymer (EPR) were blended together mechanically in the following proportions by volume: NR 100; NR 90-EPR 10; NR 75-EPR 25; NR 50-EPR 50. These blends vulcanized with either dicumyl peroxide (which crosslinks the ethylene-propylene rubber as well as the natural rubber) or sulfur (which crosslinks only the natural rubber), the vulcanizates being molded into sheets approximately 1 mm. thick. Com-

TABLE I
Mix details for the vulcanizates used

	Parts by weight			
	Peroxide cure		Sulfur cure	
NR	100	90	75	50
EPR	0	10	25	50
Dicumyl peroxide	3.0		—	
Sulfur	0.3		2.5	
CBS	—		0.6	
Stearic acid	—		1.0	
Zinc oxide	—		5.0	
Cures	60 min., 153°C.		30 min., 141°C.	

pounding details are given in Table I. In all that follows the initials NR and EPR will be used to denote the parent polymers, and particular vulcanizates will be indicated by the proportions of the constituents present and the vulcanizing system employed (e.g., 75/25 peroxide, the NR figure appearing first).

Microstructure of the Vulcanizates

The physical structure of the vulcanizates is revealed by the electron microscopy of thin sections cut with the freezing ultramicrotome described elsewhere.⁸ Figures 1 and 2 show the microstructure in a 90/10 and a 50/50 blend respectively, contrast between the two phases being enhanced by staining with osmium tetroxide. Quantitative assessment of the micrographs indicates complete separation of the two polymer phases and no solid solution can therefore have taken place. However, the size of the EPR particles (showing white in the micrographs) ranges from about 1 μ

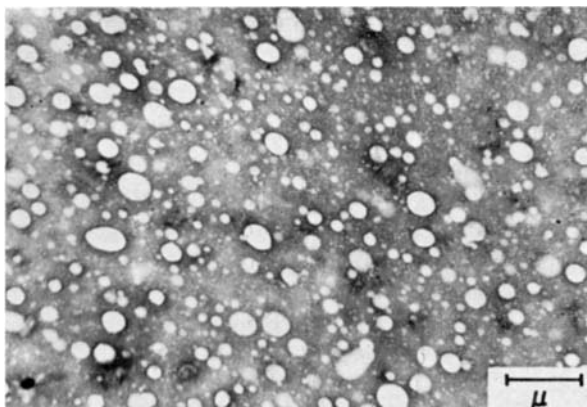


Fig. 1. Microtome section of a 90/10 blend of NR with EPR, the latter material showing white.

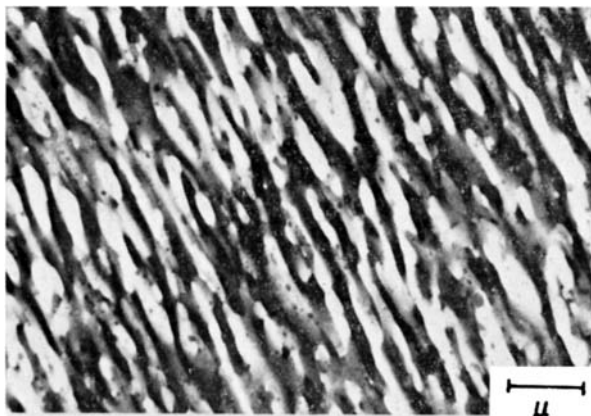


Fig. 2. Microtome section of a 50/50 blend of NR with EPR.

down to 200 Å., and the dispersion of individual molecules of EPR in the NR matrix therefore appears possible. In spite of the wide range of particle sizes it must be noted that the majority of the EPR phase is present in particles or regions of 0.3–1.0 μ and only a few per cent by volume in the smaller particles. This is important in considering the theoretical aspects of ozone cracking in these compounds. The micrographs also indicate the existence of structural anisotropy in the vulcanizates due to flow in the mould.

The microstructure of the blends is also revealed in torn surfaces which may be replicated for electron microscopy by a two-stage, gelatin-carbon technique.⁹ Although micrographs obtained in this way cannot safely be used to assess the structure quantitatively they do show the phase separation clearly and, when the specimen is exposed to ozone, the locus of chemical attack. All remaining observations, therefore, have been made on such surfaces exposed to ozone under a variety of conditions of strain.

Electron Microscopy of Ozone Cracking in Exposed Surfaces

Roughly parallel-sided strips of rubber were prepared having as one edge a straight tear, made in the sheet before marking out the strip. These strips, measuring about 1 cm. by 5 cm. were subjected to uniaxial strains of between 5 and 100% and exposed to an ozone concentration of 1 mg./l. in an apparatus described elsewhere.⁴ The torn surface was then replicated for examination in the electron microscope, the specimens being either relaxed completely before application of the gelatine or, alternatively, held at 10% extension to facilitate replication of any ozone cracks present.

Ozone cracking was observed in all blends, the crack density increasing as the proportion of EPR decreased (Table II).

TABLE II

Mean distance between parallel cracks, μ	Blend	Vulcanizing system
0.5-1	100/0	Peroxide
3-4	90/10	
3-7	75/25	
~ 20	50/50	
0.5-1	100/0	Sulfur
1-2	90/10	
3-5	75/25	
~ 20	50/50	

This suggests that one effect of the EPR phase is to reduce the number of cracks capable of growth. A further interesting, and possibly crucial, observation is that while many cracks terminate at the unreactive EPR particles, others appear to jump the particles without rupturing them. This phenomenon is illustrated in Figures 3 and 4.

If replication is carried out with the specimen under a small strain (ca. 10%), the insides of ozone cracks are replicated. The envelope of

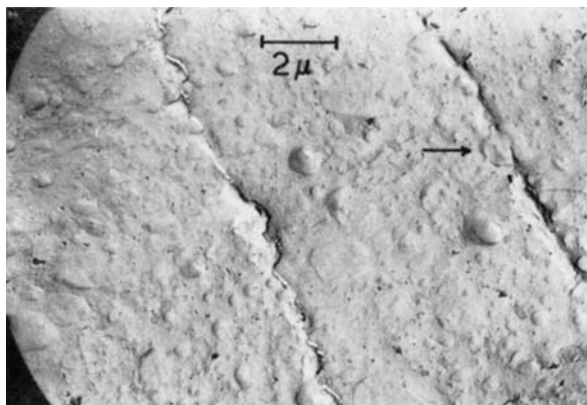


Fig. 3. Ozone cracks in the 75/25 peroxide blend showing unsevered EPR particles bridged by the crack.

carbon film thus formed stands vertically out from the final replica or else collapses sideways to show the depth profile of the crack, as indicated in Figure 5. Micrographs obtained in this manner are shown in Figures 6-8. In the 90/10 blends the ozone cracks penetrate into the surface as rapidly as they advance along it, producing a roughly semicircular crack profile which is, however, scalloped as a result of local impedance by EPR particles (Fig. 6). Some of the cracks remain closed in spite of the applied strain, and this confirms an earlier suggestion⁵ that some of the microscopic

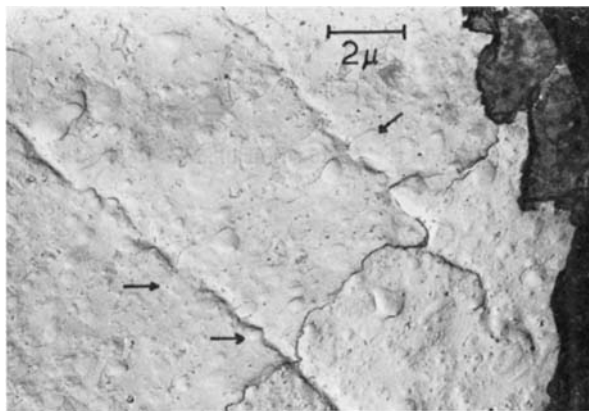


Fig. 4. As for Fig. 3.

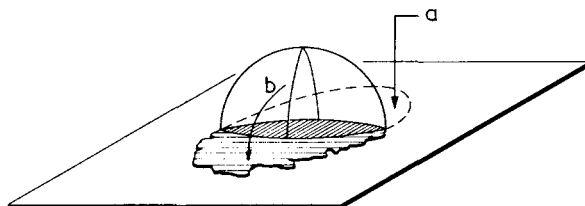


Fig. 5. Replication of ozone crack profile in specimens held under small strains: (a) shadowcast region; (b) collapse of carbon envelope.

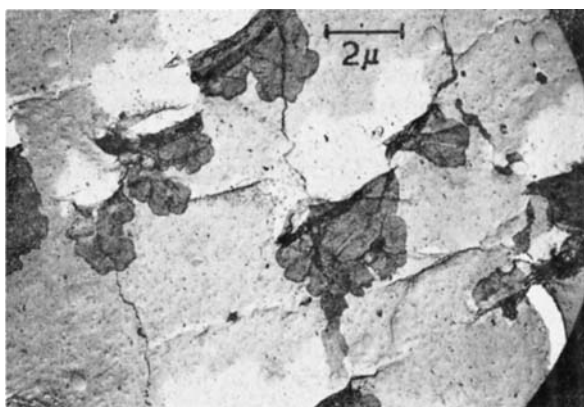


Fig. 6. Ozone crack profiles in the 90/10 peroxide blend. Replicated at 10% strain.



Fig. 7. Ozone crack profile in the 75/25 sulfur blend. Replicated at 10% strain.



Fig. 8. Ozone crack profile in the 75/25 sulfur blend showing further evidence of crack jumping. Replicated at 10% strain.

cracks propagate at the expense of others due to the mutual stress-relieving effect of neighboring cracks. The nonpropagating cracks then heal completely. In the 75/25 blends the cracks tend to spread along the surface more rapidly than they penetrate, and long, shallow envelopes are typical (Fig. 7). Here also is found further evidence of crack jumping (Fig. 8).

Determination of Critical Energy for Cracking

Braden and Gent⁴ have shown that no ozone cracking can occur in a single-phase rubber until the energy available for crack propagation reaches some small critical value. This energy derives from the elastic stored energy in the testpiece and turns out to be simply the interfacial energy required to form the new surfaces of the growing crack. The energy available (per unit surface area A of interface) to a crack of length c is

$$(dE/dA)_c = kW_0c \quad (1)$$

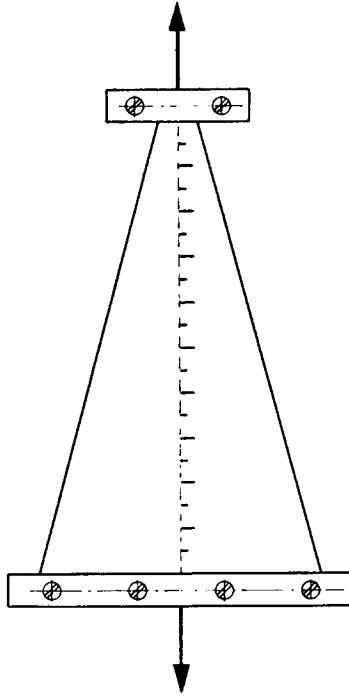


Fig. 9. Specimen used to determine critical strain for ozone cracking.

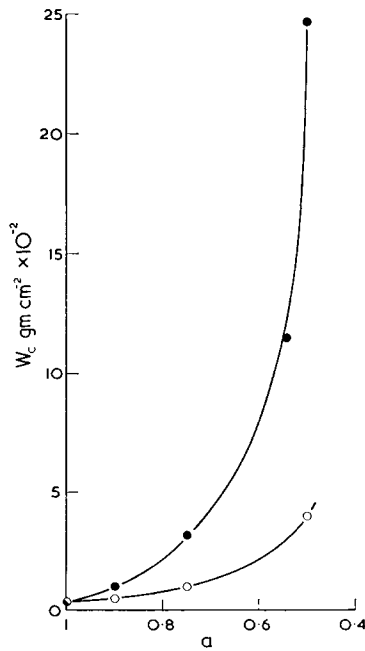


Fig. 10. Critical stored energy for ozone cracking, W_c , as a function of the proportion α of NR in the blend: (●) peroxide vulcanizate; (○) sulfur vulcanizate.

where E is the total elastic stored energy in the specimen, k is a constant, W_0 is the stored energy per unit volume, and the subscript l denotes that no work is done on the specimen during propagation of the crack. Propagation can only occur if $-(dE/dA)_l$ exceeds a critical value, and for single-phase NR, unprotected by chemical antioxidants, this value is about 50 ergs/cm.².

In a test piece containing no artificial flaw or crack there exist natural flaws of the order of 10^{-2} cm. in size at which ozone cracks are nucleated. If the average size of these flaws is regarded as a constant, eq. (1) gives as a criterion for cracking to occur,

$$\begin{aligned} -(dE/dA)_l &= T_c = k'W_c \\ W_c &= T_c/k' \end{aligned} \quad (2)$$

where T_c is written for the critical value of $-(dE/dA)_l$, W_c is now a critical value of the stored energy density in the test piece, and k' is another constant.

Values of W_c for the various blends were obtained in the following manner. Triangular specimens were cut from sheets of the blends as shown in Figure 9, and a linear scale was drawn in ink along their lengths. On stretching the specimen a distribution of strain was obtained varying from high strain at the narrow end to low strain at the base of the triangle. The strain was determined as a function of distance along the strip from measurements of the ruled scale before and after deformation, and the deformed specimen was then exposed to ozone until cracks were observed. These formed most densely in the high strain region but were absent from the low-strain region, the boundary between cracked and uncracked rubber being fairly clearly demarcated. The position of this boundary immediately provided an estimate of the critical strain for ozone cracking and the critical stored energy was then derived from the simple-extension force-strain curve of the rubber in question, being given by the area under the curve up to the previously noted critical strain. Figure 10 shows the values of critical stored energy for the blends (including unblended natural rubber) both for the sulfur and the peroxide vulcanizates. It will be our purpose in what follows to account for the dependence of critical energy upon blend composition and thus for the protective action of the inert phase.

THEORY

Physical Basis of the Theory

Although it may appear self-evident that the presence of inert particles in the elastomer blend should inhibit ozone cracking it is not easy to see how they exert this influence. A growing crack in the reactive phase must, sooner or later encounter an inert particle and come to a halt, further propagation being possible only by the crack circumventing the particle or jumping over it. Except for very small particles circumvention is un-

likely, since it would involve the crack propagating parallel to the applied stress, i.e., in a direction involving a minimum release of elastic stored energy. The alternative possibility of the crack jumping or bridging the particle leaving the latter unsevered, has actually been observed in the micrographs and clearly occurs when the presence of the crack projects a sufficient concentration of stress to the far side of the particle to initiate a new crack there. The probability of such a jump increases with the length of the crack (since the stress at the tip is related to this length) and also with the overall stress level in the specimen. The length of cracks in the reactive phase will, however, be governed by the density of unreactive particles, the presence of which will therefore diminish the probability of jumps.

The following theory has been developed on the assumption that crack jumping is the basic process involved in the production of macroscopic ozone cracks in elastomer blends containing both a reactive and an unreactive phase. Attention is focussed on the initial encounter of a crack with unreactive material; if a jump occurs it is assumed that the lengthened crack will jump all other obstacles and develop into a macroscopic crack. This assumption is completely valid if all particles have the same breadth and is probably reasonable in practice if the small volume proportion of very small particles is neglected. The elastic moduli of the two phases are assumed to be identical.

Two cases are considered, namely, the propagation of a surface (or linear) crack and the propagation of a penny-shaped (or semicircular) crack.

Crack Propagation along the Surface

Probability of a Crack of Length Greater than l . It is first necessary to calculate the probability of an uninterrupted crack of length l growing in the ozone-susceptible regions of the specimen. This probability will clearly diminish as the proportion (a) of ozone-susceptible material in the rubber decreases.

To simplify the calculation it is assumed that the ozone resistant regions are in the form of cubes of uniform size (edge length d). In actual fact, the shapes of the EPR particles vary greatly from nearly spherical to more complex forms, and the particle size is quite nonuniform. It is assumed that the effects of these variations will give rise to an apparent a which differs from the actual value by a factor which may itself be a function of a . This means that in our final formula for the probability the shortcomings of the "model" may be taken into account qualitatively simply by replacing a by the quantity $f(a)$ where f is a function of shape and size distribution. The problem is treated in two dimensions on a random plane through the solid. The proportion of the area on such a plane occupied by ozone-resistant regions will equal the volume fraction of ozone-resistant particles.

Suppose that a crack of length l is composed of n segments each of length d , and imagine that it is built up by repeatedly adding segments to its

length. The probability of placing the first segment in a permitted (i.e., ozone-susceptible) region of the plane is given simply by

$$P = a \quad (3)$$

Providing the area occupied by cracks is negligible compared with the total area available (more precisely, provided nd^2 is much smaller than the total area considered), the probability of adding another segment of ozone-susceptible material to the first is also a , and so on. The probability of generating a crack of length nd thus becomes

$$P_{nd} = a^n \quad (4)$$

If there are N_0 cracks initiated in a given area (i.e., there would have been N_0 infinitely long cracks in the absence of the ozone-resistant phase), the number N of length greater than nd becomes

$$N = N_0 \frac{\sum_{n+1}^{\infty} a^n}{\sum_0^{\infty} a^n} \quad (5)$$

Summing and dividing we obtain

$$N/N_0 = a^n \equiv \epsilon \quad (6)$$

where ϵ is now the fraction of all cracks with a length l greater than nd .

Probability of Crack Jumping an Inert Particle. The distribution of elastic stored energy along the axis of a crack in a strained elastomer is known¹⁰ to be of the form (see appendix)

$$W_x - W_0 = 2T/9(x + \alpha) \quad (7)$$

where W_x is the stored energy density at a distance x from the tip of the crack, 2α is the tip radius ($\alpha = 0$ for infinitely sharp cracks), and T is the stored energy parameter $-(dE/dA)_l$ involving the energy density W_0 in the bulk of the specimen and the crack length. For a crack of length c at right angles to the uniaxial strain direction,

$$T = kcW_0 \quad (1)$$

where $k \simeq 3$ for low overall deformation of the specimen¹¹ such as is encountered in ozone cracking.

Thus, from eq. (7):

$$W_x - W_0 = 6cW_0/9(x + \alpha) \quad (8)$$

Putting $c = nd$, $x = d$, we obtain the energy density W_d at the far side of an obstructing particle caused by a crack of length c impinging upon it, as

$$W_d - W_0 = \frac{2ndW_0}{3(d + \alpha)} \quad (9)$$

whence

$$n = [3(1 + \alpha/d)/2][(W_d - W_0)/W_0] \quad (10)$$

If the crack is to propagate beyond the particle W_d must have some critical value.

Since, from eq. (6), $\log \epsilon = n \log a$, eq. (10) gives,

$$\log \epsilon = [3(1 + \alpha/d)(W_d - W_0)/2W_0] \log a \tag{11}$$

or in terms of W_c the critical bulk stored energy necessary to ensure the survival and growth of a fraction ϵ of the original cracks,

$$W_c/(W_d - W_c) = [3(1 + \alpha/d)/2 \log \epsilon] \log a \tag{12}$$

or

$$\left. \begin{aligned} W_c/(W_d - W_c) &= C_1(\log a) \\ C_1 &\equiv 3(1 + \alpha/d)/2 \log \epsilon \end{aligned} \right\} \tag{13}$$

Growth of Cracks with Semicircular Profile

Consider the semicircular crack shown in Figure 11. An increment of growth increases the crack radius by d from nd to $(n + 1)d$ and increases the crack interface from $\pi n^2 d^2/2$ to $\pi(n + 1)^2 d^2/2$ that is, by an amount ΔA , where

$$\Delta A = [(1 + 2n)/2] \pi d^2 \tag{14}$$

The probability of selecting such an area without introducing a particle of the inert phase is

$$P_{\Delta A} = a^{\Delta A/d^2} = a^{(1+2n)\pi/2} \tag{15}$$

The probability of a crack of radius nd is then

$$\begin{aligned} P_{nd} &= a^{\pi/2} a^{3\pi/2} \dots a^{(1+2n)\pi/2} \\ &= a^{(\pi/2)[1+3+5+\dots+(1+2n)]} \\ &= a^{(\pi/4)(n^2+2n+1)} \end{aligned} \tag{16}$$

The number of cracks N of radius greater than nd thus becomes

$$N = \frac{N_0 \sum_{n+1}^{\infty} a^{(\pi/4)(n^2+2n+1)}}{\sum_0^{\infty} a^{(\pi/4)(n^2+2n+1)}}$$

or

$$\frac{N}{N_0} = \frac{\sum_{n+1}^{\infty} a^{(\pi/4)(n^2+2n)}}{\sum_0^{\infty} a^{(\pi/4)(n^2+2n)}} \tag{17}$$

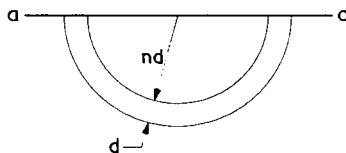


Fig. 11. Semicircular crack. Surface denoted a-a.

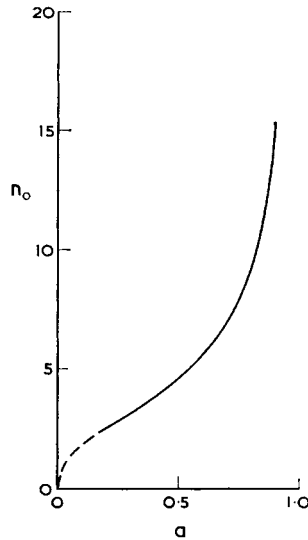


Fig. 12. n_0 as a function of a for $\epsilon = 10^{-10}$.

The quantity N/N_0 has been evaluated from eq. (17) by digital computer (ATLAS) as a function of a and of n . The question of interest is at what value of n does N/N_0 reduce to a small quantity ϵ such that no crack longer than nd is likely to occur in a test piece of reasonable size. Since cracks are spaced not less than 0.5μ apart, and a typical specimen may have a surface area of some 10 cm.^2 , a suitable value for ϵ would be 0.25×10^{-9} or, say, 10^{-10} . In Figure 12 are plotted the results of the computation showing the value n_0 of n for which $\epsilon = 10^{-10}$, as a continuous function of a . From this diagram and eq. (10) it is now possible to predict the theoretical dependence of W_c upon a for the onset of circular cracks, according to the relation

$$\left. \begin{aligned} \frac{W_c}{W_d - W_c} &= 3(1 + \alpha/d)/2n_0 = C_2 n_0^{-1} \\ C_2 &= 3(1 + \alpha/d)/2 \end{aligned} \right\} \quad (18)$$

COMPARISON WITH EXPERIMENT

Critical Energy for Ozone Cracking

The theoretical predictions embodied in eq. (13) and (18) may be tested against experiment by plotting the quantity $W_c/(W_d - W_c)$ obtained empirically against $\log a$ for the one-dimensional case and against n_0^{-1} for the penny-shaped crack. The parameter W_d , the critical energy density for ozone cracking in the absence of flaws, is however unknown. Strictly speaking, if no flaws are present, W_d is infinite, as will be seen if c is set equal to zero in eq. (1). Although in a macroscopic test piece flaws do always exist, it must be remembered that W_d is the energy density required

to initiate cracking in a very small region on the far side of an inert particle encountered by a growing crack, and the likelihood of a flaw being present there is very small. It seems reasonable therefore to assume that $W_d \gg W_c$, so that eq. (13) and (18) become

$$W_c = C_1 W_d \log a \quad (19)$$

$$W_c = C_2 W_d n_0^{-1} \quad (20)$$

These relations are plotted for both sulfur and peroxide vulcanizates in Figure 13 for the linear crack and in Figure 14 for the semicircular crack.

The predicted linearity is observed over a limited region of the curves viz. for $a > 0.7$ in the worst case and $a > 0.5$ in the best. The departures from theory are not as serious as may first appear, and in the light of the discussion which follows it is not necessary to invoke the device of replacing a by $f(a)$ to obtain agreement. It appears that the model set up above adequately represents the real material for purposes of computation. Considering first the linear crack the following points may be noted.

Firstly, the theory predicts $W_c = 0$ at $a = 1$, whereas even in pure NR some threshold value of W is required to initiate macroscopic ozone cracking. The reason for this discrepancy is obvious; the theory begins with the assumption that cracks already exist in the material and deals only with the restriction placed upon their initial length by the presence of inert particles. It thus assumes that when $a = 1$ the solid contains infinitely

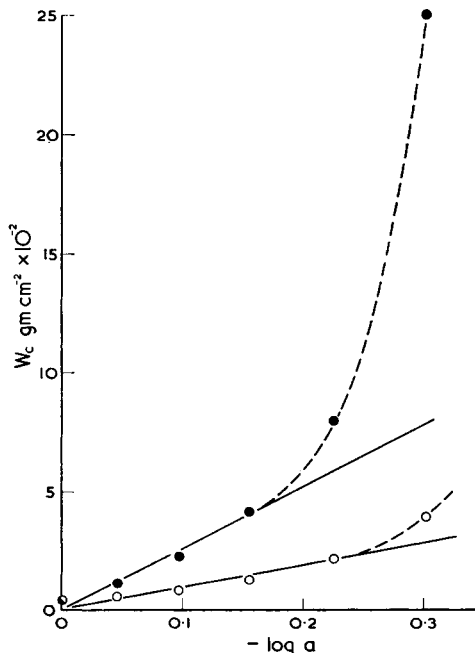


Fig. 13. W_c as a function of $\log a$ for the linear crack: (●) peroxide vulcanizate; (○) sulfur vulcanizate.

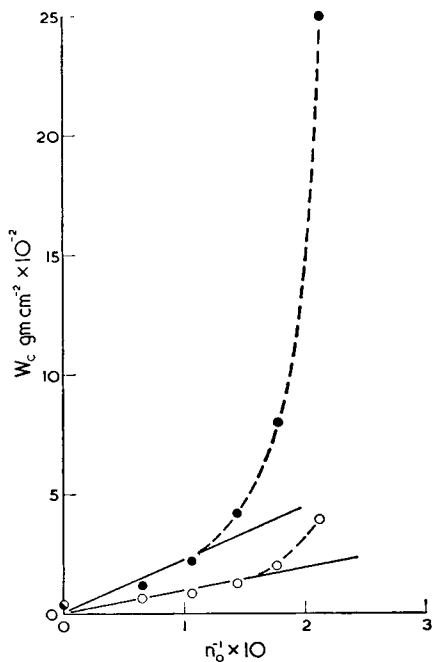


Fig. 14. W_c as a function of n_0^{-1} for the semicircular crack: (●) peroxide vulcanizate; (○) sulfur vulcanizate.

long cracks to start with, a situation which naturally predicts $W_c = 0$ for macroscopic failure. The theory does not therefore apply until W_c exceeds the value necessary to initiate cracking in pure NR, i.e., at $a = 1$ but is valid for all values of a less than unity. The situation at $a = 1$ can be met formally by supposing that at this point the number N_0 of initial cracks is zero and thus equal to the number N of surviving cracks in a material which does not fail macroscopically. The fraction ϵ is then unity, and C_1 in eq. (19) becomes infinite, leaving W_c indeterminate at $a = 1$ as the product of zero and infinity. At $a < 1$ N_0 rises immediately to a value predetermined by the density of intrinsic flaws. Strictly, N_0 should be proportional to a since only flaws in the reactive material are involved. Since however ϵ is of the order of 10^{-10} , a factor of 2 in N_0 will make very little difference to $\log \epsilon$ and thus to C_1 over the experimental range of a .

The second point to be noticed is that the actual value of W_c rises rapidly as a approaches 0.5. This effect is less marked for the sulfur vulcanizates, but even here definite departure from the theoretical prediction is evident. The cause of this departure is not difficult to find. In blends containing less than 50% NR the unreactive elastomer becomes the continuous phase (see Fig. 2), so that even if there is an infinitely long crack severing the NR phase and bridging the EPR phase, the material will not fail since there remains a continuous network of EPR. In a blend where NR is the continuous phase, the bridging of a particle of EPR by the crack must

inevitably be followed eventually by failure of the bridge either mechanically or by circumvention of the particle as the stress at the bridged particle increases with increasing length of the crack [eq. (8)]. This failure at the bridged particle is necessary if macroscopic cracks are to form and also explains why crack jumping is not observed more frequently in the micrographs. If the unreactive phase is continuous, however, circumvention is impossible and mechanical failure unlikely because multiple bridging results in sufficient load-sharing to prevent any given particle from being torn apart. An exception to this might be expected in the sulfur vulcanizates, because here the particles of EPR are uncrosslinked and therefore have little mechanical strength at low rates of strain. Rupture of the bridged particles is thus to be expected and the theory should be obeyed up to higher proportions of EPR than for peroxide cures. This is borne out by the experimental data.

Turning to Figure 14, which gives results for a semicircular crack, we find that agreement between experiment and theory is similar to that obtained for the linear crack for values of $a > 0.7$ but that departure from theory occurs more rapidly above this point for semicircular cracks than for linear cracks. This may reflect the observation that as a approaches 0.5 the cracks spread along the surface more rapidly than they penetrate into the rubber (Figs. 6 and 7).

The slopes of the linear portions of Figures 13 and 14 give the values of the parameters $W_d C_1$ and $W_d C_2$, respectively.

$$\begin{aligned} W_d C_2 &\simeq W_d C_1 = 2300 \text{ g./cm.}^2 \text{ for peroxide cures} \\ &= 930 \text{ g./cm.}^2 \text{ for sulfur cures} \end{aligned}$$

Since C_1 and C_2 differ by the factor $(\log \epsilon)$, this result shows that the value of W_d predicted on the basis of circular crack growth is smaller by this same factor than that predicted assuming linear (surface) cracking. Taking $\epsilon = 10^{-10}$ the factor represents one order of magnitude, and the actual values of W_d are as shown in Table III. (It is assumed that $\alpha/d \ll 1$.)

Of these predictions only those for the linear crack can possibly be correct, since W_d must exceed the values of W_c observed for the blends, viz., between 100 and 2500 g./cm.², and it must be concluded that the linear crack model corresponds most closely to reality. The value of 8000 for W_d in peroxide cures gives $W_d \simeq 10W_c$ for all except the 50/50 blend and so validates the assumption that $W_d \gg W_c$. The same reasoning applies to the sulfur vulcanizates.

TABLE III

	Predicted values for W_d , g./cm. ²	
	Peroxide	Sulfur
Linear crack	8030	3250
Semicircular crack	803	325

That the theory for semicircular growth turns out incorrectly does not, of course, mean that cracks with this profile do not exist. It does mean, however, that the limiting factor in the crack-jumping mechanism is the spread of the crack along the surface of the blend, penetration into the material being a secondary process.

Spacing of Cracks

A further test of the theory is available from the observations regarding crack density recorded above. Equation (11) may be rearranged to give

$$\log \epsilon = \frac{3W_d}{2W_0} \log a \quad (21)$$

for $W_d \gg W_0$ and $d \gg \alpha$. But $\epsilon = N/N_0$, and so

$$\log N - \log N_0 = (3W_d/2W_0) \log a \quad (22)$$

N is the number of surviving cracks at some value W_0 of the stored energy density, and the spacing s between cracks at this value of W_0 will be proportional to N^{-1} . Thus

$$\log s^{-1} - A = (3W_d/2W_0) \log a \quad (23)$$

where A is a constant. In Figure 15 the reciprocals of the spacings s are plotted logarithmically against a . Considering the approximate nature of the spacings, the equation describes satisfactorily their variation with blend composition. The slope of the best straight line through the points gives

$$W_d/W_0 \sim 3$$

The relevant values of W_0 are, of course, in excess of W_c , the critical value for cracking, and had a mean value of some 2500 g./cm.². This gives an

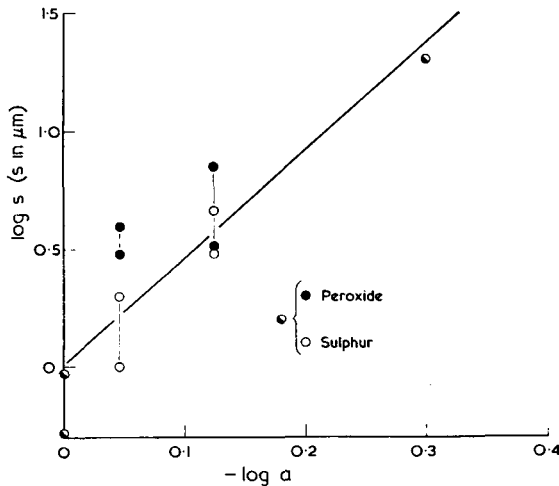


Fig. 15. Dependence of crack spacing s upon a .

independent estimate for W_d of 7500 g./cm.⁻², no distinction being possible between peroxide and sulfur vulcanizates. This compares very well with the value of some 8000 g./cm.² predicted from the critical energy data for the peroxide cures and a reasonable order-of-magnitude agreement for the sulfur cures.

CONCLUSION

The inclusion of an ozone-inert phase in an elastomer blend imparts some protection to the material in that it raises the critical stored energy necessary to initiate macroscopic ozone cracking. The role of the inert phase appears to be to hinder the development of macroscopic cracks from microscopic ones by providing physical barriers to crack propagation. These barriers may be overcome by the crack jumping or bridging the inert particle, and the likelihood of such an event is a function of the proportion of inert material in the blend and of the stored energy density in the specimen. A theory based upon the crack-jump mechanism gives good agreement with experimental results for the dependence of critical stored energy upon the composition of the blend and is independently substantiated by correct predictions of crack density and its dependence upon the proportions of reactive and inert material.

APPENDIX

The stress field around a crack in an elastomer was studied by Andrews,¹⁰ who found that the decay of elastic stored energy W along the axis of the crack could be expressed in the form,

$$1/W_x = 9(x + \alpha)/T'$$

where x is the distance along the crack axis from the tip and 2α is the tip radius. In this equation T' is twice the quantity $(dE/dA)_i$, since in its definition no account was taken of the fact that two surfaces are formed when the crack propagates. Thus $T' = 2T$. This equation furthermore applies for small x , i.e., for small distances from the crack tip and predicts that $W \rightarrow 0$ as $x \rightarrow \infty$. In fact, of course, $W_x \rightarrow W_0$ as $x \rightarrow \infty$, so that to apply the equation generally some modification must be made. A suitable amendment is to replace W_x by $W_x - W_0$, since this does not alter the form of the equation at small x where $W_x \gg W_0$ and satisfies the condition $W \rightarrow W_0$ at large distances. We thus obtain,

$$W_x - W_0 = 2T/9(x + \alpha)$$

which is the form employed in the text [eq. (7)].

The experimental work was carried out in the Laboratories of the Natural Rubber Producers' Research Association, Welwyn Garden City, Herts., England to whom the author is indebted for the facilities made available.

References

1. Newton, R. J., *J. Rubber Res.*, **14**, 27, 41 (1945).
2. Biggs, B. S., *Rubber Chem. Technol.*, **31**, 1015 (1958).
3. Andrews, E. H., D. Barnard, M. Braden, and A. N. Gent, *Chemistry and Physics of Rubberlike Substances*, Maclaren, Wiley, New York, 1963, p. 329.
4. Braden, M., and A. N. Gent, *J. Appl. Polymer Sci.*, **3**, 90 (1960).
5. Andrews, E. H., and M. Braden, *J. Polymer Sci.*, **55**, 787 (1961).
6. Braden, M., and A. N. Gent, *J. Appl. Polymer Sci.*, **6**, 449 (1962).
7. Andrews, E. H., and M. Braden, *J. Appl. Polymer Sci.*, **7**, 1003 (1963).
8. Andrews, E. H., and J. M. Stubbs, *J. Roy. Micros. Soc.*, **82**, 221 (1964).
9. Andrews, E. H., and A. Walsh, *Nature*, **179**, 729 (1957).
10. Andrews, E. H., *Proc. Phys. Soc.*, **77**, 483 (1961).
11. Greensmith, H. W., *J. Appl. Polymer Sci.*, **7**, 993 (1963).

Résumé

Le phénomène de cracking dû à l'ozone a été étudié pour des mélanges d'élastomères contenant une phase sensible à l'ozone (caoutchouc naturel) et une inerte à cet ozone (caoutchouc éthylène propylène). Des études au microscope électronique révèlent une séparation de phase dans le mélange et le lieu d'attaque par l'ozone. Les cassures provoquées par l'ozone traversent la phase sensible et sautent éventuellement au delà des particules inertes sans affecter celles-ci. Un mécanisme est à la base d'une théorie qui prédit correctement la dépendance à la fois de l'énergie critique emmagasinée pour provoquer une fissure par l'ozone et la densité de fissure en fonction de la composition du mélange.

Zusammenfassung

Die Erscheinung der Ozon-Rissbildung wurde an Elastomermischungen mit einer ozonempfindlichen Phase (Naturkautschuk) und einer ozonunempfindlichen Phase (Äthylen- Propylenkautschuk) untersucht. Elektronenmikroskopische Aufnahmen zeigen die Phasentrennung in der Mischung und den Ort des Ozonangriffs. Ozon-Risse durchziehen die reaktionsfähige Phase und überspringen gelegentlich inerte Teilchen ohne diese zu spalten. Dieser Mechanismus liefert die Grundlage für eine Theorie welche die Abhängigkeit der kritischen gespeicherten Energie für die Ozon-Rissbildung sowie der Rissdichte von der Zusammensetzung der Mischung richtig voraussagt.

Received August 13, 1965

Prod. No. 1274