Mechanism of Ozone Cracking.   II.   Nucleation and Growth of Cracks in a Plastic Film

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Synopsis

Partly unsaturated natural rubber hydrochloride films undergo stress cracking in ozonized oxygen.   The origin of cracks and the correlation between stress distribution and rate of crack growth have now been studied.   Cracks are initiated at foreign particles and/or surface fissures of microscopic dimensions.   Fracture is promoted only if the shape of the incipient crack fulfils certain geometric conditions.   These films become highly birefringent when stretched beyond the elastic limit; specific birefringence increases linearly with strain.   It follows from stress optical studies that large plastic deformations take place ahead of the crack, whereas the film is deformed only elastically.   Cut growth experiments confirm these conclusions. Fractography reveals that cracking consists mostly of a series of discontinuous events on a microscopic scale.   The influence of crack length and polymer modulus on the critical stress, necessary for the onset of ozone cracking, is predictable from the Griffith criterion.   The maximum stress at the tip was calculated from the observed dimensions of the crack and found to surpass the yield stress of the polymer.   Mechanical brittle fracturing and ozone-induced stress corrosion have been compared.   The remaining empirical element, which determines the rate of cracking, is the rate of hardening on ozonization of the fresh surface.

INTRODUCTION

Correlation between tensile stress, ozone concentration and the stress cracking of natural rubber hydrochloride films (Pliofilm) was reported in Part I.[1]   In order to analyze these phenomena in terms of a brittle fracture theory it is necessary to know the minimum size of an incipient crack and also to gain information on the stress distribution at the tip of the crack. The stress-optical properties of these films are essential for the interpretation of such microscopic observations and will be discussed first.

In fracture at small elongations, a minimum value for stress (Fig. 10 in Part I) was determined.   Unlike rapid brittle fracture produced by mechanical means alone, the growth process can be interrupted instantaneously by cutting off the ozone stream.   It is therefore possible to follow the growth phases of a crack under the microscope.   In a second approach, sufficiently large prestrain is given to the film to produce plastic flow first, and then the fracturing process is followed in the orientated material.   The locus of crack nucleation is not known *a priori* in either case and has to be found empirically.

Roesler and Benbow[2] have shown that catastrophic brittle fracture can be slowed down and controlled by localizing and restricting the area of loading necessary to produce a crack. Mechanically this is done by driving a wedge in a long beam of the material to be fractured. This can be a plastic,[2,3] an inorganic crystal,[4] or a metal.[4] In stress corrosion the wedge is replaced by a "chemical knife," ozone, which lengthens and sharpens a prepared mechanical cut. This method allows the tip of the crack to be "trained" until very low, but reproducible minimum values of stress are reached. Under these controlled, near-equilibrium conditions, fracturing is apparently taking place in an elastically deformed film.

EXPERIMENTAL

Materials and Stress-Cracking Equipment

The three types of rubber hydrochloride film Pliofilm N2, P4, and FF were the same as described in Part I.[1] Ozone production and stress-relaxation equipment have also been discussed there. Cut growth was followed by observing a growing cut at $80\times$ magnification. A strip was hung vertically through a Perspex cell with microscope slide windows (see Figs. 5 and 6 of Part I). Stress was applied by placing weights on a little platform attached to the lower end of the test piece.

Optical Quality of Films

These films are transparent and nearly colorless, which makes them suitable for light optical observations. Only small quantities of a blue dye are added during manufacture in order to compensate for yellowing on ageing. Reflectivity is high for both surfaces. As the films are produced by casting from solutions, one surface is a little rougher, corresponding to $0.5~\mu$ center line average. It is seen as a grain on the surface at large magnifications (Fig. 3). Shallow indentations of about 10–$20~\mu$ diameter are visible: they have, however, no influence on the fracturing process.

As with most polymer films, numerous impurities are found to be "cast in" or subcutaneous. Surfaces were carefully cleansed from electrostatically attached dust by rinsing with methanol. More than 360 particles to the square millimeter were frequently counted as permanent impurities. Their size distribution went from below $5~\mu$ (95%) to the range 5–$20~\mu$ (5%), and only a small number had a diameter between 20 and $40~\mu$. As some of these particles differ in birefringence from the organic matrix, they are seen as a galaxy of bright spots in several of the photographs taken with polarized light.

Stress-Optical Properties

Small elastic deformations make the film only weakly birefringent, but near the yield point at about 20% elongation, birefringence changes sign

and now increases rapidly with plastic flow (Fig. 1). In order to correlate strain and birefringence accurately, the following method was used. The strain of a small area was measured between markers. Birefringence of the same area was then estimated by applying either an Ehringhaus or a De Sénarmont compensator; results agreed well for both methods.

Positive birefringence increases linearly with strain in the plastic region. It is therefore possible to deduce the degree of strain of an area from observation of the amount of birefringence and the thickness of the film at the
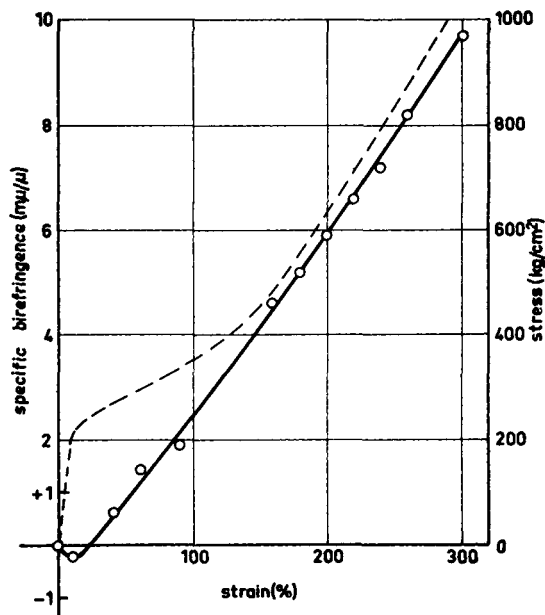

Fig. 1. Plots of (——) strain-dependent birefringence of Pliofilm type P4 (the positive sign means indicatrix in accordance with the direction of stress); (- - -) actual stress vs. strain curve for the same material (from Fig. 2 of Part I).

area. That indeed strain, and not stress, determines the degree of birefringence is borne out by the fact that stress relaxation, even at high degrees of strain, does not influence birefringence, while in contraction, due to partial elastic recovery, birefringence is reduced to a degree predictable from Figure 1.

A change in sign as shown in Figure 1 is well known and even more pronounced for polystyrene, where it is related to the gradual orientation of the phenyl groups. Amorphous natural rubber hydrochloride, like other aliphatic polymers, is probably only weakly stress-birefringent corresponding to the small, negative value found in the elastic region. The large positive birefringence observed on plastic deformation is essentially due to orientation of the crystalline phase. It is known that the latter process is related rather to strain than to stress.[5]

RESULTS

Initiation of Cracks

Unlike rubbers, these films show little stress relaxation in an ozonized atmosphere until the first cracks become visible with the naked eye (compare Figs. 7 and 9 of Part I).   At about 20% strain, when this induction period becomes short, such cracks rapidly grow to 50–100 μ length.   On relaxing the stress, they close to a gap width of a few microns and can now be studied under the microscope (Fig. 2).   It is seen that most of the cracks
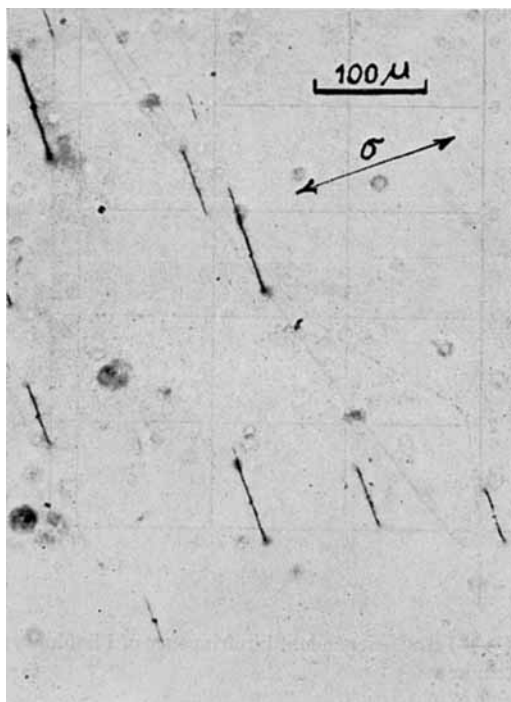

Fig. 2. Cracks produced by exposure of a film, type P4, to 5 ppm ozone after 3 min. Strain 10%, stress about 100 kg./cm². Photographed in phase contrast after release of stresses. Foreign particles are seen in the center of cracks.

are growing from a small foreign particle seen in their center.   A few apparent exceptions in the left top corner of the picture are cracks initiated also by a central foreign particle, but at the back of the film and piercing this surface at the moment of observation.

At higher magnifications, and with considerable patience, this nucleation process was observed at an earlier phase (Fig. 3).   After 2 min. exposure to 5 ppm ozone a crack of some tenths of a micron width had grown about 5 μ in length in both directions from the largest of the visible built-in foreign particles.   Quite similar phenomena have been observed for rubbers.[10]
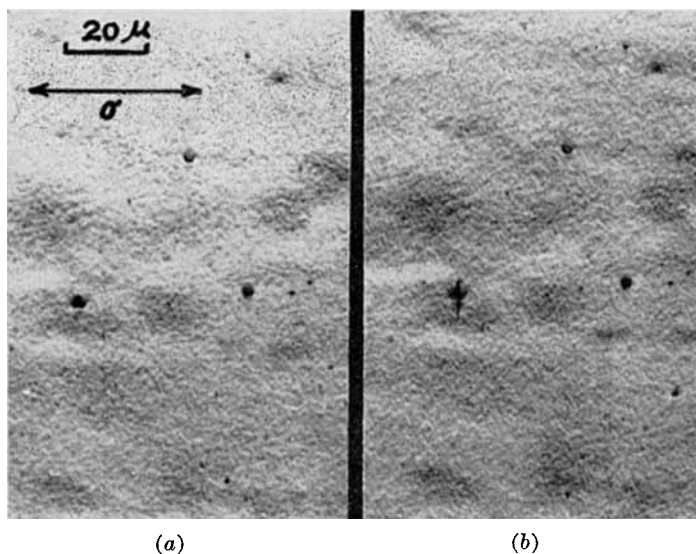
(a)   (b)

Fig. 3. Formation of a crack in the same film and under similar conditions as Fig. 2: (a) before exposure to ozone; (b) after exposure to ozone. Vertical illumination. Only at one of a number of foreign particles has a crack nucleated.

Growth of Cracks

These observations were extended by time-lapse photography (2 frames/sec.) in polarized light; a number of frames has already been reproduced elsewhere[6] (Fig. 5 *loc. cit.*). It is seen there and in Figure 4 of the present work that foreign particles clearly exhibit stress fields. Again, a crack nucleates at the largest particle (Fig. 5 *loc. cit*). From the crack length and the exposure time a nearly constant rate of primary crack growth was calculated to about 12 μ/sec.

Initiation is not always caused by foreign particles. A rare case of a dangerous surface fissure is shown in Figure 4. The strain chosen was again sufficient to cause localized plastic flow at the edges of foreign particles, which therefore show bright stress fields. However, no cracks are formed at these stress raisers. After 1 sec. a crack is seen to grow from a surface damage, a fissure of about 100 μ length, but only 1–2 μ in width (visible in the original copy of the first frame reproduced here). This fissure happens to be exactly perpendicular to the direction of tensile stress, a necessary condition for crack growth.

Attempts were made to reproduce such surface fissures by mechanical means, and to initiate crack growth by exposure to ozone. The surface was scratched with (1) hard powders, (2) emery paper, (3) fine needles, and (4) sharp blades; finally elongated pinholes were formed by stretching the film. All these artificial damages remained inactive, and cracks developed either at foreign particles or at fortuitously formed surface fissures. Obviously, all the mechanically produced incisions are too blunt to serve as a nucleus for an ozone crack.
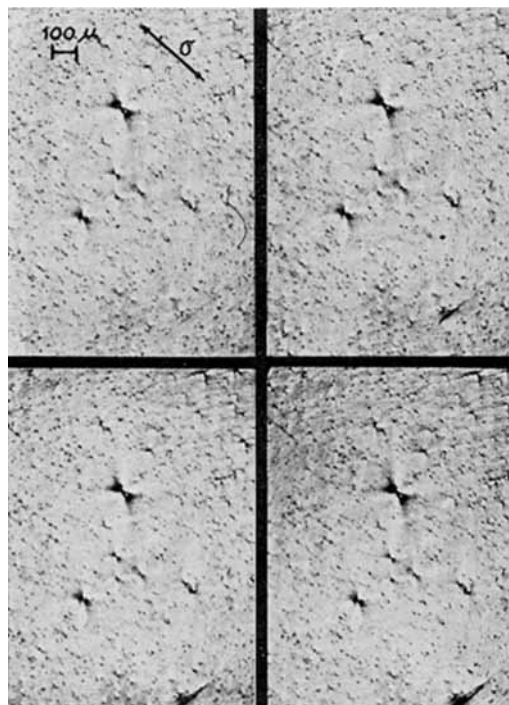
Fig. 4. Activation of surface damage; time-lapse photography. Film type P4, 30% strain, about 200 kg./cm.² stress, 5 ppm ozone; between crossed polarizers, 2 frames/ sec. Frames 1, 3, 13, and 21. A crack is initiated at a sharp fissure (top left); the crack grows rapidly while numerous stress raisers remain inactive.

It seems that the *shape and position* of an inhomogeneity are the decisive factors. As any shallow indentation will ease redistribution of stresses, and will therefore remain inactive, the shape of the nuclei has to be that of a wedge. Ratios actually observed on growing cracks were as much as 30 to 1 for length to width. The principal axis of such an incipient crack has to be perpendicular to the direction of stress. In order to activate a nucleus it may be necessary that the tip first grows to a capillary which, by external stresses, is pulled open sufficiently for continuous supply of ozone.

At low external stresses only a few points in the surface will fulfill these requirements; the chance of crack nucleation remains small and the in- duction period is therefore long. Not only are more local stress centers de- veloped with increasing external stress, but the chance for the formation of cavities at the edge of a foreign particle increases as well. It is well known in polymer technology that a vacuole is frequently formed at the filler– matrix interface on stretching. Particles firmly bound by the polymer matrix may be stress raisers, but they cannot act as nuclei, unless a vacuole is formed first at the particle–polymer interface.

The active area, where fracturing is taking place, is the center of a field of high-stress concentration. Plastic deformation occurs there even when the
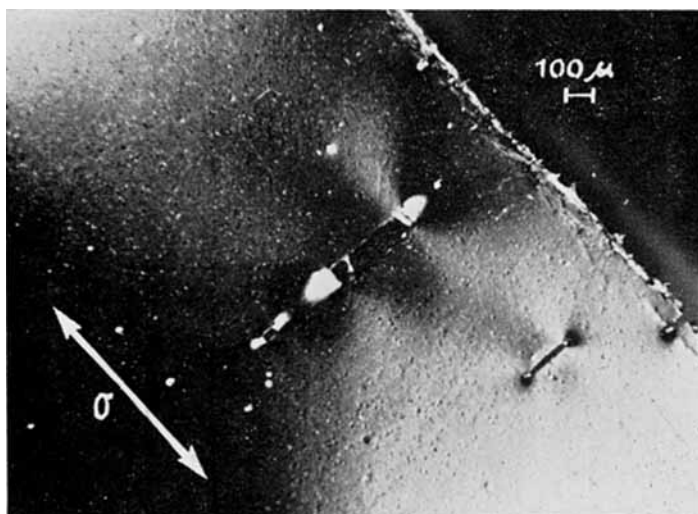
Fig. 5. Photograph of several larger cracks grown under the same conditions as in Figure 4. Areas of high specific birefringence indicate localized plastic flow at the tip of growing cracks.

film as a whole has not yet yielded. Viewed in polarized light, this region of plastic flow looks very bright, whereas the adjoining region is only elastically deformed and therefore remains dark. Typical examples are shown in Figure 5. Several cracks, 50–200 μ long, are terminated by brightly illuminated areas of plastic flow. Dark areas surrounding these bright zones, and the edges of the largest crack, indicate partial relaxation of the material. Residual bridges of material keep the edges together. These bridges are thin and yet very bright; therefore they must have flowed to a still larger extent. A small crack penetrates the dark field ahead of the large one; the two cracks would be joined a little later.

Growth History of Some Cracks

A semiquantitative analysis of the strain at the tip of a crack and the rate of polymer deformation during cracking will now be attempted.

The profile of a crack is obtained by shifting the focus of the microscope gradually from the surface to successively deeper levels (in unpolarized light) and drawing the contour of the crack at a given height. In order to determine the location of a submerged tip accurately, the apparent depth has to be corrected for the refractive index of the polymer film. The cross sections shown in Figure 6 have been constructed from a series of such measurements.

A film type FF 60 μ thick has been penetrated to about 30 μ (Fig. 6, top). The relaxed elliptical hole has an extension of 32 μ, while the stretched crack is 80 μ long. The plane of fracturing has shifted gradually from the surface to the center, as becomes apparent from the sawtooth profile. While the crack is growing in the shape of a capillary, visible under the

microscope, it tends also to penetrate to the lower surface.   This final situa-
tion is shown in Figure 6 (bottom).

Three areas, differing in degree of birefringence, can be distinguished;
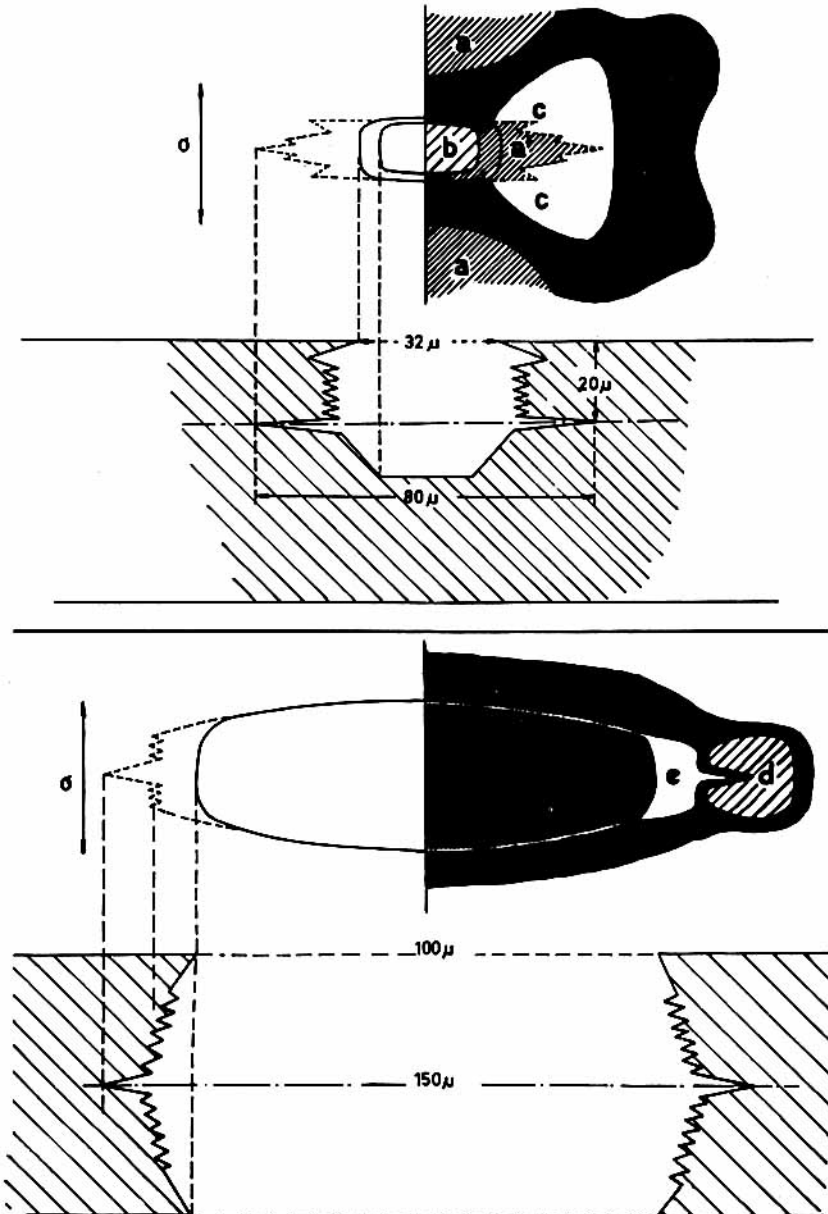they are drawn schematically as regions a, b, and c in Figure 6, top.   The

Fig. 6. Cross sections and surface topography of two cracks.   Areas a–e differ in
birefringence (see text).   Drawn from microscopic observations at successive levels of
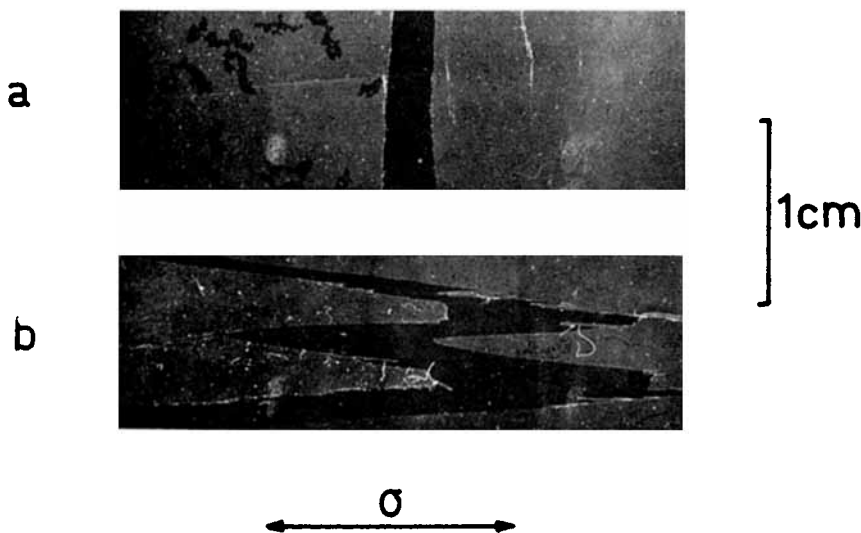depth.

Fig. 7. Influence of orientation on mechanism of fracture of high modulus film N1, prestretched about 200%: (a) high degree of sensitivity to stress cracking (stressed 175 kg./cm.^{2} perpendicular to the direction of orientation; strain less than 1%; exposed to 5 ppm ozone; time to fracture less than 0.2 sec.); (b) very low degree of sensitivity to stress cracking (stressed 600 kg./cm.^{2} parallel to direction of orientation; strain 8%; exposed to 1% ozone; time of tearing process 10 min.).

thickness of the film was 60 μ near area a, but only 30 and 20 μ at areas b and c. The optical path difference was now estimated with the aid of a De Sénarmont compensator, and the specific birefringence (for the wavelength of 589 mμ) was calculated. The values of 1, 3, and 8 mμ/μ for regions a, b, and c, respectively, correspond to strains of 60, 120, and 250% (see Fig. 1). Although the ragged area a' has the same grey tint as areas a, the degree of strain near a' cannot be estimated, because the optical path length is uncertain. The same method applied to region d near the hole (Fig. 6, bottom), yields also a strain of about 120% and finally the bright bridges e are stretched to 250%. A series of measurements on other cracks produced at similar strains always lead to the same conclusion. Plastic flow of the polymer takes place ahead of the crack, and there is partial recovery near the edges. At a nominal elongation of 20%, the average stress is only about one-fifth of the fracture stress, but the actual strain at the tip is so high that a small reduction in fracture strength by ozonization will be sufficient to propagate the crack.

At higher tensile stresses the traveling crack tends to open up, the tip becomes blunted, and the rate of fracturing is reduced. This is the reason for the peculiar shape of the fracturing versus prestrain curves shown in Figures 4, 9, and 10 of Part I. Finally, by prestraining to 300%, a highly anisotropic material is formed. Loaded perpendicular to the fiber axis, a rapid clean cut is produced on exposure to ozone (Fig. 7a). However,

when stressed parallel to the fiber axis, fracture develops with difficulty and only at very high ozone concentrations (Fig. 7b). Further evidence has already been published elsewhere.[7,8] Orientation may contribute to formation of a sawtooth profile on a microscopic scale.

Cut Growth

An ozone crack grown from a mechanical cut offers the advantage of controlled formation of a tip and also of a reproducible fracture surface for microscopic inspection. Strips, 1 cm. broad, were cut at the edge and an ozone crack grown to about 2 mm. length. The rate of crack growth near
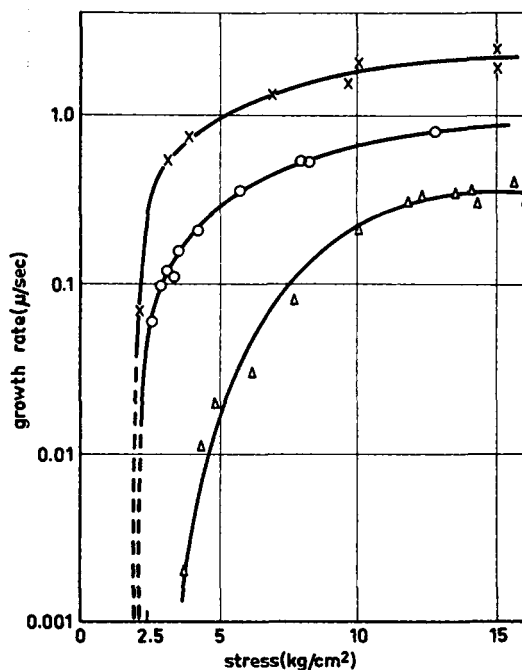

Fig. 8. Rate of cut growth in 5 ppm ozone as a function of stress: (×) film type N2, $E = 11 \times 10^9$ dynes/cm.,[2] thickness 20 μ; (△) film type P4, $E = 8 \times 10^9$ dynes/cm.[2], thickness 30 μ; (○) film type FF, $E = 6 \times 10^9$ dynes/cm.[2], thickness 60 μ. Stresses normalized for an initial cut length of 2 mm. [eq. (2)].

this length was now determined under the microscope. Values for nominal stresses were normalized to 2 mm. crack length by applying eq. (2) given below. Results for three films differing in modulus and thickness are summarized in Figure 8.

The critical load for a crack 2 mm. long is only 2–3 kg./cm.[2] A growth of only 10–20 μ/hr. is quite reproducible, if mechanical vibrations and temperature fluctuations are avoided. The growth rate is at first extremely stress-sensitive: a doubling of the nominal load results in nearly a hundred-fold increase in the growth rate. At higher loads the tip is gradually pulled
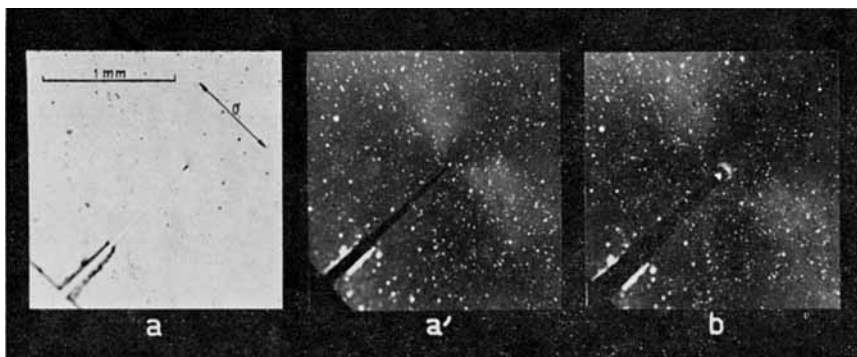
Fig. 9. Crack grown from a cut. Film type FF, 5 ppm ozone. A fine (dark) tip visible in incident light (a) at 18 kg./cm.² stress shows only as a tiny (bright) spot of plastic deformation between crossed polarizers (a'). At a higher load (24 kg./cm.²) it has been enlarged considerably (b).

open; stress concentration is thus reduced, and the growth rate becomes finally insensitive to higher stresses.

The three films differ in modulus (Table I of Part I) and corresponding rate of stress relaxation. It could be expected that the rate of cut growth will increase with modulus. The rate for the softest type, FF, falls in fact between the two others. This film, however, is twice as thick as types N and P. A more pronounced effect of modulus and instantaneous stress relaxation becomes obvious at high ozone concentrations, when catastrophic splitting of the hard film (type N2) is difficult to prevent.

Such experiments at the 5 ppm level (Fig. 8) are well reproducible. At 0.01–0.1% ozone, the critical load is slightly lower, the stress dependence is even more pronounced, and crack rates of 10 μ/sec. are readily produced; the shape of the curves is quite similar to those reproduced in Figure 8.

Viewed under the microscope, the picture of a growing crack changes considerably with both load and growth rate. At 0.01 μ/sec. a fine fissure is seen moving; it is stress-optically empty. Ahead of the tip a weakly illuminated stress field becomes visible; it disappears after stress relaxation and is therefore due to elastic deformation caused by the moving crack. At higher loads, stress fields become more pronounced, and once a growth rate of 1 μ/sec. has been reached a small, plastically deformed area is observed (Fig. 9). Viewed with incident light the difference between the edge of the original mechanical and the subsequent chemical cut is obvious; at the tip a dark area, diameter 10–20 μ, indicates the fracture zone (Fig. 9a). In polarized light (Fig. 9a') a tiny bright spot, permanent after stress relaxation, reveals a small area of plastic flow. Only when the load is increased beyond the scale shown in Figure 8, the onset of plastic deformation ahead of the tip becomes visible (Fig. 9b). Again the degree of birefringence can be measured and the local deformation estimated. While the strip is stretched only 0.4%, material ahead of the tip is strained a hundred times more to about 40%. The extent of the transient zone, where sudden

stretching is taking place, can be estimated only at the largest magnifica-
tion; it is about 4 μ broad.   Therefore, at a growth rate of 1 μ/sec., the
material in cut growth is strained at 70%/sec., a figure similar to the value
given above for crack growth.   However, at a controlled slow growth,
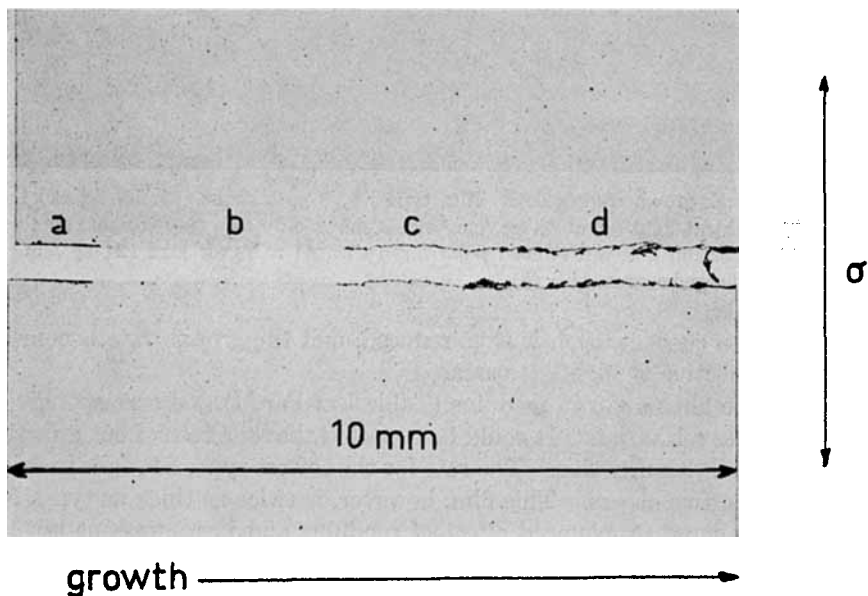0.01 μ/sec., the rate of flow ahead of the tip becomes also very low.   It is

Fig. 10. Change in profile of a crack with increasing stress in film type P4: (a) mechanical
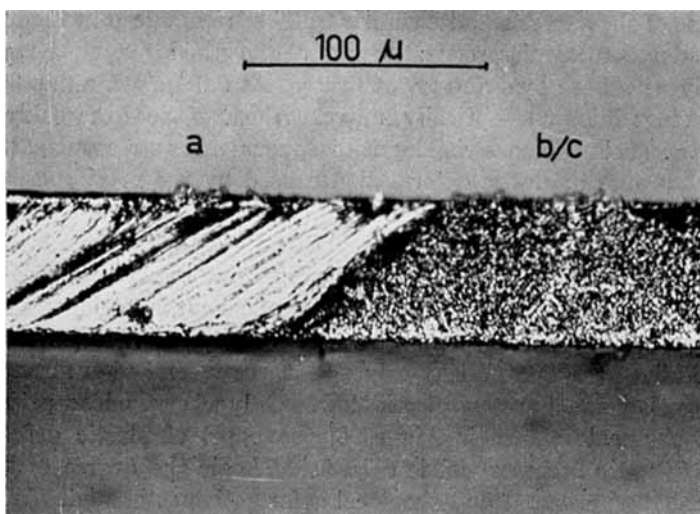cut; (b) very low stress; (c) 30 kg./cm.²; (d) 60 kg./cm.².

Fig. 11. Fractograph of cut and cracked surface of film type FF: (a) mechanical cut;
(b, c) ozone crack at about 15 kg./cm.² stress.

shown below that plastic flow is still taking place under these conditions, but the area of plastic deformation is now reduced to submicroscopic dimensions.

Determination of growth rates and stress-optical observations are necessary, but not sufficient for the understanding of the primary fracturing process. Morphology of the fractured area reveals additional information. A film was successively cut, (a) mechanically, (b) with ozone at a rate of 0.01 μ/sec., (c) at the five thousand times higher rate of 50 μ/sec. and finally (d) at a very high load (Fig. 10).

The difference between profile a and profile b has already been illustrated in Figure 9. The mirror formed under condition b is obviously very flat. It is formed only at the singular combination of low tensile stresses with a low ozone concentration. The surface roughness, determined by interference microscopy, is 0.2 μ or less; this surface is therefore highly reflective. At a crack growth rate of 100 A./sec., diffusion of ozone through the fresh surface and mechanical flow of the deformed material at the tip occur probably at similar rates; any sudden changes in stress concentration are thus avoided. These areas of smooth ozone cutting extend almost over the total cross section of the film and are in the length direction interrupted only by growth steps of about 1 μ. However, at a constant load the growth becomes accelerated with time as the stress at the tip is increased by the lengthening of the crack, see eq. (2) below. There is, therefore, a gradual change from the smooth surface profile b to the rougher surface type c.

Some typical surface structures are shown in Figure 11. The difference between the flow lines, about 2 μ deep, produced by mechanical cutting (Figs. 10a and 11a) and the grain structure produced by ozone (Figs. 10c and 11b/c) is clearly seen. Measured at 800$\times$ magnification the grain resolves into a dense population of little cylinders, 3 μ high and 1–2 μ in diameter. Ozone cracking of this grain type can be produced by a combination of high stress with a low ozone concentration, or vice versa. The phenomenon is comparable to adhesive peeling: a succession (in time) of minute fracturing events separated (in space) on a microscopic scale. This surface roughness is probably due to the subtle interplay of mechanical and chemical forces. The flow process is interrupted by fracture over a distance of a few microns. Stress concentration is relaxed by this fracture and it is building up again ahead of the fractured area.

The gradual change to coarser surfaces (c to d in Fig. 10) is readily understood. At high loads fracture tends to become catastrophic; forking and splitting of the advancing ozone crack is taking place, bridges of material being left behind and torn mechanically at a later phase.

THE BRITTLE FRACTURE CRITERION

Reduced to the idealized model of a two-dimensional crack, the Griffith criterion can be written:

$$\sigma_c{}^2 = (2/\pi) \, (2E\gamma_0 \, \gamma_1/l) \qquad (1)$$

where σ_c is the critical stress for the onset of fracture and l the length of the crack. E, the modulus of the polymer film, varied in the present investigation only between 6×10^9 and 11×10^9 dynes/cm.^{2} The free surface energy γ_0 of this polymer should be of the order of 50 erg./cm.^{2}; it is only moderately sensitive to structural changes. In addition, it is assumed that fracture of primary bonds either does not take place at all, or that it does not contribute to the energy equilibrium.

The curve-fitting factor γ_1 should be about unity for true brittle fracture. It is known that most solids absorb more energy under conditions of apparently brittle fracture, values of 10^3–10^5 for γ_1 being quite common. As the Pliofilm foils are rather brittle, the value estimated from the fracture stress of a strained film is only $\gamma_1 = 200$–400. Inserting the experimental values for E, l, and the σ_c value for ozone cracking, it is found indeed that $1 < \gamma_1 < 5$. This means that less fracture energy is needed in the presence of ozone.

The only real experimental variable is crack length l. It is accurately known for cut growth, 2000 μ, and about 2–5μ for crack initiation at impurities. The critical stress should therefore increase by $(1/l)^{1/2}$, 20 to 35 times, from cut growth to crack growth. Indeed, the critical value for crack growth determined in Part I was about 75 kg./cm.^{2} compared with only 2–3.5 kg./cm.^{2} found for cut growth (Fig. 8). By inserting the E value for rubbers in eq. (1) and the length either of a crack or a cut, a critical stress value can be predicted, as shown previously,[6] in excellent agreement with the experimental results obtained with rubbers by Braden and Gent.[9] Moreover, this calculation shows that the size of initiating impurities should be similar for plastics and rubbers, about 2–5 μ, which is in good agreement with our observations.[6]

The question why the idealized eq. (1) should hold so well for this complicated situation of stress corrosion needs closer inspection. It was shown that fracturing takes place in a narrow capillary or wedge with a very fine tip of nearly submicroscopic dimensions. For a linear elastic solid either the classical engineering approach of Inglis[10] or the molecular reasoning of Smekal[11,12] could be applied. Both models predict that the maximum stress at the tip, σ_m, should depend only on radius r of the tip at constant crack length:

$$\sigma_m = K\sigma_c \, (l/r)^{1/2} \qquad 1 < K < 2 \qquad (2)$$

As these films do not deviate much from linearity in the elastic region, eq. (2) can be used to predict whether the yield stress, about 200 kg./cm.^{2}, is reached at the tip. The diameter of the traveling capillary was found to be independent of crack length: always about 0.4 μ at the limit of microscopic resolution. Therefore, a value $r = 0.2 \mu$ becomes reasonable.

A cut of 2 mm. is nominally half a crack and therefore $l/r = 4000/0.2 = 2 \times 10^4$. On inserting this value in eq. (2) it follows that, even for $\sigma_c = 2$ kg./cm.^{2}, $280 < \sigma_m < 560$ kg./cm.^{2}. This σ_m value is far in excess of the yield point. Therefore, the material around the tip must flow. A *crack*

of only 5 μ length and the same tip diameter has a stress concentration factor $(l/r)^{1/2} = (5/0.2)^{1/2} = 5$. As $\sigma_c > 75$ kg./cm.^{2} the value of $\sigma_m > 5 \times 75$ kg./cm.^{2} again is quite sufficient to explain the occurrence of plastic flow at the moving tip. Thus it is seen that the plastic deformation actually observed is predictable from the dimensions of a crack and the stress-strain curve of the material.

DISCUSSION

True brittle fracture, i.e., the validity of eq. (1) has been established only for a small number of ionic crystals and metals mostly at low temperatures.[4] It has been known for many years[13] that rubbers still deform (thermo)plastically at temperatures far below their brittle point; only at the temperature of liquid hydrogen were indications for true brittle fracture of rubbers obtained.[14] The more recent experience that a viscous mechanism of energy dissipation is operative in the apparent brittle fracture of hard plastics, at temperatures far below their brittle point[15] agrees well with these earlier observations on rubbers.

The plasticized Pliofilms become brittle only at low temperatures. The apparent paradox of true brittle fracture of Pliofilm and rubbers at ambient temperature in ozonized air can be understood if volume effects are taken into account. True brittle fracture in a crystal is facilitated by existing cleavage planes, where stresses are concentrated. The radius of the travelling tip in ozone cracking is always very small (0.2 μ), whether fracture is propagated by a crack of 5 μ or a cut of 2 mm. length. Stresses are therefore more concentrated and extend over a narrower field in ozone cracking than in mechanical fracture of the same material or of organic glasses. This "chemical knife" has thus a sharper edge than any razor. The area attacked by ozone is about 0.05–0.1 μ thick.[1] The deformed colored layers observed in the fracture of some organic glasses are indeed of similar thickness,[16] but the zone of plastic deformation in ozone cracking is limited to a much smaller area. It may be because of this difference in fracturing volumes that observed nuclei in stress corrosion and crazing measure only a few microns,[17] whereas the size of inherent flaws in organic glasses is conjectured to be about 10 times as large.[18]

The remaining empirical element is whether a fine wedge will actually be formed and maintained. This, the problem of crack geometry, depends on the chemorheology of ozonized surface layers. The virginal, fractured polymer surface reacts instantaneously with ozone and hardens (Part I). Qualitative observations on ozone cracking of other high modulus polymers such as incompletely chlorinated rubbers and high-styrene/butadiene copolymers make probable that these materials are also ozone-sensitive, because ozonization leads to hardening.[7] However, this conclusion must not be generalized. Indications have been obtained that the ozone resistance of elastomers depends, at least in part, on the balance between hardening and softening reactions.[6,19]

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Résumé

Dans un film de caoutchouc naturel hydrochloré, partiellement insaturé tendu en présence d'oxygène ozonifié se forment des crevasses. L'origine des crevasses et la relation entre la distribution des tensions et la vitesse d'accroissement des crevasses ont été étudiées à présent. Les crevasses prennent leur source aux particules étrangères et/ou des fissures superficielles des dimensions microscopiques. La cassure se développe seulement si la forme des crevasses en formation remplit certaines conditions géométriques. Ces films deviennent fort biréfringents quand ils sont étirés plus loin que leur limite élastique; la double réfraction spécifique augmente proportionnellement avec l'allongement. Des études optiques de la tension résultent que des grandes déformations plastiques prennent place devant la crevasse alors que le film est seulement déformé élastiquement. Ces conclusions sont confirmées par des essais avec l'accroissement des incisions. Des études fractografiques démontrent que la cassure consiste généralement d'une série d'événements discontinus sur dimensions microscopiques. Par le criterium de Griffith on peut prédire l'influence de la longueur des crevasses et du module du polymer à la tension critique, nécessaire au début des crevasses ozoniques. On a comparé la fragilité causée par les moyens mécaniques et la corrosion en tension causée par l'ozone. Le facteur empirique restant qui détermine la vitesse de cassure, est la vitesse du durcissement durant l'ozonisation d'une surface naissante.

Zusammenfassung

In Folien aus teilweise ungesättigtem Naturkautschukhydrochlorid entstehen Spannungsrisse in ozonhaltigem Sauerstoff. Der Ursprung der Risse und die Beziehung

zwischen Spannungsverteilung und Risswachstumgeschwindigkeit wurde nun untersucht. Risse werden ausgelöst an Fremdteilchen und/oder mikroskopisch feinen Haarrissen in der Oberfläche. Nur wenn der sich bildende Riss bestimmte geometrische Bedingungen erfüllt wird der Bruch entwickelt. Wenn diese Folien über die elastische Grenze verstreckt werden, tritt starke Doppelbrechung auf; die spezifische Doppelbrechung nimmt proportional mit der Dehnung zu. Aus spannungsoptischen Studien folgt, dass grosse plastische Verformung dem Riss vorausläuft, während der Film nur elastisch gedehnt wird. Dies wird durch Untersuchungen an wachsenden Einschnitten bestätigt. Studium der Bruchoberfläche (Fractographie) zeigt, dass Rissbildung sich meistens aus einer Serie diskontinuierlicher Prozesse im mikroskopischen Bereich zusammensetzt. Der Einfluss der Länge eines Risses und des Modulus eines Polymeren auf die kritische Spannung, die für die Auslösung des Ozonrisses notwendig ist, kann mit Hilfe des Kriteriums von Griffith vorausgesagt werden. Die maximale Spannung an der Rissspitze wurde aus den beobachteten Abmessungen des Risses berechnet, sie überschreitet die Fliessgrenze des Polymeren. Mechanischer Sprödbruch und durch Ozon ausgelöste Spannungskorrosion wurden miteinander verglichen. Der empirische Faktor, der übrig bleibt und die Risswachstumsgeschwindigkeit bestimmt, ist die Geschwindigkeit mit der die neue Oberfläche während der Ozonisierung gehärtet wird.