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Flexcracking of Polymers

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INTRODUCTION

One of the difficulties encountered in studying flexcracking of polymers is a lack of precision in the experimental data. One cannot hope to construct a sound theory of flexcracking on average data that individually scatter by 50% or more.

It is desirable that we learn to pinpoint the cause of each individual failure. In this paper we will show that it is possible to test the cracking resistance of polymers with a high degree of accuracy. We shall do so by elaborating upon one particular method of testing.

THE FLEXING MACHINE

To obtain a clear-cut evaluation of the flex resistance of a polymer sample, one needs a careful description of the kind and the degree of the damage done and a complete set of controlled destructive manipulations that can be expressed in numerical form.

We obtained from the research department of the U. S. Rubber Tire Company a flexing machine which had been developed there by Mr. S. A. Lippmann. The machine takes a grooved polymer sample identical with that used in the DeMattia flexing machine, but the sample is subjected to a straight pull rather than to bending. The machine shown in Figure 1 features four speeds. An eccentric moves the upper jaw up and down over a distance that may be varied from 0 to $^1/_2$ in. A highly viscous dashpot holds the floating lower jaw at an equilibrium position which is attained shortly after flexing starts. This equilibrium position is determined by the elastic and hysteretic force together and can be controlled by weighting the floating jaw with a variable load. The machine has been found to give fairly consistent values for cut growth in pierced samples, as in the DeMattia test. It was, however, unable to induce cracking in unpierced samples of some polymers. Upon stroboscopic inspection we found a small but measurable motion in the lower jaw. This yielding apparently robbed the imposed sinusoidal strain cycle of its final and decisive snap. Adding balanced inertia weights of 50 lbs. each, shown in Figure 1, stopped this motion and enabled us to induce cracking in every case. Elongating the jaws to the form shown in

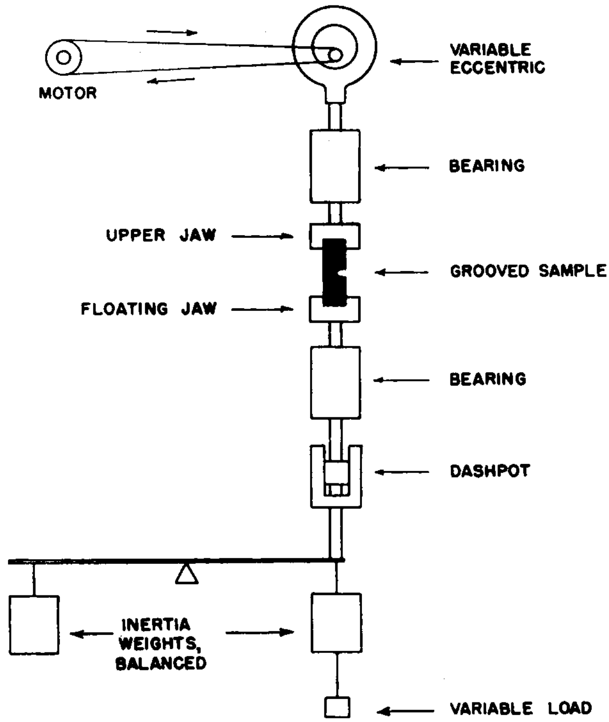


Fig. 1. Schematic side view of the flexing machine.

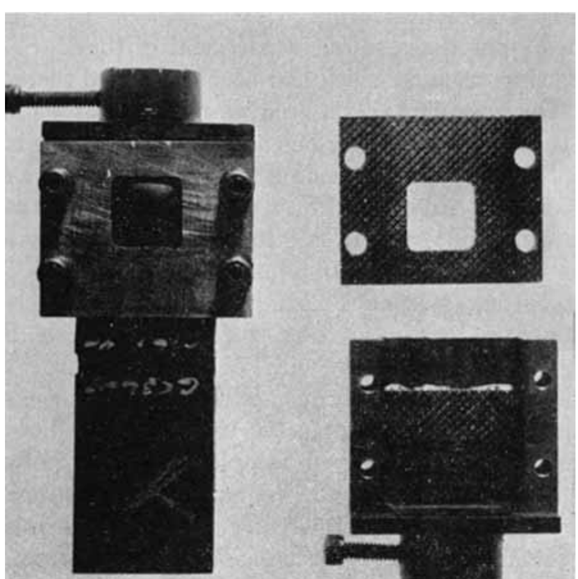


Fig. 2. Long jaws hold the sample securely and in a fairly reproducible way.

Figure 2 increased the maximum attainable effective strain cycle in the groove, as less of it was taken up by the other parts of the sample, and completed our control over this part of the operation.

Under our standard test conditions at ambient temperature, all polymers tested, except Hevea, warm up to 190–200°F. Hevea runs at about 20°F. less. We made no use of the heating chamber in which the sample is enclosed.

OBSERVATION TECHNIQUES

As we wished specifically to examine spontaneous crack initiation, it was necessary to observe the sample almost continuously during flexing. Therefore, an automatic still camera was attached rigidly to the frame of the flexing machine together with a high-speed electronic flashlight. The camera was a Beattie-Coleman Varitron Model E, equipped with interchangeable magazines taking 35 or 70 mm. film and a data chamber recording the moment of exposure and sample identifying information. The whole groove was photographed at slightly reduced size, on 35 mm. film. On the 70 mm. film almost all of the groove was recorded at 4× magnification. Our light source was a General Radio Strobolume, flash duration 20 μsec., capable of stopping motion even under magnification. The standard sealed-beam type of light was used and the light was concentrated on the sample by means of two concave microscope mirrors. The machine is shown in Figure 3. The light is mounted on the side door.

The camera was actuated by one of a set of timers which gave a choice

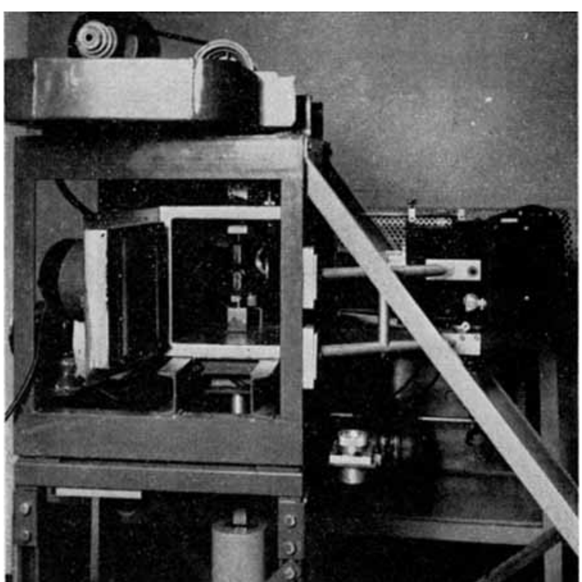


Fig. 3. Side view of the flexing machine. The door on which the light is mounted has been opened.

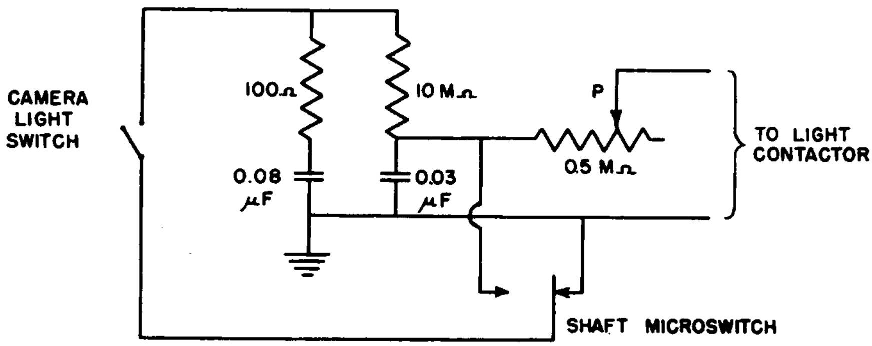


Fig. 4. The synchronizing circuit.

of three intervals between exposures: 2.5 sec., 10 sec., and 60 sec., depending on the expected life of the sample and the desired completeness of the coverage. The camera comes equipped with a light switch for flash synchronization. Another microswitch was actuated by a cam on the driving shaft of the machine. The circuit, shown in Figure 4, insures that the sample is photographed by means of one flash at the moment of its highest elongation. The light source is actuated by a condenser discharge which takes place once and only once during each closure of the camera light switch. The charging of the condenser is controlled by the potentiometer P which has to be adjusted for each different setting of the eccentric.

MEASURING TECHNIQUES

As said before, measurements in this field come in two groups: (*1*) the kind and the extent of the damage done by flexing and (*2*) the characterstics of the flexing itself. The failure occurs in many forms that have to be classified rather arbitrarily and will be discussed under Experimental Results. The flex cycle has only a small number of well-defined parameters (speed of the machine, length of the stroke, and static load); we shall discuss it first.

To obtain highly consistent and reproducible data, it is not sufficient to state just the length of the stroke as set on the eccentric. The way in which the operator mounts the sample cannot be completely controlled. The jaws clamp the sample very tightly, and variable amounts of stock will be squeezed out. This leads to variation in the elongation that is actually attained in the groove. These variations are small in magnitude, but they may lead to considerable differences in cracking behavior, especially at the shorter strokes. It is, therefore, necessary to read the maximum groove width that prevailed during the test off the photographic record. The groove width is subject to change during the test, and we use a reading taken 30 sec. after the start as one decisive parameter of the flex cycle.

The readings may be linearly transformed to per cent maximum elongation at the bottom of the groove by an obvious experimental calibration.

This method of measuring elongation results from the present photographic arrangement. It is clear that an additional stress measurement would help to establish differences that now escape us. But apart from this, another parameter needs to be considered which we have avoided by keeping it constant, namely, the curvature in the groove. Its importance, through the biaxial stress it generates, may be gathered from the scatter that occurs if insufficient care is taken to mount the sample straight in the jaws and, in particular, to keep the jaws in good alignment. In a new machine we are building, the jaws will run in tracks, to eliminate this problem. In the present paper the term "elongation" refers to the simple maximum elongation measured in the above manner.

EXPERIMENTAL RESULTS

The experimental results in this section are of two kinds. They are graphs obtained by plotting some kind of failure against one of the parameters of the machine and photographs of stages of the cracking process that may be of fundamental interest.

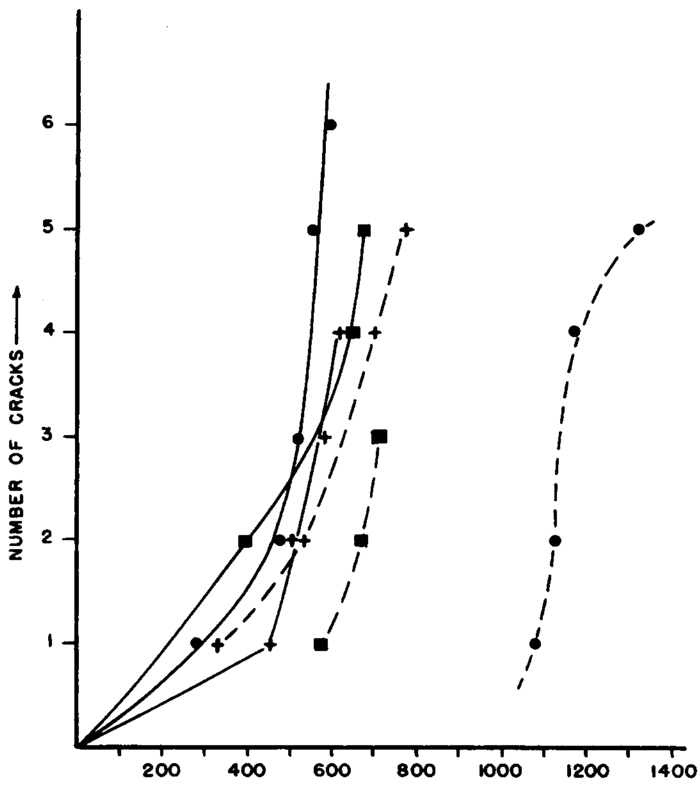


Fig. 5. The increase of the number of spontaneous cracks in time, measured on extracted samples: (—) without antiozonant; (---) with antiozonant.

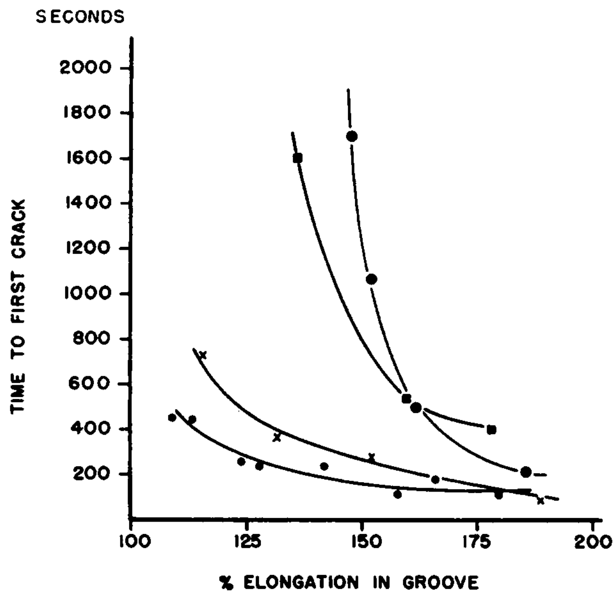


Fig. 6. Time from the start of flexing to the initiation of the first crack, plotted against elongation for four closely related vinylpyridine stocks.

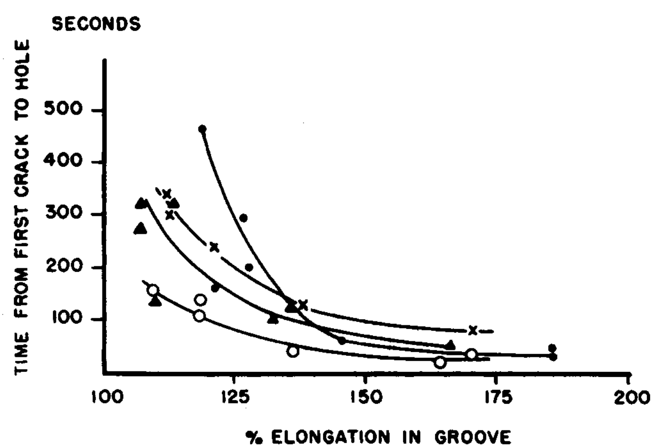


Fig. 7. Time for the first crack to penetrate the sample, plotted against elongation for four closely related SBR stocks.

We can note, in general, that there is a vast difference in spontaneous cracking between SBR and Hevea stocks. In Hevea, after a short induction period, one crack opens up, soon followed by a number of further cracks. They grow and merge relatively slowly; i.e., their growth covers most of the life span of the sample. In SBR the induction period covers most of the life span. Then one crack opens up and total failure follows relatively rapidly.

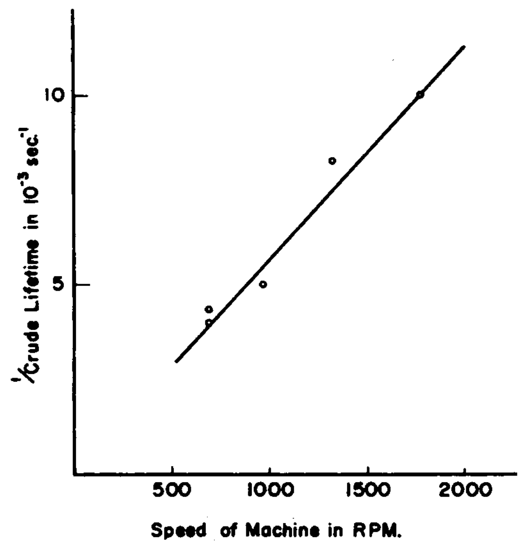


Fig. 8. The lifetime of the sample is inversely proportional to the speed of the machine; therefore, in this range the cracking process does not depend on the rate of flexing.

By special treatment, however, multiple cracks may be induced in SBR, as in the following experiment, which concerned an antiozonant, Flexzone 3C (Figure 5).

There were six samples, three control samples protected by an antioxidant, three others by Flexzone 3C. We extracted one control and one Flexzone sample for 24 hr. with benzene in a Soxhlet apparatus and all the others for 48 hr. All were subsequently dried at 20°C. in a stream of air for 72 hr. For each of the six samples we have plotted the number of cracks against time. The Flexzone sample that had been extracted for 24 hr. shows an appreciable induction period, whereas the performance of the other two had been brought down to the low level of the extracted controls. We conclude that the antiozonant interferes with crack initiation.

The moment at which the first and, in SBR often the only, crack appears is a fairly reproducible quantity, but it is very sensitive to proper alignment. Curves obtained are shown in Figure 6. The stocks are of approximately equal modulus. The differences between them are differences in compounding. After the crack has been initiated, it grows both in length and in depth. At a certain moment it penetrates the sample, forming a neat round hole, well before it reaches the edges of the sample. The time between the moment of initiation and the moment the hole appears is one of the most poorly reproducible quantities we have been dealing with but occasionally one obtains good curves as in Figure 7.

The machine is equipped with a limit switch, mounted on the balance arm, that carries the inertia weights and the static load. When the sample fails completely, the load pulls the balance arm away from its horizontal

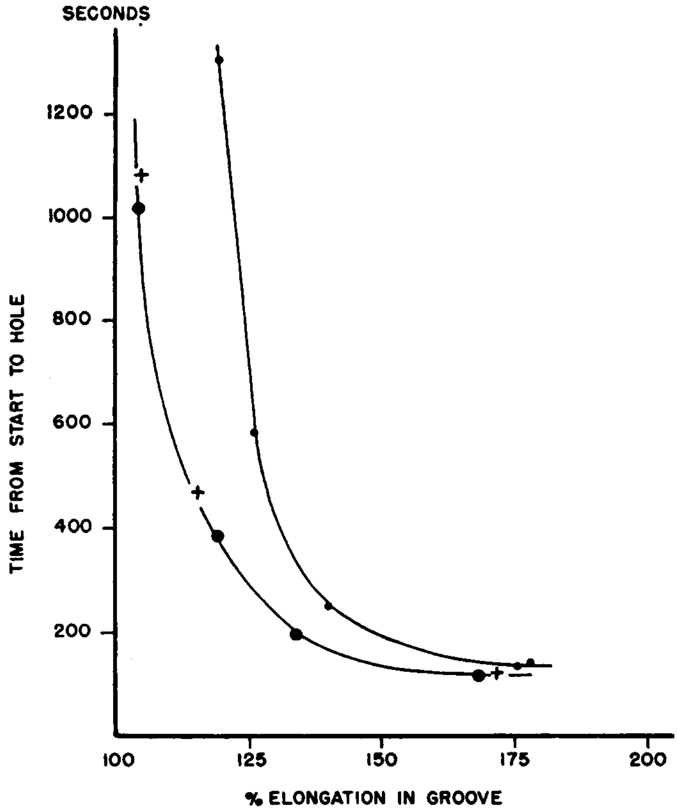


Fig. 9. Time for a pierced sample to develop a hole, measured on one stock at three different curing times (the plateau at the optimum cure is apparent): (•) 30 min. at 45°; (+) 45 min. at 45°; (●) 60 min. at 45°.

position, the switch pushes against a fixed bar, and the machine is shut off automatically, making it possible to let it run unattended. The length of time between the start of an experiment and the automatic shut-off, in combination with the length of the stroke gives an impression of the flex resistance of a stock. As this measurement does not involve the accuracy of the camera, we call it the crude lifetime. In SBR the crude lifetimes do not scatter too badly because by far the largest portion, as explained before, is taken up by the induction period. This is reproducible, particularly at the longer strokes. In Figure 8 the inverse of the crude lifetime is plotted against the speed of the machine, and this quantity is seen to be of little or no importance. In all cases the sample failed after about 3000 cycles. The stroke length was 0.5 in.

The more classic type of failure occurs in a sample that has been pierced, as in the DeMattia test. Here again there are several forms to be considered. One of these is analogous to one already encountered in spontaneous cracking, namely, the moment when the crack growing out of the puncture reaches the back of the sample, forming a round hole: The time to this event is measured from the start of the experiment. This length of time gives the best measurement we have been able to make, consistently yielding curves with very little scatter.

In Figure 9 we have plotted times from start to hole against per cent maximum elongation in the groove, varied by varying the stroke. In Figure 10 we have combined variations in stroke length (0.2, 0.3, and 0.5

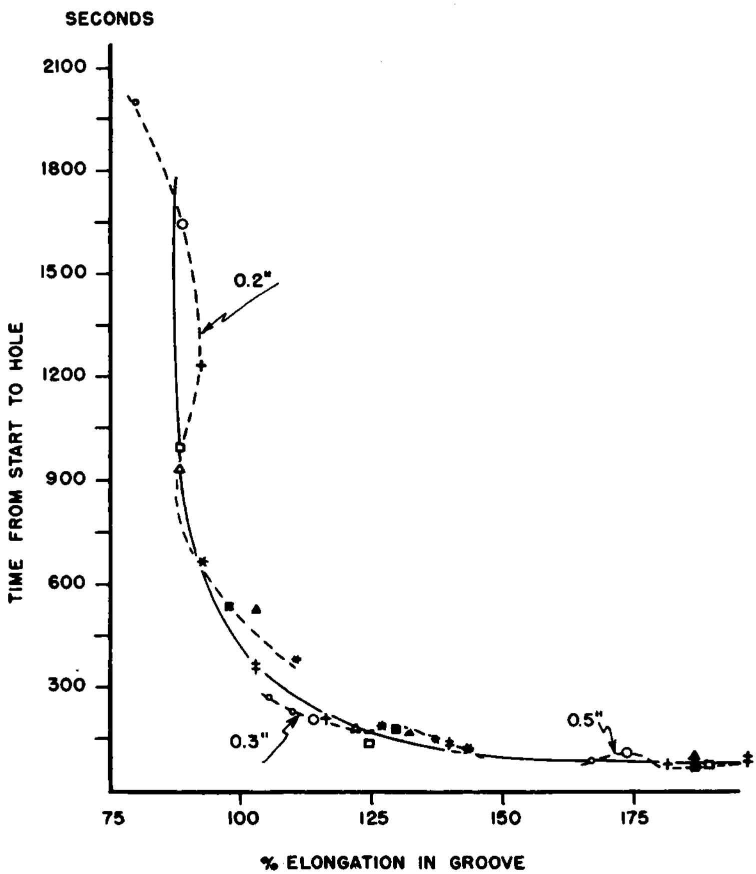


Fig. 10. Penetration times at varying loads and stroke length of pierced samples. In each segment the load increases in steps of $^1/_2$ kg., starting at 1 kg.

in.) with variations in load. In a first approximation all data could be covered by one master curve, similar to the curves in Figure 9. Apparently, the cut growth is to a large extent determined by the maximum elongation, no matter how this elongation is obtained. As the elongation is determined by the length of the stroke and the equilibrium position of the lower jaw, this shows that the hysteretic and the elastic force are equivalent in their effect on cut growth, approximately.

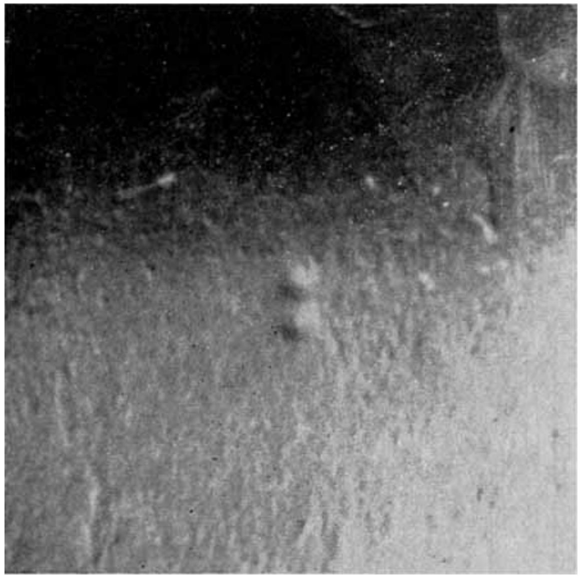


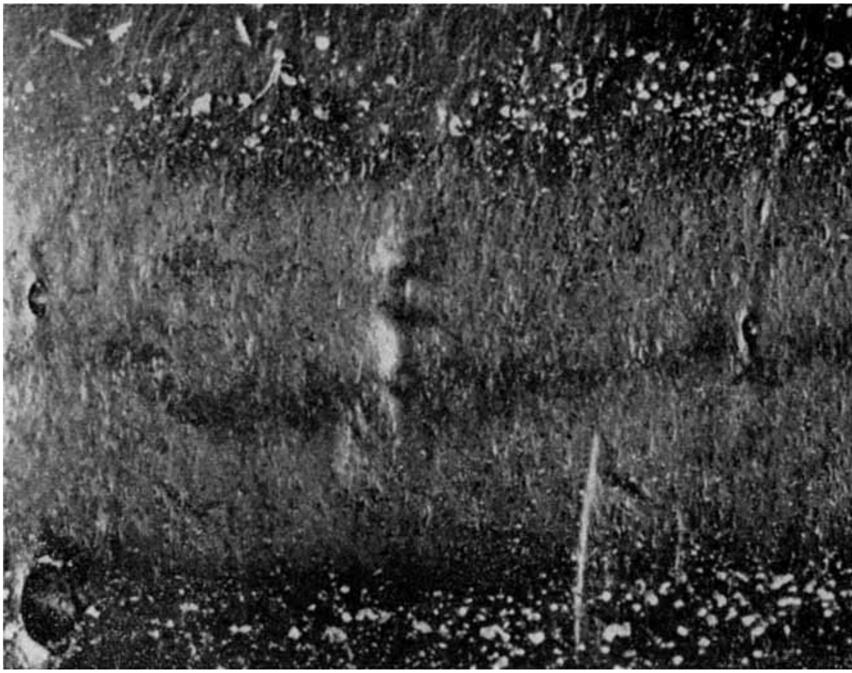
Fig. 11. Double flaw. This twin, or dumbbell, type is quite common.

It still remains to be determined which type of failure correlates with the practical behavior of the stock. We have found correlation between the type of failure in Figure 9 in SBR tread stocks and the severity of cracking of tires manufactured with those stocks, that cracked during auxiliary road testing in Texas. We also have found a substantial difference in crack initiation between stocks that had been very carefully processed and similar stocks that had been mixed less carefully, though not unreasonably so.

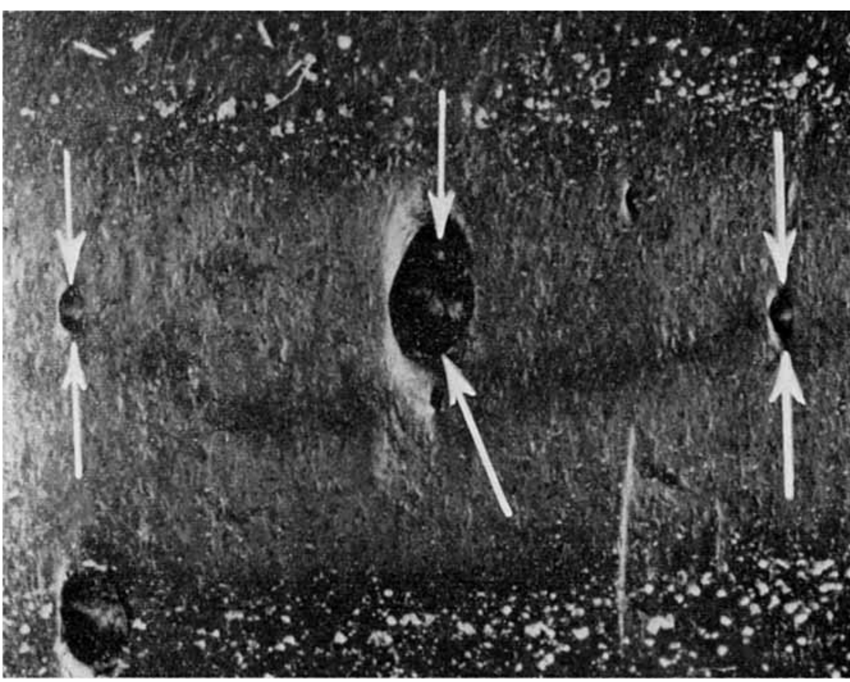
Concerning the most immediate causes of cracking, we may note that cracking does not necessarily start in the surface. Subsurface flaws became visible through flexing. At the outset the surface was smooth. Flexing, in this and all other photographs, was done at 20 cycles/second. All magnifications are 12×. Stocks are Dicup-cured H.A.F. Hevea.

A sizeable cavity forms under the surface and opens up suddenly. There is a 1-min. interval between photographs 12(*a*) and 12(*b*). The time lapse between 13(*a*), 3(*b*), and 13(*c*) was 10 sec. We here seem to have caught the twin character of the original flaw in the way the cavity broke.

More often than not in these cases the original inhomogeneity may be shown to be of a polymeric nature rather than to consist of inelastic foreign matter. In Figure 14 (*a*) through (*d*), a crack opens up showing a core or bridge of elastic material connecting the opposite walls of the crack. The bridge stretches until it breaks, and upon retraction leaves two small protrusions, indicated by arrows. Close inspection of Figure 12(*b*) shows these protrusions in a number of cracks. One is not always fortunate



(*a*)

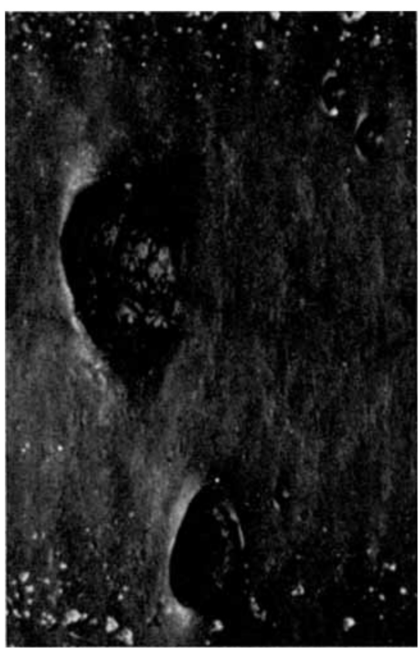


(*b*)

Fig. 12. A subsurface hole opening up: two pictures taken 1 min. apart.

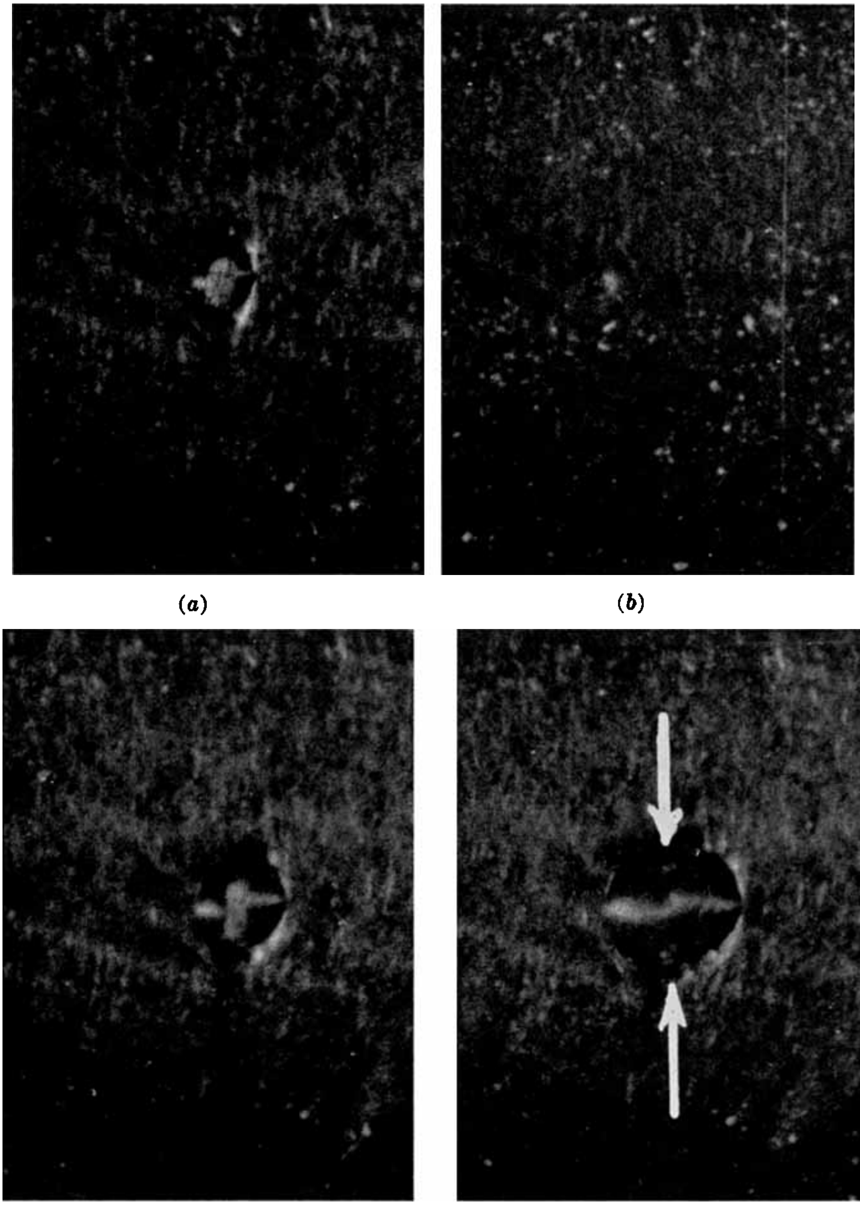
(a)

(b)



(c)

Fig. 13. Pictures taken 10 sec. apart, showing the twin character of the flaw in the way it opens up.



(a) (b) (c) (d)

Fig. 14. These photographs demonstrate the polymeric nature of the flaw by its elasticity.

enough to catch the bridge in the act of breaking, owing to the length of the time lapse between frames. In two years of operation, we have photographed only a few cases such as Figure 14. The indicated protrusions have been noticed frequently.

We wish to thank Dr. F. W. Boggs for his interest and valuable suggestions, Dr. D. R. Elliott for his help in constructing the synchronizing circuit, and Mr. G. Bastedo for running the machine.

Synopsis

Accurate measurement of several types of fatigue failure in polymers was obtained with a flexing machine equipped with an automatic camera. The technique is described at length. Observations made include that an antiozonant interferes with crack initiation, that a crack may well start under the surface, and that in the growth of a crack the elastic force is equivalent to the hysteretic force. Several photographs show aspects of crack initiation.

Résumé

On obtient une mesure précise de divers types de rupture à la fatigue dans les polymères en employant une machine à flexion équipée avec une caméra automatique. On décrit la technique en détail. Les observations faites concluent qu'un antiozonant interfère avec l'initiation par rupture et que la rupture peut débuter sous la surface, et que lors de la croissance de la rupture, la force élastique égale la force d'hystérésis. Divers clichés montrent les aspects de l'initiation de rupture.

Zusammenfassung

Genaue Messung einiger Typen von Ermüdungsschädigung bei Polymeren wurde mit Benützung einer mit einer automatischen Kamera ausgestatteten Biegemaschiene durchgeführt. Das Verfahren wird ausführlich beschrieben. Es wurde unter anderem gefunden, dass Antiozonmittel die Rissbildung hemmen, dass ein Riss unterhalb der Oberfläche beginnen kann und dass beim Risswachstum die elastische Kraft der Hysteresiskraft gleichwertig ist. Mehrere Aufnahmen zeigen das Aussehen des Rissbeginnes.

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