JOURNAL OF APPLIED POLYMER SCIENCE VOL. VI, ISSUE NO. 23, PAGES 497-502 (1962)

Some Chemical Effects in Fatigue Cracking of Vulcanized Rubbers

A. N. GENT*

The National Rubber Producers' Research Association, Welwyn Garden City, Herts., England

I. INTRODUCTION

A recent study[1] of the failure of rubber strips due to repeated extension—fatigue failure—has indicated that the process is caused by the growth by cumulative tearing steps of a small flaw, present initially, until catastrophic failure occurs. This simple tearing theory is remarkably successful in predicting quantitatively the fatigue life of strips of soft vulcanized rubbers over a wide range of extensions, in terms of the cut-growth resistance of the rubber and the size of the initial flaw. The former property is readily determined experimentally,[1,2] while the latter is deduced by extrapolation from the effects of artificial flaws to be of the order of 10^{-3} cm. for test pieces produced by die-stamping from thin sheets—a not unreasonable value. The success of this "mechanical" theory of fatigue failure suggests that chemical processes play little part. That some chemical mechanism is involved, however, is suggested by the beneficial effect of including certain additives[3-5] known as antiflex antioxidants, and of conducting fatigue experiments in an inert atmosphere.[3,6]

In order to examine the influence of the surrounding atmosphere on the fatigue life of rubber strips under repeated tensile strains, the equipment described in Section II below was constructed. With it, tests were carried out on some soft natural rubber vulcanizates containing a variety of additives, and on one butadiene-styrene vulcanizate. The experimental results are described in Section III.

It must be emphasized that no serious increase in temperature of the test pieces occurred in the present measurements, in contrast to some earlier studies of fatigue under repeated deformations. This was due to the small bulk, relatively large surface area, and low hysteresis of the test pieces employed. Although no measurements were made of the temperature rise, an overestimate may be obtained by equating the energy dissipated in the rubber (assumed to be 10% of the maximum stored energy) to the direct radiation loss by Stefan's Law. The values calculated in this way were only 14°C. for repeated extensions of 200%, and 27°C. at 300%, the highest extension employed. Conduction and convection effects would diminish these still further, so that the actual temperature rises would be quite small.

* Present address: The Institute of Rubber Research, University of Akron, Akron, Ohio.

II. EXPERIMENTAL

Test Pieces

The test pieces used were dumbbell-shaped with a parallel-sided central region about 1.4 cm. long and 0.28 cm. wide. They were die-stamped from sheets of vulcanized rubber about 0.075 cm. thick, immediately before testing. The mix formulations and vulcanization conditions employed in preparing the sheets are given in the Appendix.

In some cases additives were incorporated into the vulcanized sheets by swelling the sheets to equilibrium with a 1% solution of the additive in diethyl ether and then allowing the ether to evaporate, the last traces being removed by pumping. The amount of material incorporated was estimated from the gain in weight relative to a control sample.

Mechanical Arrangement

The freshly die-stamped test piece was mounted in the apparatus shown in Figure 1. The large ends were secured in two grips, one (the upper one in the figure) attached to a U-shaped spring that permitted a small amount of movement of the grip, under the action of a tensile force in the specimen, before further motion was prevented by a stop. This limited travel of the "stationary" grip was employed in operating an automatic failure indicator, to be described later.

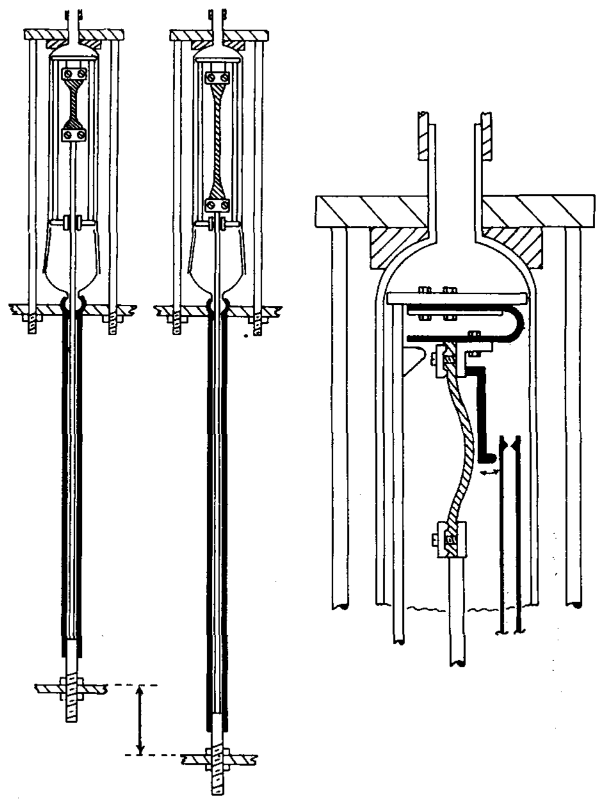

Fig. 1. Sketch of apparatus: (*a*) test piece in the unstretched state, (*b*) test piece stretched, (*c*) detail of failure-indicating mechanism.

The other test-piece grip (the lower one in the figure) was attached by means of a long rod to a reciprocating carriage driven by an eccentrically mounted circular cam, not shown in the figure. The degree of eccentricity, and hence the throw of the carriage and the attached rod and grip, could be adjusted in the range 0 to 10 cm. The cam was driven at a constant speed of 100 rpm, and thus the central region of the test piece was subjected to repeated simple extensions at this frequency.

The minimum extension of the test piece was always zero; indeed, the test piece adopted a bent configuration, the bending strains being negligibly small. The maximum extension was made to vary between 150 and 300% by adjusting both the degree of eccentricity of the cam and the total length of the test piece secured between the grips. Fine adjustments were made by varying the length of rod between the carriage and the grip, by means of a pair of locking nuts on the threaded rod. The value of the maximum extension was determined by measuring in the stretched state the separation between two ink marks placed on the central region of the test piece in the unstretched state at an axial distance of 1.27 cm.

Method of Sealing

The test piece was surrounded by a glass vessel having outlet tubes at either end. Through one, the upper one in the figure, the vessel could be evacuated to a pressure of about 10^{-2} mm. of mercury by means of a vacuum pump. The reciprocating rod passed through the other outlet tube and was connected to it by means of a special flexible seal. This consisted of a long rubber tube surrounding the rod, fastened at one end to the outlet tube of the glass vessel, and at the other to the rod, as shown in the figure. The rubber tube was about 45 cm. in length, so that the reciprocating motion of the rod imposed extensions of only about 20% or less. This is much smaller than the extensions imposed on the test pieces, and fatigue failure of the rubber tube was not encountered during the entire test series, involving several million extensions. To obtain the maximum fatigue life for the tube, it was assembled with an initial extension of about 10% so that it did not return to the undeformed state at any time.[7]

Automatic Failure Indicator

The small movement of the "stationary" grip as the test piece was extended closed a pair of post-office relay contacts, as shown in the figure. Electrical leads from the contacts passed through the wall of the glass vessel, by means of tungsten–glass seals, to an external indicator. This consisted of a lightly sprung metal stylus resting on a strip of Teledeltos electrically sensitive recording paper,[8] fastened to the circumference of a metal drum. A transformer supplied 60 v. across the paper, through the contacts and a current-limiting resistor of 10 kohm. The drum was rotated by a clock mechanism so that the paper moved under the stylus at a speed of about 0.1 mm./min. At each closure of the contacts, therefore, a black spot was formed on the recording paper, the spots merging at the frequency of extension employed to yield a continuous trace, each millimeter corresponding to about 11 min., i.e., to about 1100 extensions of the test piece.

When the test piece eventually broke, the contacts ceased to close on each movement of the moving grip, and the recorder trace was therefore ended. Thus, the number of extensions before failure occurred was determined from the length of the trace on the recording paper.

III. EXPERIMENTAL RESULTS

The Failure Process

Toward the end of the life, the fatigue crack which would eventually sever the test piece reached a visible size. It generally grew inwards from one of the die-stamped edges, indicating that it had originated as a small flaw in these cut surfaces. Occasionally, however, it appeared in one of the major surfaces of the test piece. The flaws produced in the process of die-stamping thus seem to be somewhat more severe, but not much more, than those produced in moulded surfaces.

The experimental scatter in the measured fatigue lives was surprisingly small. The coefficient of variation was calculated for 18 replicate tests in air, and 11 *in vacuo*, for vulcanizate A subjected to extensions of 200%. The values obtained were 24 and 21%, respectively.

In the following sections, the mean value of four or more replicate tests is quoted without qualification. The total range of such measurements was generally ±30% of the mean value. When a smaller number of tests was made, or a greater spread of results was encountered, this is indicated.

Effect of the Test Atmosphere

A standard natural rubber vulcanizate A was examined under repeated extensions of 200%, in four different atmospheres. The average lives in air and in cylinder oxygen at a pressure of 760 mm. of mercury were closely similar: 10.4 and 11.4 kc., respectively. The life *in vacuo* was much greater, 102 kc. In cylinder nitrogen, let into the apparatus after prolonged evacuation to remove residual oxygen, it was 55.5 kc.; presumably, a small proportion of oxygen is present in the nitrogen and somewhat reduces the fatigue life.

It is clear that the atmosphere has a striking influence on the fatigue life; indeed, the quite moderate vacuum used in these experiments has resulted in a tenfold improvement.

A limited number of measurements was carried out with test pieces of a vulcanizate C of a butadiene–styrene copolymer (SBR) subjected to repeated extensions of 250% in air and *in vacuo*. The fatigue lives were far less reproducible for this material, the results covering a range of somewhat more than ten to one in 15 replicate measurements in each atmosphere. However, the average life *in vacuo*, 50.5 kc., was about five times that in air, 11.5 kc., so that a highly significant influence of the test atmosphere seems to exist. Further measurements and detailed analysis would be necessary to compare the effect quantitatively with that found for the natural rubber vulcanizate; the present observations merely suggest that they are of a similar order.

Effect of Degree of Extension

The average fatigue lives for vulcanizate A at several extensions in air and *in vacuo* are given in Table I. The relative improvement in fatigue life due to conducting the experiments *in vacuo* is evidently greater at low extensions than at high ones. At 150% extension, for example, the life is increased more than tenfold, whereas at 300% it is only about five times the life in air. The contribution to fatigue crack growth due to mechanical rupture would be expected to become the major component at large extensions, so that the diminishing effect of the surrounding atmosphere is not unexpected.

TABLE I
Fatigue Lives of Two Natural Rubber Vulcanizates A and B, in Air (N_a) and *in Vacuo* (N_v)

	Max. extension, %			
	150	200	230	300
	Vulcanizate A			
N_a, kc.	32.7	10.4	8.0	3.5
N_v, kc.	402[a]	102	66.5[a]	16.6
Stored energy, W, erg./cm.^{3} × 10^6	11.2	18.5	23 8	39 0
W^2N_a, erg.^{2}/cm.^{6} × 10^{18}	4.1	3.6	4.5	5.3
W^2N_v, erg.^{2}/cm.^{6} × 10^{18}	50.5	35	38	25
	Vulcanizate B			
N_a, kc.	132	37.1	23.1	9.8
N_v, kc.	462[a]	118	80.7	19.0

[a] Average of two results only.

The fatigue lives in air satisfy the relation recently derived[1] for the dependence of the life N upon the degree of extension for natural rubber vulcanizates. It has been shown that the life is inversely proportional to the square of the maximum elastically stored energy W per unit volume of the test piece, to a first approximation. The values of W obtained from the load–extension relation in simple extension are given in Table I for each extension, together with the values of the product W^2N. They are seen to be substantially constant for the tests in air. Because of the differing effect of the atmosphere at different extensions, however, the values of W^2N for the tests *in vacuo* depart correspondingly from constancy.

Effect of Additives

The average fatigue lives in air and *in vacuo* for vulcanizate B at several extensions are included in Table I. This vulcanizate is similar to A, with the addition of 1% by weight of phenyl-β-naphthylamine (PBN), a widely used antioxidant, to the mix formulation. The fatigue lives in air are markedly increased at all extensions, being three to four times larger than for vulcanizate A. *In vacuo,* however, the lives of the two materials are closely similar.

A number of other additives have also been examined. Small quantities of them were added to test pieces of vulcanizate A by swelling with dilute solutions in diethyl ether and allowing the solvent to evaporate. The fatigue lives were then measured in air and *in vacuo,* under repeated extensions of 200%. The results are listed in Table II.

TABLE II
Effect of Additives on Fatigue Life of Vulcanizate A in Air (N_a) and *in Vacuo* (N_v), under Extensions of 200%

Additive	Wt. addn., %	N_a, kc.	N_v, kc.
—	—	9.4	100
Phenyl-β-naphthylamine (PBN)	2	33.6[a]	120[a]
N-Isopropyl-*N*′-phenyl-*p*-phenylenediamine (IPPD)	1	41.2	100[a]
N-Cyclohexyl-*N*′-phenyl-*p*-phenylenediamine (CPPD)	1–2	37.6	87.5
Thio-β-naphthol	2–6	32.4	72.5
Trinitrobenzene	2	16.5	101[a]

[a] Average of two results only.

A comparison of the values given in Table II for the control samples, and those with PBN incorporated, with the corresponding values in Table I shows that the swelling process did not appreciably affect the subsequent fatigue behavior.

The additives increased the average fatigue lives in air by considerable amounts. The well-known "antiflex-antioxidants," IPPD and CPPD, seemed slightly more efficient than PBN and the radical acceptor, thio-β-naphthol, but lives more than three times that of the control test pieces were obtained with all these additives. The other radical acceptor examined, trinitrobenzene, showed a much smaller effect.

The fatigue lives *in vacuo* were not greatly affected by the incorporation of any of the materials. The antioxidants and trinitrobenzene did not have any significant effect, while thio-β-naphthol appeared to cause a small, but probably significant, decrease in the fatigue life.

Possible Forms for the Oxidation Process

The results reported above indicate that (*a*) an oxidative process forms a substantial part of fatigue failure under the present experimental conditions, and (*b*) it may be partially suppressed by suitable antioxidants and radical acceptors.

Two forms for the oxidative reaction may be envisaged. The first is oxidative deterioration in the neighborhood of the fatigue crack tip, possibly initiated by the reactive molecular endgroups formed by mechanical rupture. This would effectively contribute to crack growth, because the degraded rubber would have low strength and would rupture easily on subsequent deformation.

The second mechanism arises from the possibility that some degree of recombination of the reactive molecular endgroups occurs when the test piece is relaxed. The proposed oxidation reaction in this case would consist of the consummation of rupture by reaction of oxygen with the endgroups to stabilize them. Thus, the first process would yield *additional* crack growth, while the second would merely permit the effective development of mechanical rupture.

It seems possible to distinguish between these alternative mechanisms by studying the effect of oxidation inhibitors and radical acceptors, respectively. Unfortunately, the additives do not readily separate into these categories, which may, indeed, be coextensive to some degree, but the action to be expected of "active" materials would be quite different in the two cases. On the first hypothesis, oxidation inhibitors would confer improved fatigue resistance in air, but not, of course, *in vacuo.* This is precisely the behavior found with the majority of the additives studied, so that the first hypothesis is strongly supported.

On the second hypothesis, suitable radical acceptors would be expected to act in the same manner as oxygen, and the fatigue life *in vacuo* would therefore be seriously diminished in their presence. Since oxygen is particularly efficient, their addition would not be expected to cause appreciable further reduction of the fatigue lives observed in air. None of the additives, including the recognized radical acceptors thio-β-naphthol and trinitrobenzene, caused a reduction in the fatigue life in any way comparable to that caused by oxygen (in air), so that the second hypothesis seems unlikely to be valid.

Oxygen is known, however, to be a particularly efficient radical acceptor[9]; moreover, the vulcanizate employed in these experiments might well have contained active materials already, either in the form of impurities in the raw rubber or arising from the vulcanization reagents. The relative inefficiency of additional materials *in vacuo* is not completely convincing, therefore, and the possibility that some recombination occurs *in vacuo*, and less in air, cannot be altogether discounted. However, the present results make it appear improbable.

Effect of Ultraviolet Irradiation

In order to examine the consequences of the presence of ozone in the test atmosphere, test pieces of the standard vulcanizate A were subjected to repeated extensions of 200% while they were simultaneously illuminated by an ultraviolet lamp[10] held about 25 cm. away. The ultraviolet irradiation of air is known to generate ozone, which would be expected to accelerate crack growth and result in premature failure. No such effect, of course, would be expected *in vacuo.*

TABLE III
Effect of Ultraviolet Irradiation on Fatigue Life of Vulcanizate A in Air (N_a) and *in vacuo* (N_v), under Extensions of 200%

Illumination	N_a, kc.	N_v, kc.
None	14.9	98
During fatigue test	18.6	197
Before fatigue test		
1 hr. at 50% extension	—	151[a]
2 hr. in unstrained state	13.8	84[a]

[a] Average of two results only.

The average fatigue lives in air and *in vacuo* are given in Table III. They show a surprising *increase* in air and, even more so, *in vacuo*, so that some other process is clearly present.

Further experiments were carried out in which the test pieces were illuminated for 1 hr. at 50% extension, and for 2 hr. in the unstrained state. The fatigue lives were then determined in the normal way, without illumination. The results are included in Table III.

Irradiation in the stretched state *in vacuo* was found to prolong the subsequent fatigue life, whereas irradiation in the unstretched state was found to shorten it somewhat. These results are consistent with a further crosslinking of the test piece under the ultraviolet irradiation,[11] because the stored elastic energy associated with a given extension will be increased by crosslinking in the unstrained state and decreased by crosslinking in the strained state, leading to shorter and longer fatigue lives respectively.

The effect of irradiation in the unstretched state in air was small, but again consistent with further crosslinking of the test piece.

IV. DISCUSSION

The present experiments completely confirm the early work of Neal and Northam,[3] and fatigue cracking in air appears to be largely a consequence of oxidative deterioration, the direct mechanical rupture being small in comparison. The growth step in the cumulative tearing process which constitutes fatigue[1] can therefore be considered as a small rupture step accompanied by a larger growth due to oxidation. The fact that the whole growth step per cycle is governed by a simple energy criterion[1] suggests that the amount of oxidative growth is directly dependent upon, and thus a consequence of, the mechanical rupture. This does not seem improbable; indeed, the production of reactive molecular endgroups is known to be a powerful oxidation stimulus.

Eccher[12] has suggested that the oxidative process is, in fact, due to ozone present in the atmosphere. This does not appear to be the case in the present experiments (in air), for the following reason. Similar results were obtained in the laboratory atmosphere, with the test vessel containing air sealed from communication with the atmosphere, and with cylinder oxygen. The latter two procedures should have largely eliminated even the small amount of ozone present indoors. It appears, therefore, that this had a negligible effect.

Substantially higher ozone concentrations, of course, would probably have had a marked effect on the fatigue life. Attempts to demonstrate this by ultraviolet irradiation were unsuccessful, however, as has been described, due to the overriding influence of structural changes brought about by the irradiation.

This work forms part of a program of research undertaken by the Natural Rubber Producers' Research Association. The assistance of D. J. Hill in constructing the appraatus and carrying out the experiments is gratefully acknowledged.

APPENDIX

The mix formulations in parts by weight, and the vulcanization conditions employed in preparing the thin sheets from which the test pieces were cut, are given below.

	A	B	C
Natural rubber (smoked sheet)	100	100	—
Butadiene–styrene copolymer (75/25, Polysar S)	—	—	100
Zinc oxide	5	5	5
Stearic acid	2	2	2
N-Cyclohexylbenzthiazyl sulfenamide	0.6	0.6	1
Sulfur	2.5	2.5	1.75
Phenyl-β-naphthylamine	—	1	1
Vulcanization time, min. at 140°C.	40	40	50

References

1. Gent, A. N., P. B. Lindley, and A. G. Thomas, to be published.
2. Thomas, A. G., *J. Polymer Sci.*, **31**, 467 (1958).
3. Neal, A. M., and A. J. Northam, *Ind. Eng. Chem., Ind. Ed.*, **23**, 1449 (1931).
4. Crawford, R. A., *ibid.*, **26**, 931 (1934).
5. Buist, J. M., and G. E. Williams, *India Rubber World*, **124**, 320, 447, 567 (1951).
6. Winn, H., and J. R. Shelton, *Ind. Eng. Chem.*, **37**, 67 (1945).
7. Cadwell, S. M., R. A. Merrill, C. M. Sloman, and F. L. Yost, *ibid.*, *Anal. Ed.*, **12**, 19 (1940).
8. Teledeltos recording paper, Creed & Company Ltd., Croydon, England.
9. Pike, M., and W. F. Watson, *J. Polymer Sci.*, **9**, 229 (1952).
10. Low-pressure mercury vapor lamp, Type 100, Hanovia Ltd., Slough, England.
11. Dunn, J. R., J. Scanlan, and W. F. Watson, *Trans. Faraday Soc.*, **54**, 730 (1958).
12. Eccher, S., *Gomma*, **4**, 1 (1940); *Rubber Chem. Technol.*, **13**, 566 (1940).

Synopsis

An apparatus is described for studying the fatigue of rubber strips under repeated simple extensions in different atmospheres. The fatigue life is shown to be greatly increased *in vacuo* for vulcanizates of natural rubber and SBR. The effect of oxidation inhibitors and radical acceptors has been examined; they are found to prolong the life in air, but have little effect *in vacuo.* The results suggest that a substantial proportion of crack growth in air is due to oxidative deterioration of the rubber at the crack tip, probably initiated by mechanical rupture.

Résumé

On a décrit un appareil pour l'étude de l'usure des bandes de caoutchouc sous l'effet d'extensions simples répètées dans différentes atmosphères. On a démontré que le temps d'usure s'accroît fortement *sous vide* pour les vulcanisats de caoutchouc naturel et de SBR. On a examiné l'effet des inhibiteurs d'oxydation et des accepteurs de radicaux; on a trouvé qu'ils prolongent la durée de vie dans l'air libre mais qu'ils ont peu d'effet *sous vide.* Ces résultats suggèrent que la proportion substantielle d'augmentation des fissures à l'air libre est due au fait que l'oxydation détériore le caoutchouc au bout des fissures, probablement initiée par rupture mécanique.

Zusammenfassung

Es wird ein Apparat zur Untersuchung der Ermüdung von Gummistreifen bei wiederholten einfachen Dehnungen unter verschiedener Atmosphäre beschrieben. Es wird gezeigt, dass die Ermüdungszeit für Naturkautschuk und SBR *im Vakuum* stark ansteigt. Der Einfluss von Oxydationsinhibitoren und Radikalacceptoren wurde untersucht; sie verlängern die Lebensdauer in Luft, haben aber *im Vakuum* nur geringen Einfluss. Diese Resultate weisen darauf hin, dass ein wesentlicher Teil des Risswachstums in Luft auf oxydative Spaltung des Kautschuks an der Risspitze zurückzuführen ist, die vielleicht durch mechanische Spaltung eingeleitet wird.

Received March 22, 1961