

librium constant of unity, the equilibrium concentrations of B and C are 0.7 and 0.6. By taking therefore β gel as 0.7, the degree of acid reaction at gelation is $0.7 + 0.5/0.7 + 0.6 = 0.92$, as compared with 0.75 for the irreversible case.

(b) A triol A reacts with an anhydride B-C and a fatty acid F in balanced proportions. For gelation $2\alpha + 2\gamma/\beta + \lambda + \zeta = 1$ so that $\gamma = 3/4$ at gelation. In the first stage $3\alpha = \beta + \gamma$, so that the equilibrium concentration of C is $3/4$, giving an equilibrium concentration of B of $(1 - 0.75/2)$ or 0.625. If all B and F are consumed, β and ζ are 0.625 and 1 at gelation. The degree of acid reaction at gelation is, therefore, $0.75 + 0.625 + 1/0.75 + 1 = 1$, compared with 0.92 for the irreversible case.

If the anhydride is taken as a dibasic acid, then gelation will be calculated to occur at 0.85.

These calculations illustrate the considerable error likely to be introduced by neglect of reversibility and by treating phthalic anhydride as a dibasic acid.

References

1. Jonason, M., *J. Polymer Sci.*, **4**, 129 (1960).
2. Case, L. C., *J. Polymer Sci.*, **26**, 333 (1957).
3. Wekua, K., and W. Reiser, *Farbe u. Lack*, **58**, 297, 345 (1952).
4. Wekua, K., and W. Klausch, *ibid.*, **59**, 85 (1953).
5. Geitel, A. C., *J. prakt. Chem.*, **55**, 429 (1897).
6. Frost, A. A., and W. D. Schwemer, *J. Am. Chem. Soc.*, **74**, 1268 (1952).
7. McMillan, W. G., *ibid.*, **79**, 4838 (1957).
8. Schulz, G. V., *Z. physik. Chem.*, **A182**, 127 (1938).
9. Wiltshire, J. P. (unpublished work).
10. Shkolman, E. E., and I. I. Zeidler, *J. Appl. Chem. U.S.S.R.*, **23**, 79 (1950).

H. S. LILLEY

Research Department, Paints Division
Imperial Chemical Industries Ltd.
Wexham Road, Slough, Bucks, England

Received April 17, 1961

Rate of Oxidative Stress Relaxation and the Extension

A number of experimenters¹⁻³ have reported the rate of thermal oxidative stress relaxation of sulfur vulcanizates of natural rubber as independent of the extension given to the strip, up to moderately high values. Similar independence has also been reported⁴ for a sulfurless peroxide vulcanizate in photochemical aging. Some recent work of Mullins and Watson⁵ on hot mastication of unvulcanized natural rubber indicated, however, that stress markedly accelerates the oxidative scission of the rubber molecules even when inadequate to rupture the chains mechanically as during cold mastication. The lack of dependence of rate of relaxation on extension up to about 300% is important practically if stress relaxation is used to follow oxidative degradation and, since it is believed⁶ that sulfurless vulcanizates, at least, degrade by the same mechanism as the unvulcanized rubber, it appeared that a further check would be worthwhile for the case of thermal degradation of a peroxide vulcanizate.

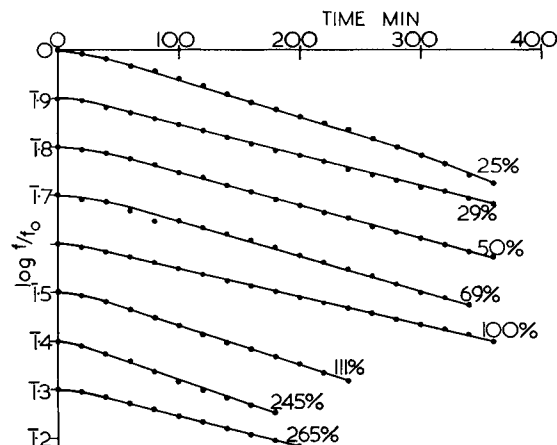


Fig. 1. Stress relaxation in air at 100°C. of a natural rubber peroxide vulcanizate at varying elongations. The figures against the curves give the corresponding extensions.

A natural rubber vulcanizate was prepared from the following recipe: highly purified rubber (U. S. Rubber Co.) 100, dicumyl peroxide 0.75, and HAF Black 5, cured 60 min. at 153°C. The cure time was extended to reduce residual peroxide and, in fact, corresponds to about 8 half-lives. Stress relaxation was carried out without extraction which, it was considered, might introduce inhomogeneity. Without the small loading of black the more highly extended strips tended to break after very brief heating.

The results of the continuous stress-relaxation measurements at 100°C. in air are given in Figure 1. There is some scatter in the observed rates but there is no indication of a trend of rate with extension over a range from 25% to 265%.

The lack of any apparent effect of stress on rate in these experiments is not necessarily in conflict with the results in hot mastication, as the elastic strains exerted during mastication, although unknown, are probably considerably higher. The strain energy for moderate to high extensions will rise at least as rapidly as the square of the extension ratio, and any contribution made by this energy to the activation energy for oxidation will rise similarly.

References

1. Tobolsky, A. V., I. B. Prettyman, and J. H. Dillon, *J. Appl. Phys.*, **15**, 380 (1944).
2. Berry, J. P., *J. Polymer Sci.*, **21**, 505 (1956).
3. Scanlan, J., and W. F. Watson, *Trans. Faraday Soc.*, **54**, 740 (1958).
4. Dunn, J. R., J. Scanlan, and W. F. Watson, *Trans. Faraday Soc.*, **54**, 730 (1958).
5. Mullins, L., and W. F. Watson, *J. Appl. Polymer Sci.*, **1**, 245 (1959).
6. Dunn, J. R., J. Scanlan, and W. F. Watson, *Trans. Faraday Soc.*, **55**, 667 (1959).

L. J. MAISEY
J. SCANLAN

Rubber and Plastics Research Association of Great Britain,
Shawbury, Shrewsbury, Shropshire, England

Received January 13, 1961