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CRYSTALLISATION AND TENSILE STRENGTH OF VULCANISED NATURAL RUBBER COMPOUNDS

by

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Crystallisation and Tensile Strength of Vulcanised Natural Rubber Compounds

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SUMMARY

The effect which changes in the degree of cross linking have on the crystallisation of stretched rubber has been studied by observing the densities of a series of peroxide-cured natural rubber compounds. It was found that at any one elongation, crystallisation first increased and then decreased with increase in the degree of cross linking. The significance of this maximum and the relation between crystallisation and tensile strength are discussed.

INTRODUCTION

It is generally accepted that the tensile strength of rubber-like materials depends critically on crystallisation. Flory's[1] investigation of the influence of the molecular weight of raw rubber on the tensile strength of the vulcanisate and the work of Gee[2] and Flory, Rabjohn and Shaffer[3] on the relation between the degree of cross-linking and the tensile strength yielded results which could be satisfactorily interpreted on this basis. However, while several authors have given estimates of the degree of crystallisation in stretched rubber,[4,5,6] it appears that the relation between crystallinity, cross-linking, and tensile strength has not hitherto been investigated systematically. The present paper has for its subject a study of this relation for a series of natural rubber compounds vulcanised with di-*tert.*-butyl peroxide. Peroxide-cured rubbers are highly suitable for physical measurements; they are probably C-C cross-linked and may thus be presumed to contain a minimum of structural irregularities. They are sufficiently transparent for flaws to be detected by inspection and are free from solid ingredients which are known to give rise to vacuoles[7] and comparatively large volume changes on stretching. This last fact is of special importance in the present investigation where a measure of the degree of crystallisation was obtained from measurements of the change of volume. The degree of cross-linking was estimated from observations of the equilibrium swelling of the compounds in benzene.

EXPERIMENTAL

Materials.

Best quality pale crepe or smooth smoked sheet was used in all experiments. The intrinsic viscosities $[\eta]$ of the rubbers in benzene solution fell in the range 5·3–5·5. This probably corresponds to a molecular weight range of 1,000,000–1,200,000.[8] The di-*tert.*-butyl peroxide was a commercial sample purified by washing with alkali, drying over sodium sulphate, and distilling under reduced pressure. A.R. benzene was used in all swelling measurements.

The compounds were vulcanised *in vacuo* by a method similar to that of Farmer and Moore.[9] For the crystallisation experiments small rings (vol. *ca.* 0·1 c.c., i.d. 1 cm.) were cut from pale crepe which had been cast into sheets, using a standard mould and heating for 15 minutes at 130°. About 12 of these rings were fitted over a uniform glass tube (o.d. 1 cm.), leaving at least $\frac{1}{8}$ in. gaps between rings, and placed in a Carius tube. The Carius tube was drawn out, connected to a vacuum line, and the system evacuated for 30 minutes. An amount of peroxide, varying from 2 to 8 per cent. on the volume of rubber, was next added from a pipette. The Carius tube was protected with a calcium chloride tube and frozen in liquid air before being reconnected to the vacuum line. After degassing the tube in the usual way by alternate freezing, pumping, and melting, the system was evacuated to 10^{-5} mm. with the peroxide frozen, and the Carius tube sealed. The rubber and peroxide were allowed to equilibrate for at least 48 hours and then cured for 6 hours at 140° C. The tertiary butyl alcohol formed in the reaction was pumped off. For the tensile measurements, pieces of smooth sheet were similarly vulcanised at 140° C., varying the amount of peroxide and the time of cure. Standard dumb-bell test pieces were cut from the vulcanisate. A few crystallisation experiments were also made with lightly degraded samples: the rubber was milled to a Mooney viscosity of about 60, corresponding to $[\eta] \simeq 2{\cdot}8$ and a molecular weight of *ca.* 500,000. The peroxide (1·5–2 per cent.) was added on the mill and the mix cured in the form of 6 × 6 × $\frac{1}{8}$ in. sheets at 160° C. The time of cure varied between 8 minutes and an hour, no precautions being taken to exclude oxygen. Rings for the measurements were then cut from the cured sheet.

Measurements of the Volume Changes.

The volume changes were measured by the method of hydrostatic weighing. The frame used, which has been described elsewhere,[7] carried 8 rings which could be stretched in pairs to elongations* ranging from 40–570 per cent. Measurements were made as follows: the frame and the unstretched rings were immersed in water and their combined weight observed on an automatic analytical balance over a period of about 15 minutes, until frame and rings had reached equilibrium with the bath. The rings were then stretched and the weight observed for 6–8 minutes, after which the rings were released and the weight again observed for several minutes. The volume change on crystallisation was calculated from the difference in weight of the stretched and unstretched states. Four values of the volume change were obtained for each elongation.

If the volume changes are to be related quantitatively to the degree of crystallisation, it is necessary to show that there are no spurious volume

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* The elongations quoted are corrected, by a method due to Mullins (private communication), to make them equivalent to the true elongations obtained, e.g. with dumb-bell specimens. If α_r is the apparent elongation of the ring, calculated on the internal diameter, and r_1 r_2 are the internal and external radii of the unstretched ring, the corrected elongation ratio, α is given by:

$$\alpha = \tfrac{1}{2}\left[\alpha_r + \left(1 + r_1 r_2^{-1}(\alpha_r^{3/2} - 1)\right)^{2/3}\right]$$

changes caused by vacuoles formed about solid impurities, or flaws when the rubber is stretched. The absence of such vacuoles was shown by observing the volume changes on stretching at elongations of 40, 115 and 200 per cent., i.e. below the crystallisation point. Owing to the small volume of rubber used the expansion could not be *measured* at these low elongations but was less than the sensitivity of the method (*ca.* 0·01 per cent.) in all cases at 40 per cent. and at 115 per cent., and less than 0·025 per cent. at 200 per cent. The expansion calculated from the stress-strain curve and the compressibility of rubber[7] is of the order of $\sim$0·01 at 100 per cent. elongation and $\sim$0·02 per cent. at 200 per cent. elongation for the type of compound used in the experiments.

The quantitative aspects of the results are also affected by irreversible changes in the rubber, such as stress relaxation and permanent set. An estimate of these was obtained by measuring the internal diameter of the rings with a travelling microscope some weeks after the completion of the experiments. This proved difficult as the edges of the rings were not very well defined and permanent set alters the shape as well as the size of the rings. However, in no case was there a change in the diameter greater than 2 per cent. and this factor was, therefore, neglected in calculating the elongations.

Variations in the temperature affect the degree of crystallisation and thus affect the results. Goppel[5] found that at 17° C. and for an elongation of 460 per cent. the degree of crystallisation changed by about 1 per cent. per degree. The present experiments were made in an insulated room in which the temperature change in the course of an afternoon was less than 1° C. and the drift during the determination of a volume-elongation curve usually considerably less. All volume-elongation curves were determined in the temperature ranges 16·5 ± 2° C.

An additional source of error is the effect of the variations in temperature on the volume of the rubber, but it follows from the consistency of the readings for the unstretched rubber that these factors do not interfere with the measurements.

The most troublesome feature of the crystallisation experiments was the time-dependence of the degree of crystallisation. Holt and McPherson[6] found that the volume of stretched rubber continued to change for months without apparently reaching equilibrium. Similar observations were made by Flory.[10] The rate of stretching is of secondary importance.[5,6] In the present experiments the final reading was taken after 6–8 minutes: the short interval was chosen in order to make the conditions compare more nearly with those obtaining in tensile tests. It is doubtful if true thermodynamic equilibrium is attainable when rubber is allowed to crystallise on stretching, and in any case, undue prolongation of the experiments was clearly undesirable for practical reasons. The procedure adopted was thus a compromise, made with the object of achieving equilibrium with respect only to the rapidly changing parameters. In practice, after 8 minutes there were no further volume changes within the sensitivity of the method at elongations above 350 per cent., and at elongations up to 200 per cent. the volume did not change after the first reading. At intermediate elongations there were indications that whereas the major portion of the density change had doubtless occurred, the volume was still changing at a rate just detectable on the balance (viz. 0·01 per cent. over 1–2 minutes).

Measurement of the Degree of Cross-linking.

For the swelling measurements a weighed sample of the rubber (*ca.* 0·5 gm.) was immersed in benzene in a tube provided with a ground glass stopper. The tube was swept out with nitrogen and kept in a thermostat at 25° C. After 4–5 days the samples were taken out, surface dried, and weighed. In all cases the samples were re-weighed after swelling for a further day and the invariable result was that the volume of benzene absorbed was reproducible to a greater extent than 1 per cent. From the ratio of the volumes of benzene and rubber, Qm, the molecular weight between cross-links, M_c, was calculated from the equation[12]:—

$$\ln\left(1 + \frac{1}{Qm}\right) - (Qm + 1)^{-1} = \mu(Q_m + 1)^{-2} + \frac{\rho_r V_o}{M_c}(Q_m + 1)^{-1/3} \quad \ldots\ldots(1)$$

The value taken for μ, the interaction constant of the system rubber-benzene, was $0{\cdot}39_5$[2] the densities of rubber, ρ_r, and benzene (required for the calculation of the molar volume of benzene, V_o) were determined as 0·917 and 0·873 at 25° C. All M_c values were corrected for soluble matter in the rubber.

Measurement of the Tensile Strength.

Tensile strength measurements were carried out on a conventional Goodbrand testing machine using standard dumb-bell test pieces, as it was found impossible to measure satisfactorily the tensile strengths of the rings used in the experiments. Unless otherwise stated, the tensile strengths refer to the cross-section at break.

RESULTS AND DISCUSSION

Volume-extension curves for the compounds investigated are given in Fig. 1. In Fig. 2 the change of volume is plotted against the degree of cross-linking for several elongations. Fig. 3 shows a graph of the tensile strength and ultimate elongation against the degree of cross-linking, and Fig. 4 relates the extrapolated volume change at break to the degree of cross-linking.

Recently, Flory, Rabjohn and Shaffer[3] have suggested that M_c-values calculated from equation 1 are erroneous, more especially for lightly cross-linked rubbers. Any such errors should, however, only affect the absolute values of M_c without invalidating the discussion which follows.

From Figs. 1 and 2 it will be seen that the volume changes first increase and then decrease with increasing degree of cross-linking, but the effect is not very large, especially at higher elongations. Initially, at any given elongation, a greater number of cross-links causes greater alignment of the chains, suppresses flow and leads to higher degrees of crystallisation. Beyond a certain degree of cross-linking, progressively greater portions of the chain will be incapable of taking part in crystallisation; this will finally lead to a decrease in the degree of crystallisation with cross-linking. We have also to consider other factors which may be responsible for the lower crystallinity of the highly cross-linked samples. Firstly, it is a well-known fact that the rate of crystallisation of unstretched rubber decreases sharply with cross-linking. Observations of the rate of change of volume indicate that this factor is probably unimportant in the present

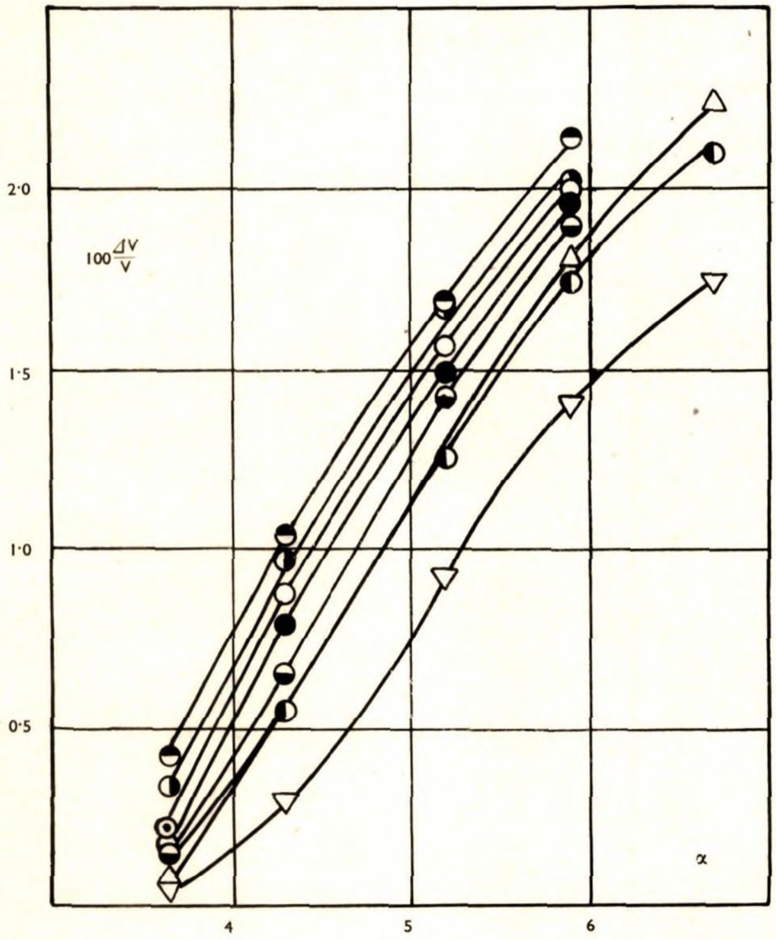

FIG. 1.

Volume-elongation curves for peroxide cured rubber samples.

Tube cures:

(a) ◐ $10^4/M_c = 0{\cdot}893$ (d) ○ $10^4/M_c = 1{\cdot}299$
(b) ◒ $10^4/M_c = 1{\cdot}031$ (e) ◓ $10^4/M_c = 1{\cdot}639$
(c) ● $10^4/M_c = 1{\cdot}163$ (f) ◑ $10^4/M_c = 1{\cdot}786$

Press cures:

(g) ▽ $10^4/M_c = 1{\cdot}020$ (h) △ $10^4/M_c = 1{\cdot}429$

experiment. Secondly, chemical interaction other than cross-linking may take place between the rubber and peroxide leading to chain scission, a reduction in the proportion of active network chains, and thence of the degree of crystallisation. That this factor is very important for lightly cross-linked compounds cured in the presence of oxygen can be seen from the data for press-cured samples included in Fig. 1. The effect is very great for the sample of $\frac{10^4}{M_c} = 1{\cdot}02$ (g), and much less for the more highly cross-linked sample of $\frac{10^4}{M_c} = 1{\cdot}43$ (h). The reduction in the degree of crystallisation is presumably due partly to the lower primary molecular weight of these compounds, and partly to further degradation due to the presence of oxygen during the cure. In the case of the vacuum cures care was taken to exclude oxygen. Whereas the possibility of slight degradation of the samples cannot of course be definitely excluded, no evidence for this was found, and its effect must have been very small. It was found impossible to prepare suitable vacuum-cured samples of high degrees of cross-linking. Highly cross-linked peroxide compounds were prone to tear (when stretched on the frame) and they frequently broke at elongations well below those found in the usual tensile test before the volume change could be measured. After many attempts data were obtained for a press-cured sample of $\frac{10^4}{M_c} = 2{\cdot}5$ at two elongations, and these are included in Figs. 2 and 4. We believe that the effects of degradation and lower primary molecular weight will be small at the

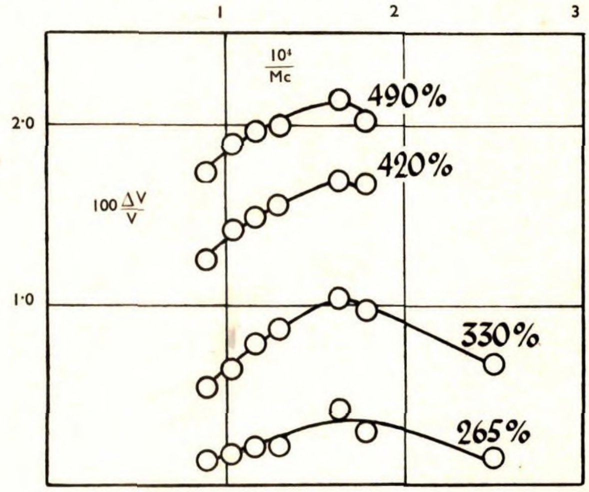

FIG. 2.

Dependence of volume change on cross-linking at 265 per cent., 330 per cent., 420 per cent. and 490 per cent. extension.

high degree of cross-linking of this sample, and that, although the values of $\frac{\Delta V}{V}$ are not strictly comparable, the error involved in their use will be small.

Finally, a factor difficult to assess is the magnitude of the expansion due to the hydrostatic component of the applied force.[7] The magnitude of this expansion cannot be predicted,[11] but it must be greater for the more highly cross-linked (high modulus) compounds. Rough calculations on the lines of those described[7] show that the effect would certainly be important, possibly up to 0·1 per cent. of the original volume at 400 per cent. elongation; there are, however, grounds for believing[11] that in the region of high extensions when the rubber is no longer isotropic, the expansion will be less than that calculated from theory. Nevertheless this uncertainty is one of the major hindrances to the precise determination of the degree of crystallisation by measurement of the volume change.

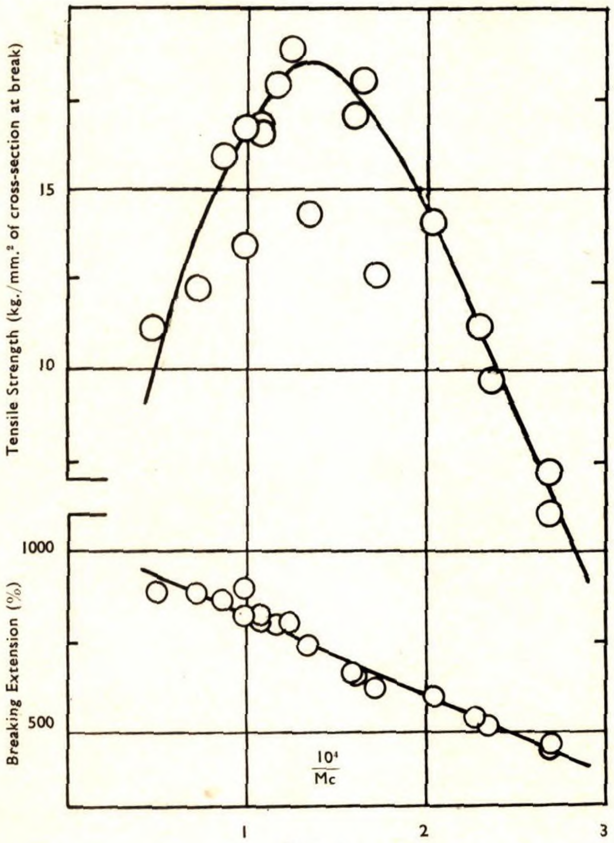

FIG. 3.

Effect of cross linking on tensile strength and ultimate elongation.

However, it is considered that the *difference* in the magnitude of the effect for the lightly and highly cross-linked samples is not sufficient to affect materially the general shape of the crystallisation curves, which are believed to be substantially correct.

The shape of the tensile strength ~ cross-linking curve and the position of the maximum in the tensile strength, are in reasonable agreement with the result of previous investigations, but the tensile strengths throughout are lower than those found by Gee.[2]

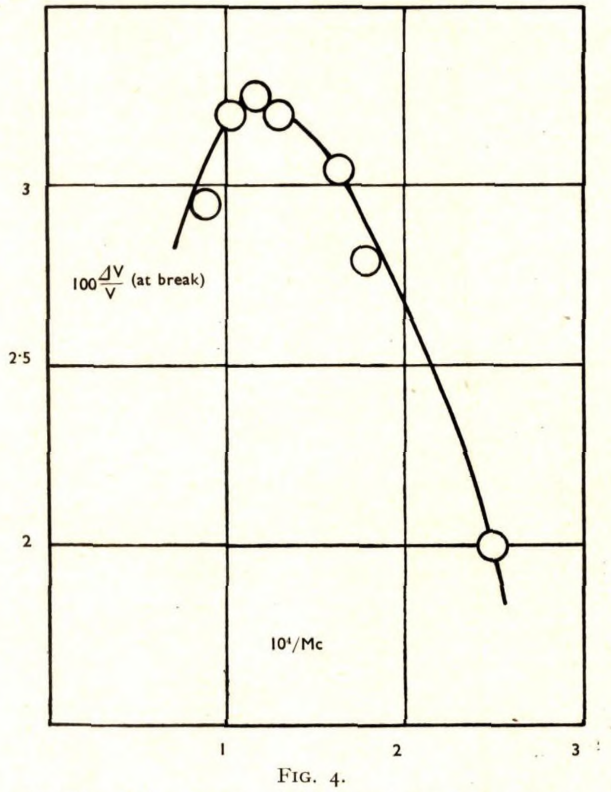

FIG. 4.
Relation between cross linking and the (extrapolated) volume change at break.

An attempt was made to correlate tensile strength with crystallisation at break. For this purpose it was necessary to extrapolate the volume-extension curves some considerable way and the uncertainty in the value of $\frac{\Delta V}{V}$ at break is correspondingly large. Consequently the relation between $\frac{\Delta V}{V}$ at break and $\frac{10^4}{M_c}$ could not be determined with any great precision. The results are shown in Fig. 4 where it is seen that the curve of $\frac{\Delta V}{V}$ at break is similar in shape to the tensile strength curve, and the maxima occur roughly in the same region showing the close interdependence of these quantities. The lower crystallisation at break and tensile strength of the lightly cross-linked samples $\left(\frac{10^4}{M_c} < 1\right)$ can at least in part be attributed to the lower slope of the $\frac{\Delta V}{V} \sim \alpha$ curves and the necessary higher elongation for incipient crystallisation of these compounds. In addition flow phenomena, which will tend to reduce both crystallisation and tensile strength must become increasingly important as the degree of cross-linking is reduced.

The main cause of the decrease in the crystallisation at break and tensile strength at high degrees of cross-linking, on the other hand, must be sought in the high modulus of highly cross-linked samples which leads to high loads and rupture at low elongations before the material has become sufficiently strengthened by crystallisation.[2] The tensile strength and crystallisation at break are further diminished by the decrease in crystallisation at high degrees of cross-linking.

Experimental data indicate that compounds breaking at elongations below *ca.* 350 per cent. must do so without crystallising to any appreciable extent. Fig. 3 shows that such compounds like many non-crystalline polymers are very weak (t.s. of *ca.* 1 kg./mm.^{2}).

In conclusion, it should be pointed out that although it is possible to explain the general tensile behaviour of the peroxide-cured samples satisfactorily in terms of crystallisation, other factors, chemical and physical, must affect the tensile strength of rubber. This is clear from the work of Gee[2] who found tensile strengths nearly 100 per cent. higher for boosted sulphur cures (containing 5 per cent. ZnO) over a comparable range of cross-linking.

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