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A Semi-empirical Theory for Deriving Isochronal Stress-strain Curves of Rubbers

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A theory has been proposed whereby isochronal stress-strain curves of rubbers may be derived by the use of a single stress relaxation curve together with a single constant rate of extension curve. Agreement between data from this theory and experimental results for unvulcanised and lightly-crosslinked rubbers is good.

The deformation behaviour of uncrosslinked and crosslinked rubbers may be represented by their stress-strain relations. The stress-strain curves normally obtained are generally not equilibrium data; in uncrosslinked rubbers, the rate of relaxation of stress may be considerably higher than in vulcanised rubbers[1]. Isochronal stress-strain relations may be used to characterise the deformation behaviour, and these relations may be derived from a series of stress relaxation experiments at various levels of strain. However, in practice this is difficult to carry out. In the case of unvulcanised rubbers, a new piece is required for each relaxation experiment, which is inconvenient and, because of possible inhomogeneities in the sheet from which the specimens are prepared, liable to inaccuracies. In principle, these isochronal stress-strain curves may also be derived from a series of constant extension stress-strain curves at different rates. A theory is proposed whereby, with a single stress relaxation curve and a single constant rate of extension curve, the isochronal stress-strain curve may be derived. These are compared with the experimentally-obtained curves for uncrosslinked and very lightly crosslinked natural rubber and a synthetic *cis*-polyisoprene.

THEORY

The problem is to deduce (approximately) the isochronal stress-strain relation from a measured constant extension rate stress-strain curve and the measured stress relaxation behaviour, assuming the latter to be strain-independent. Referring to *Figure 1*, the idea is to find the relation between the time (t_1) after beginning a stress relaxation measurement which will duplicate the stress and strain in a constant rate of extension experiment at a particular time (t_2) after beginning the stretching.

A full rigorous solution is clearly difficult, if not impossible, for a non-linear material. Even a linear material with a complicated stress relaxation behaviour will create significant problems.

Initially therefore one models the rubber by a simple spring/dashpot model *(Figure 2)* appropriate to stress relaxation[1]. Intuitively, it would be expected that, in *Figure 1*, $t_1 \simeq t_2/2$. If a relation such as this can be established, albeit approximately, then an isochronal stress-strain curve can be constructed from the constant rate experiment.

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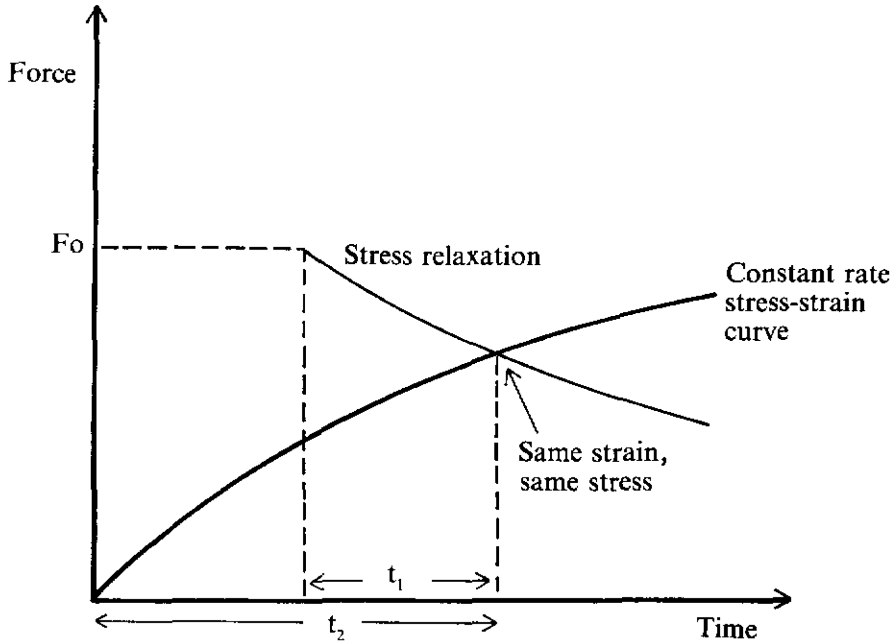
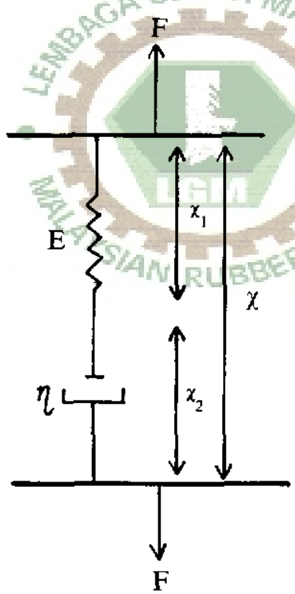


Figure 1. Schematic stress relaxation and constant rate of extension curves.



$$F = Ex_1$$
$$= \eta \frac{dx_2}{dt}$$
$$dx_1 + dx_2 = dx$$
$$\frac{dx}{dt} = v$$

Figure 2. A simple visco-elastic model.

We have *(Figure 2)* for constant stretching,

$$\frac{dx}{dt} = v = \frac{dx_1}{dt} + \frac{dx_2}{dt} \qquad \ldots 1$$

i.e.

$$v = \frac{1}{E}\frac{dF}{dt} + \frac{F}{\eta}$$

$$v - \frac{F}{\eta} = \frac{1}{E}\frac{dF}{dt}$$

$$\frac{dF}{(v - F/\eta)} = Edt$$

$$-\eta \; ln \; (v - F/\eta) = Et + \text{constant}$$

For $F = 0$, $t = 0$, giving

$$ln \; (1 - F/v\eta) = -Et/\eta \qquad \ldots 2$$

For stress relaxation, we have

$$x \doteqdot \text{constant} = x_o, \text{ say}$$

$$\therefore \quad dx_1 = -dx_2$$

$$\frac{dx_1}{dt} = -\frac{dx_2}{dt}$$

$$\frac{1}{E}\frac{dF}{dt} = -\frac{F}{\eta} \qquad \ldots 3$$

This gives $ln \; \frac{F}{F_o} = -\frac{E}{\eta}t$ ... 4

where F_o is the initial force after rapid extension to X_o

$$F_o = Ex_o \qquad \ldots 5$$

as the dashpot will not have moved at this point.

We wish to determine the relation between t_1 and t_2 in *Figure 2*. Thus we have to have the same values of F and x ($= x_o$ say) in *Equations 2, 4,* and *5* when t in *Equation 2* equals t_2 and t in *4* equals t_1.

We have

$$x_o = vt_2$$

giving

$$v = \frac{X_o}{t_2} \qquad \ldots 6$$

Then *Equation 2* becomes

$$1 - \frac{Ft_2}{x_o} = e^{-\frac{E}{\eta}t_2} \qquad \ldots 7$$

and *Equation 4* becomes, with $F_o = Ex_o$

$$\frac{F}{Ex_o} = e^{-\frac{E}{\eta}t_2} \qquad \ldots 8$$

Thus

$$1 - \frac{t_2}{\eta} \cdot E\, e^{-\frac{E}{\eta}t_1} = e^{-\frac{E}{\eta}t_2} \qquad \ldots 9$$

Writing for convenience,

$$\alpha_1 = t_1 \cdot \frac{E}{\eta}, \; \alpha_2 = t_2 \cdot \frac{E}{\eta} \qquad \ldots 10$$

Equation 9 becomes

$$1 - \alpha_2 e^{-\alpha_1} = e^{-\alpha_2}$$

$$\frac{1}{\alpha_2} - e^{-\alpha_1} = \frac{1}{2}\, e^{-\alpha_2}$$

i.e.

$$e^{-\alpha_1} = \frac{1}{2}(1 - e^{-\alpha_2}) \qquad \ldots 11$$

or

$$-\alpha_1 = ln\,(1 - e^{-\alpha_2}) - ln\,\alpha_2 \qquad \ldots 12$$

Figure 3 shows the variation of α_1/α_2 for various values of α_2. For moderate values of α^2, the ratio α_1/α_2 is, as guessed, about 0.5. As a more general linear visco-elastic material can be modelled by a series of these elements in series, the conclusion is likely to be approximately true in general, provided the experimental relaxation rate is not too high. For a non-linear material, the accuracy cannot be predicted with any certainty, but the stress, strain point during an extension reached at time t_2 after the start of the extension is likely to correspond quite closely to the stress in a relaxation measurement after time $t_2/2$ from an instantaneous stretch to the same strain.

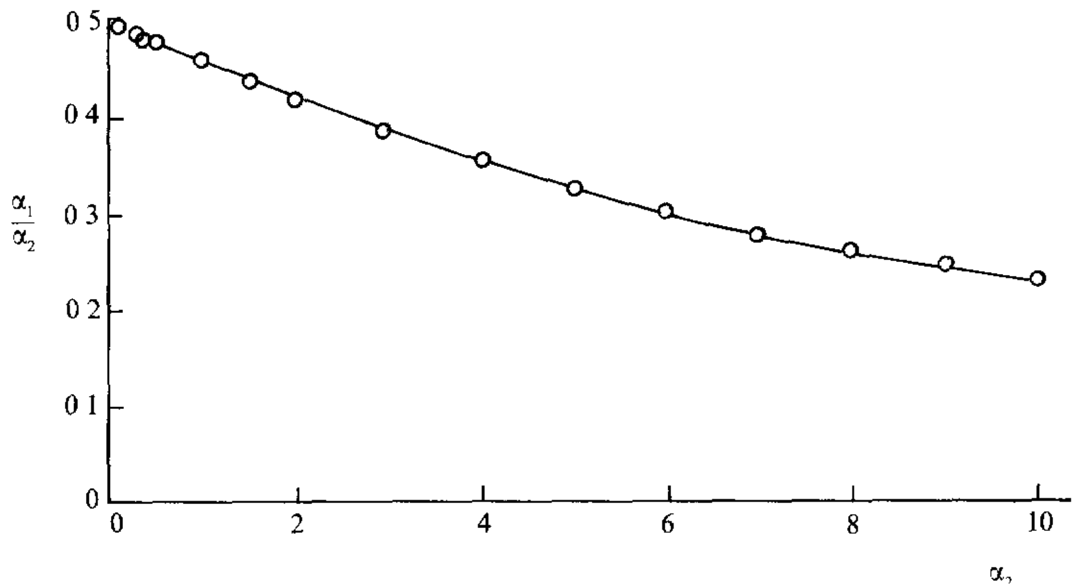


Figure 3 Variation of α_1/α_2 with α_2

EXPERIMENTAL

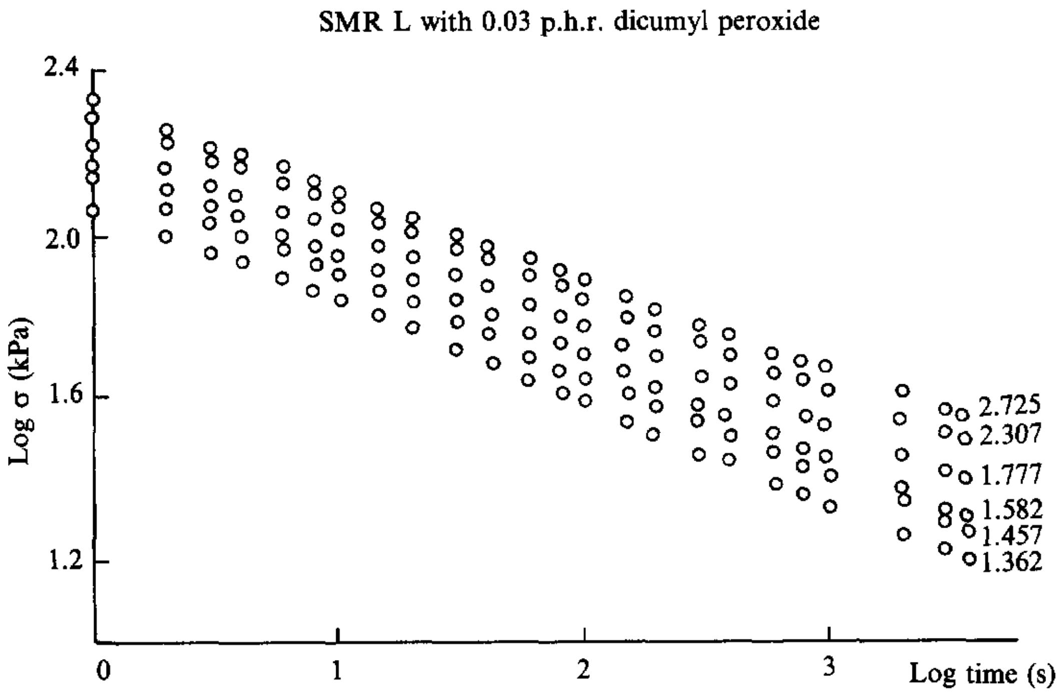
The initial objective of the above theory was the provision of a method to obtain isochronal stress-strain relations of unvulcanised rubbers which would characterise their behaviour under deformation, a method which would circumvent the necessity of performing a large number of experimental tests, which in the case of uncrosslinked rubber has experimental difficulties such as in the preparation of satisfactory test pieces As such the above theory was tested with uncrosslinked and very lightly crosslinked samples of a natural rubber (SMR L) and a synthetic polyisoprene (Natsyn 2000) Samples of SMR L and Natsyn 2200 corresponding to different levels of crosslink densities were prepared by the incorporation of dicumyl peroxide from 0 01 p h r to 0 1 p h r The samples were press-moulded between melenex sheets at 150°C for 30 min and from which samples for stress relaxation tests were die-stamped Stress relaxation tests (RRIM relaxometer) and constant rate extension tests (on a tensile tester, Instron 1122) were carried out at room temperature

RESULTS AND DISCUSSION

Figure 4 shows typical stress relaxation curves at various levels of strain for natural rubber and Natsyn 2200 The fact that these curves are parallel confirms the strain independence of the relaxation behaviour in the time-scale of the experiment, which is an essential assumption of the theory

Figure 5 shows 10-s isochronal stress-strain curves for natural rubber uncrosslinked, lightly crosslinked with 0 03 p h r and 0 06 p h r dicumyl peroxide, and isochronal curves derived using the above theory together with the constant extension curves at two different crosshead speeds The latter curves do not differ much and agreement with the experimental curve is quite good This is also the case with Natsyn 2200 *(Figure 6)* The agreement between the experimentally obtained curve at 100 s and that derived from the theory is also shown in the *Figure*

The following are some possible sources of error which may account for the discrepancy observed between the isochronal



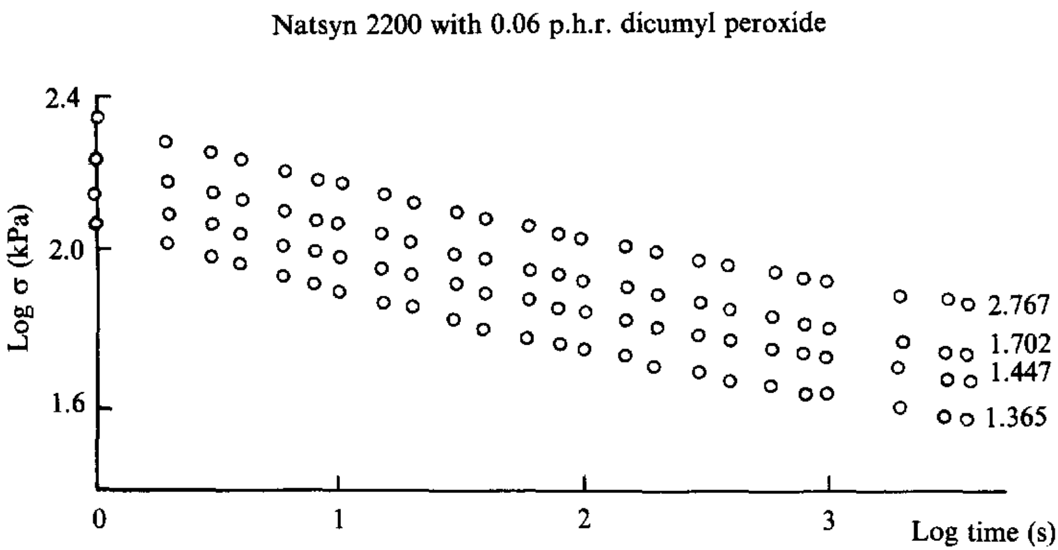


Figure 4. Stress relaxation at different strains.

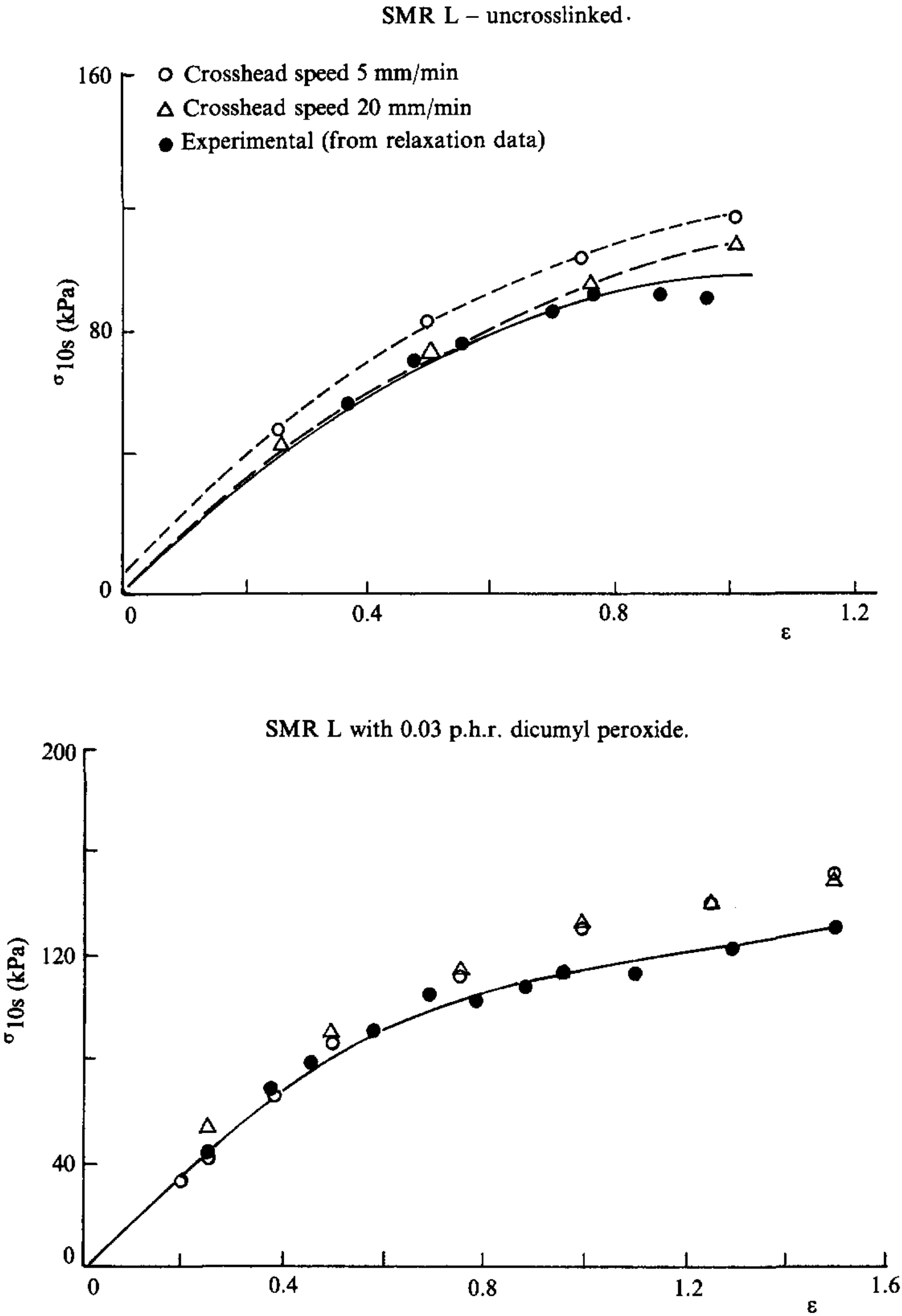


Figure 5. Comparison of 10-second isochronal stress-strain curve with that derived from theory.

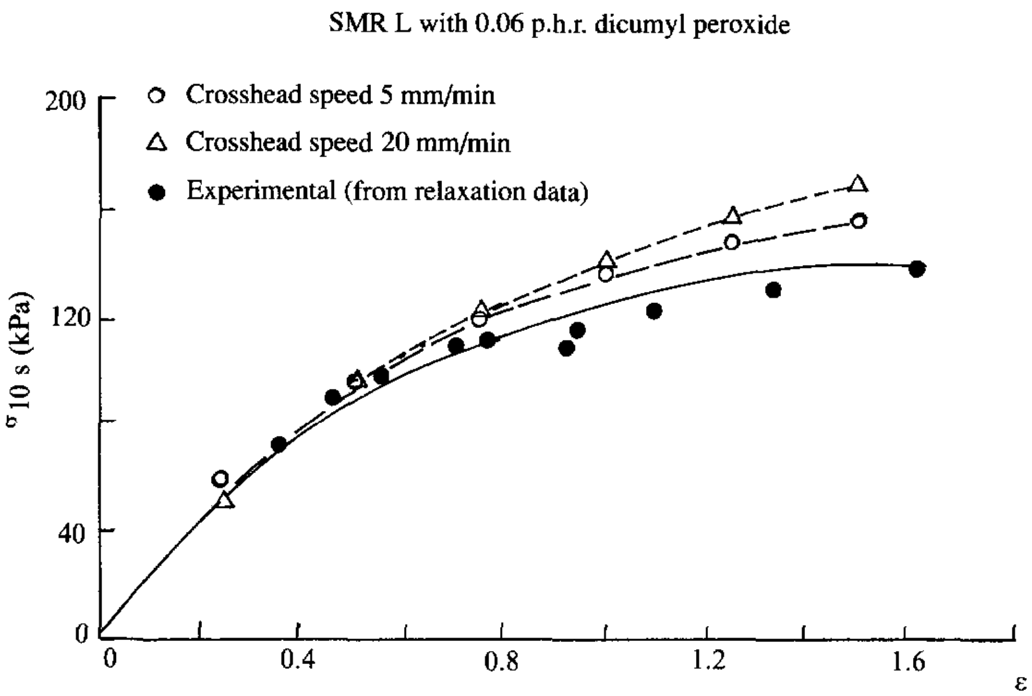


Figure 5. (Contd.) Comparison of 10-second isochronal stress-strain curve with that derived from theory.

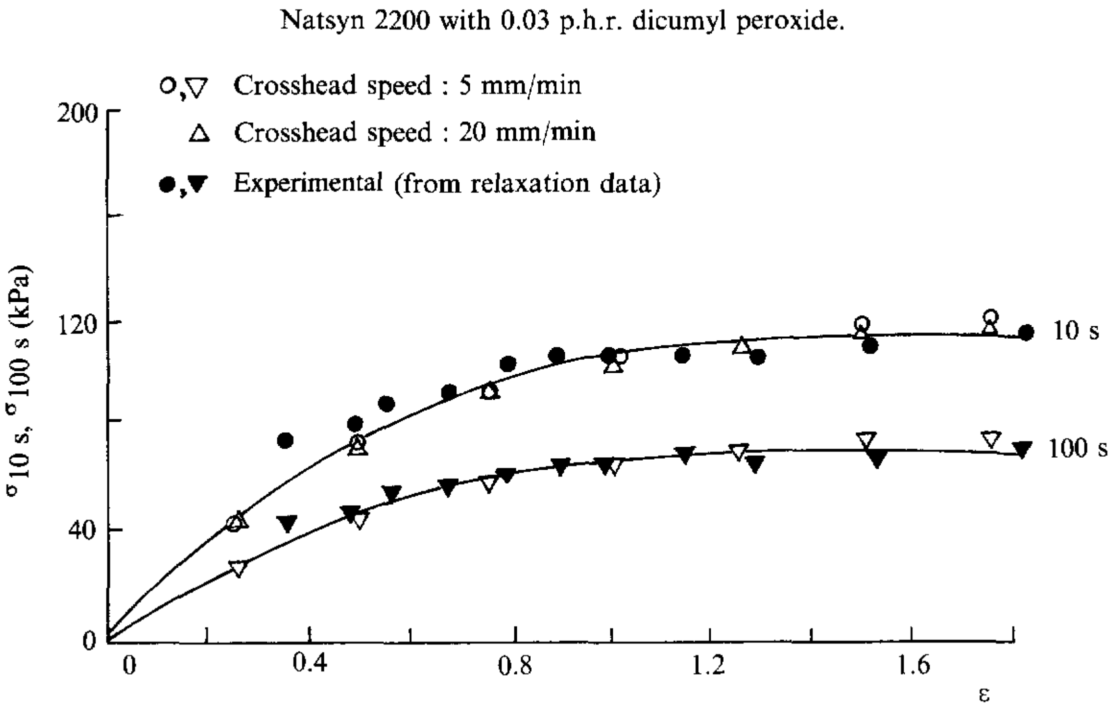


Figure 6. Comparison of 10 s and 100 s isochronal stress-strain curves with that derived from theory.

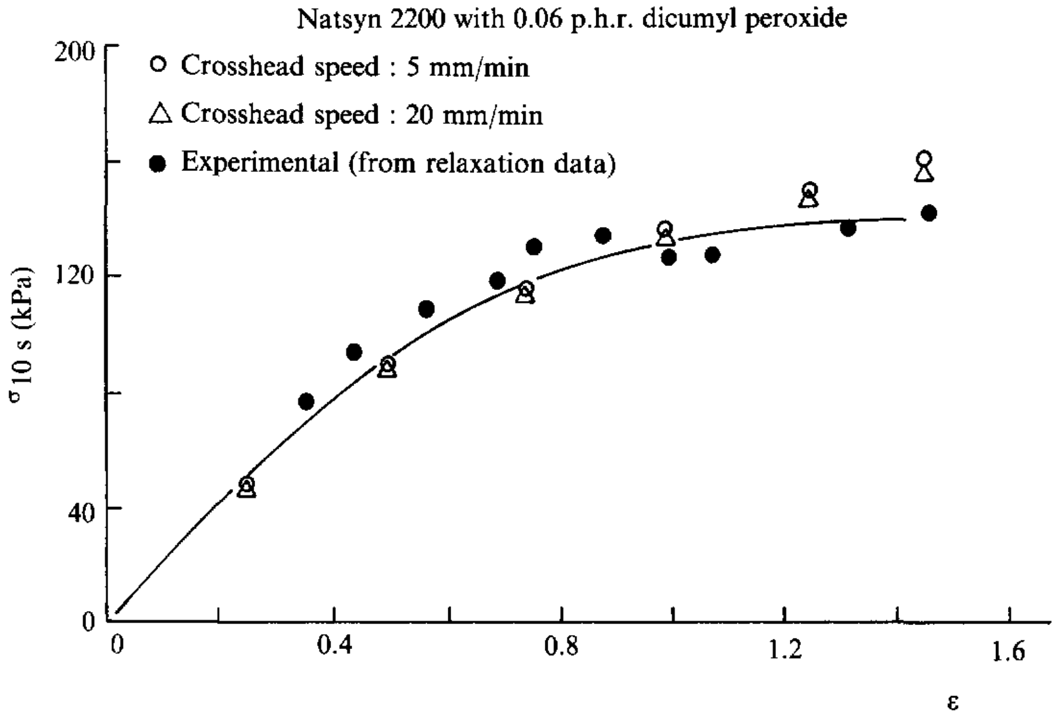


Figure 6. (Contd.) Comparison of 10 s and 100 s isochronal stress-strain curves with that derived from theory.

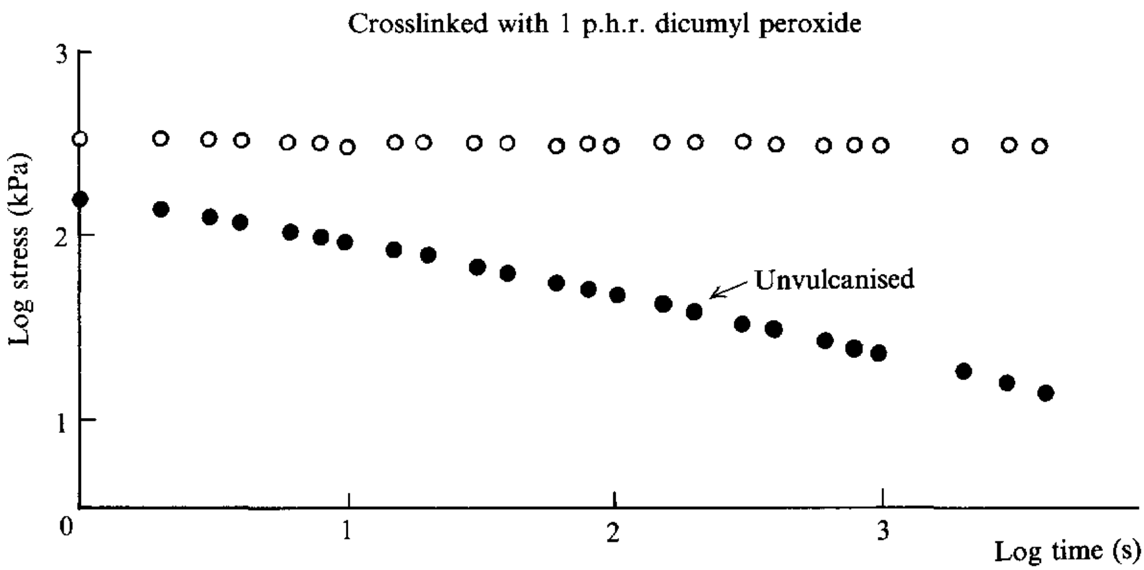


Figure 7. Relaxation of stress with time of SMR L at 50% extension.

stress-strain curves obtained from a series of stress relaxation tests and the curves derived with the above theory:

- As far as the unvulcanised material is concerned, the application of the theory may be limited by the very high rate of relaxation *(Figure 7)* where the rate of relaxation of the unvulcanised rubber is seen to be considerably higher than that crosslinked with 1 p.h.r. dicumyl peroxide.
- The assumption of $t_1 = t_2/2$ is approximately true only for moderate values α^2.
- The assumption of complete constant rate of extension in the tensile test may not have been achieved; there is some degree of non-uniformity of stretch, especially in the early stages.
- The precision of the experimentally-obtained isochronal curve which is based on a series of stress relaxation curves is inadequate; for uncrosslinked material, there may be some errors due to non-uniformity of samples.
- The use of a simple model in the derivation of the theory may not be realistic.

Notwithstanding the possible contribution of the above sources of error, the curves derived from the theory fit the experimental curves reasonably well.

CONCLUSION

A semi-empirical theory has been proposed for deriving the isochronal stress-strain curves of rubbers; this being based on a single stress relaxation measurement together with a single constant rate of extension curve. Such a procedure may be useful, for example, in the case of uncrosslinked or very lightly-crosslinked rubbers where the preparation and testing of a large number of satisfactory test samples may present a problem.

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REFERENCE

1. NIELSEN, L.E. (1962) *Mechanical Properties of Polymers*, Chap. 4. Van Nostrand Reinhold Co.