European Polymer Journal, 1971, Vol. 7, pp. 433–443. Pergamon Press. Printed in England.

DYNAMIC AND EQUILIBRIUM STUDIES OF SILICONE RUBBER VULCANIZATES

DEREK A. SMITH† and J. K. THOMAS

National College of Rubber Technology, Northern Polytechnic, Holloway, London, N.7

(*Received* 3 *July* 1970)

Abstract—Values of the modulus factor for polydimethylsiloxane/peroxide networks have been obtained by use of the Weissenberg Rheogoniometer, the Monsanto oscillating disk rheometer, and the reticulometer (swollen compression method).

At full cure, values of the viscous moduli are negligibly small and values of the elastic moduli are independent of frequency in the range $2{\cdot}5 \times 10^1$ to 1×10^{-5} cycles per second at temperatures in the range 85 to 105°. The values of elastic modulus obtained using the two dynamic methods are in good agreement with those measured by the "equilibrium" method at 25°, provided that the values are corrected to the same reference temperature.

These results support the view that fully cured silicone rubber networks exhibit an extended rubbery plateau within which they conform to the Gaussian elastic theory and are virtually non-hysteretic.

1. INTRODUCTION

THE USEFULNESS of the Monsanto oscillating disk rheometer as a control instrument in the rubber industry is widely recognized. Among the many advantages of the instrument are the speed of operation and reproducibility of results, qualities which have led several workers$^{(1-4)}$ to explore the possibility of using the instrument as a research tool for measurement of physically effective network chain density. However, it is not immediately obvious that an experimental quantity, $|G^*|$, obtained using this instrument may be used as an estimate of the equilibrium modulus factor, G_{eqm}, since $|G^*|$ embodies contributions both from the dynamic elastic (storage) and viscous (loss) moduli. In the absence of long range entanglement forces, the dynamic elastic modulus (G') might be expected to provide a better estimate of G_{eqm}. Under certain conditions, the loss modulus (G'') will be negligibly small, in which case

$$|G^*| \approx G' \approx G_{\mathrm{eqm}}.$$

The purpose of this paper is to test these approximations for well-cured polydimethylsiloxane rubber.

2. OUTLINES OF METHODS

2.1 *Weissenberg rheogoniometer*

In the Weissenberg rheogoniometer,$^{(5)}$ the specimen is contained between two plates the lower of which performs small amplitude forced sinusoidal oscillations while the upper is constrained by a torsion bar.

In the present study, the parallel plate geometry is used throughout.

If a_1 is the angular amplitude of the constrained plate and a_2 that of the plate performing forced oscillations, the amplitude ratio (a) is defined as (a_1/a_2). The phase lag of the "forced" plate behind the "constrained" plate is defined as δ.

---

† Present address: Industrial Materials Research Unit, Queen Mary College, University of London, Mile End Road, London, E1 4NS.

Walters and Kemp(6) have shown that the relationship between a and δ is

$$\frac{\exp(i\delta)}{a} = \cos(\alpha h) + S\alpha h \sin(\alpha h) \tag{1}$$

where, in terms of the elastic and viscous moduli

$$\alpha = \left(\frac{-4\pi^2 n^2\, id}{G'' - iG'}\right)^{\frac{1}{2}} \tag{2}$$

α is a fundamental parameter found to occur in the theory for oscillatory experiments for all geometries.(7–9)

S in Eqn. (1) is given by

$$S = \frac{2}{\pi d r^4 h}\left(\frac{K}{4\pi^2 n^2} - I\right) \tag{3}$$

where d is the density of specimen,
r is the radius of the parallel, circular plates,
h is the gap between the plates,
K is the restoring constant of the torsion bar,
I is the moment of inertia of the constrained plate about its axis,
n is the frequency of oscillation.

When αh is small (i.e. thick fluids) and fluid inertia is negligible, Eqn. (1) can be approximated to

$$\frac{\exp(i\delta)}{a} = 1 + \alpha^2 h^2 S. \tag{4}$$

If we write

$$C = Sh^2 d \tag{5}$$

Separating real and imaginary parts, Eqn. (4) leads to

$$G' = \frac{4\pi^2 n^2\, Ca(\cos\delta - a)}{(a^2 - 2a\cos\delta + 1)} \tag{6}$$

$$G'' = \frac{-\,4\pi^2 n^2\, Ca\sin\delta}{(a^2 - 2a\cos\delta + 1)}. \tag{7}$$

Values of the elastic and viscous moduli can thus be calculated from experimentally observed quantities, i.e. a and δ. However, as will be shown in 2.2, the Monsanto rheometer can only measure a dynamic modulus factor $|G^*|$ and so for purposes of comparison the values of G' and G'' may be converted into values of $|G^*|_w$ by use of the relationship

$$|G^*|_w = [(G')^2 + (G'')^2]^{\frac{1}{2}}.$$

2.2 *Monsanto oscillating disk rheometer*

The basic principle of the Monsanto rheometer(10) involves the oscillation of a biconical disk, embedded in a rubber specimen, which exerts a shear strain sinusoidally on the specimen. The force (stress) needed to oscillate the disk is measured as "rheometer torque".

From the experimentally observed quantities (torque and applied strain) and from considerations of the geometry of the system, Wise(11) has derived the following expressions for the elastic and viscous moduli:

$$G' = \frac{T \cos \delta'}{(A + B)\,\theta_m} \tag{8}$$

$$G'' = \frac{T \sin \delta'}{(A + B)\,\theta_m} \tag{9}$$

where δ' is the phase angle between stress and strain,
T is the observed torque,
θ_m is the applied strain.

A and B are constants obtained from the geometry of the system. In the type MP rheometer used in this study, it can be shown that

$$(A + B) = 294{\cdot}242 \text{ cm}^3.$$

Unfortunately, the phase angle, δ', is not experimentally accessible with the present rheometer. However, it is still possible to calculate values of the dynamic modulus factor, $|G^*|_m$, since

$$|G^*|_m = [(G')^2 + (G'')^2]^{\frac{1}{2}} = \left[\frac{T^2 \cos^2 \delta'}{(A + B)^2\,\theta_m{}^2} + \frac{T^2 \sin^2 \delta'}{(A + B)^2\,\theta_m{}^2}\right]^{\frac{1}{2}} \tag{10}$$

i.e.
$$|G^*|_m = \frac{T}{(A + B)\,\theta_m} \tag{11}$$

using the relationship $\sin^2 \delta' + \cos^2 \delta' = 1$. Wise has also proposed a small correction to θ_m to allow for bending of mechanical components in the rheometer

$$\theta_t = \theta_m - \beta\, T \tag{12}$$

where θ_t is the true rotor displacement, and
β is a correction factor $= 0{\cdot}0001$ radians per in. lb of torque.

Thus,

$$|G^*|_m = \frac{T}{(A + B)\,\theta_t} = \frac{T}{(A + B)\,(\theta_m - \beta T)}. \tag{13}$$

A value of $|G^*|_m$, which in general is likely to be an overestimate of G_{eqm}, can therefore be obtained directly from the torque measurements.

2.3 *Swollen compression modulus*

The Smith–Wallace reticulometer(12) is a modified Wallace microhardness tester used to determine swollen compression modulus. The method utilizes small samples which reach swelling equilibrium in a few hours, a stress–strain curve being obtained in 20–30 min.

For a compressed swollen rubber, the compressive force (f) acting on unstressed unswollen area (A_0) is given by

$$f = A_0 v_r^{-\frac{1}{3}} G_{sc} (\lambda^{-2} - \lambda) \tag{14}$$

where v_r is the volume fraction of polymer in the solvent/polymer system,
λ is the extension ratio, and
G_{sc} is the experimentally determined Gaussian modulus factor in swollen compression. Evidence for natural rubber(2) and polybutadiene(13) networks indicates that G_{sc} is a good estimate of G_{eqm}.

λ is defined in compression as

$$\lambda = \frac{\text{Compressed swollen height}}{\text{Uncompressed swollen height}} = h_c h_s^{-1}. \tag{15}$$

The change in height on compression (Δh) is therefore defined as

$$\Delta h = h_s - h_c$$
$$\text{i.e. } h_c = h_s - \Delta h.$$

Substituting for h_c in Eqn. (15) gives

$$\lambda = 1 - \Delta h \, h_s^{-1}. \tag{16}$$

Equation (14) now becomes

$$G_{sc} = \frac{f v_r^{\frac{1}{3}}}{A_0} [(1 - \Delta h \, h_s^{-1})^{-2} - (1 - \Delta h \, h_s^{-1})]^{-1}. \tag{17}$$

Using the relation

$$v_r^{\frac{1}{3}} = h_0 \, h_s^{-1}$$

Eqn. (17) becomes

$$G_{sc} = \frac{f v_r^{\frac{1}{3}}}{A_0} [(1 - \Delta h \, v_r^{\frac{1}{3}} h_0^{-1})^{-2} - (1 - \Delta h \, v_r^{\frac{1}{3}} h_0^{-1})]^{-1}. \tag{18}$$

The use of Eqn. (18) was suggested by Moore(14) who has shown it represents reticulometer data for natural rubber more accurately over a wide range of strain than do the approximate equations of Cluff *et al.*,(15) Loan,(16) and Khan Khadim and Smith.(17)

3. EXPERIMENTAL

A sample of polydimethylsiloxane (PDMS) gum rubber was supplied by Midland Silicones (Barry) Ltd. The curing agent was 2,4-dichlorobenzoyl peroxide supplied as a 50% paste in dimethylphthalate by Laporte Industries Ltd.

The PDMS sample, as received, was found to contain 10% by weight of low molecular weight materials. These were removed by heating the sample for 24 hr in an air circulating oven at 150°. A Mechrolab 502 high-speed osmometer (using toluene as solvent and with a cellulose membrane) gave the number average molecular weight of the PDMS sample as 110,000.

The peroxide vulcanizing agent was purified by successive extractions with and recrystallizations from acetone. Mixing of the peroxide and PDMS was carried out on a 2 × 4 in. two-roll mill. A peroxide concentration of 2 parts per hundred of rubber was used throughout.

The procedure of operation of the Weissenberg rheogoniometer was as outlined in the handbook.(5) Flat plates of 2·5 cm radius and a torsion bar of diameter 0·25 in. were used throughout this study. The oscillatory input signal from the forced plate and the resultant output signal from the constrained plate were recorded by an ultraviolet recorder on the same co-ordinates.

With the rheogoniometer used in the present study, the platens are heated by an electrical heating chamber. A drawback in the use of such a heating system is the fall in temperature which occurs when a sample is being loaded. This drawback becomes a major problem when the system being studied is a curing system with no induction time, as is the case with the silicone gum/peroxide system. In order to reduce the temperature fall during sample loading, we have modified the design of the heating chamber. Details of this modification will be published later.

Temperature monitoring has shown that the variation in sample temperature during cure is within $\pm 0{\cdot}5^\circ$ and that, after loading, the small samples used in the rheogoniometer attain the required temperature within 5 sec.

The rheogoniometer used in this study has a frequency range of $2{\cdot}5 \times 10^1$ to $1{\cdot}0 \times 10^{-5}$ c.p.s. Testing of the PDMS/peroxide stock was as follows:

(i) over the frequency range $2{\cdot}5 \times 10^1$ to $5{\cdot}0 \times 10^{-2}$ c.p.s., samples were cured in the instrument and the changes in their dynamic properties with temperature and time of cure noted;

(ii) over the frequency range $1{\cdot}0 \times 10^0$ to $1{\cdot}0 \times 10^{-5}$ c.p.s., measurements were carried out on a circular disk vulcanizate samples (radius 2·50 cm, thickness 0·051 cm) which were prepared by press curing. These vulcanizates were post-cured for 24 hr at 150° to eliminate peroxide decomposition products and other volatile materials.

The Monsanto oscillating disk rheometer was set up and adjusted as described in the handbook.(10) Samples of the PDMS/peroxide stock were cured in the rheometer at 85°, 95° and 105° using both modes of operation, i.e. disk oscillation frequencies of 0·1667 and 15·00 c.p.s. The disk was oscillated through a nominal angle of 0·0524 radians.

The operation of the reticulometer has been outlined elsewhere.(12) Vulcanizates of nominal thickness 0·10 cm were prepared by press curing the stock at 85°, 95° and 105°, the time to full cure at each temperature being obtained from the rheometer and rheogoniometer data. Small specimens were then cut from these vulcanizates by using an I.S.O. tensile strength test piece cutter in two directions at right angles to give square plan pieces of side nominally 0·64 cm. The unswollen dimensions of these specimens were then determined accurately using a Projectina 4014 measuring microscope (×20 magnification). The specimens were swollen in toluene for 48 hr, the solvent being renewed after 24 hr to eliminate sol. Reticulometer measurements at 25° were made on the swollen samples which were then weighed swollen and finally dried to constant weight under vacuum.

4. RESULTS AND DISCUSSION

4.1 *Rheogoniometer and rheometer measurements on curing samples*

From changes in amplitude ratio and phase lag (as measured from u.v. records) for the PDMS/peroxide stock samples cured in the rheogoniometer, the change in $|G^*|_w$ with time and temperature of cure was calculated by means of Eqns. (6) and (7). Typical changes in $|G^*|_w$ at cure temperatures of 85°, 95° and 105° are shown in Fig. 1, the frequency of oscillation (0·1990 c.p.s.) in the example shown being as near as possible to the frequency used in the rheometer. This is believed to be the first time that the cure of an elastomer has been followed in the Weissenberg rheogoniometer.

Figure 2 shows the variation of $|G^*|_m$ with time and temperature of cure, the frequency of oscillation of the disk in the example shown being 0·1667 c.p.s.

A comparison of Figs. 1 and 2 shows a very close similarity between the cure curves obtained for the PDMS/peroxide stock in the rheogoniometer and in the rheometer. As an example of this similarity, analysis of the two 95° cure curves is shown in Table 1.

It can be seen that the values of $|G^*|_w$ and $|G^*|_m$ are in close agreement throughout the whole of the cure. Similar agreement was found for the stocks cured at 85° and 105°; the closeness of the values appears to be strong evidence that the Monsanto rheometer and the Weissenberg rheogoniometer are measuring the same modulus function

$$\text{i.e. } |G^*|_m = |G^*|_w.$$

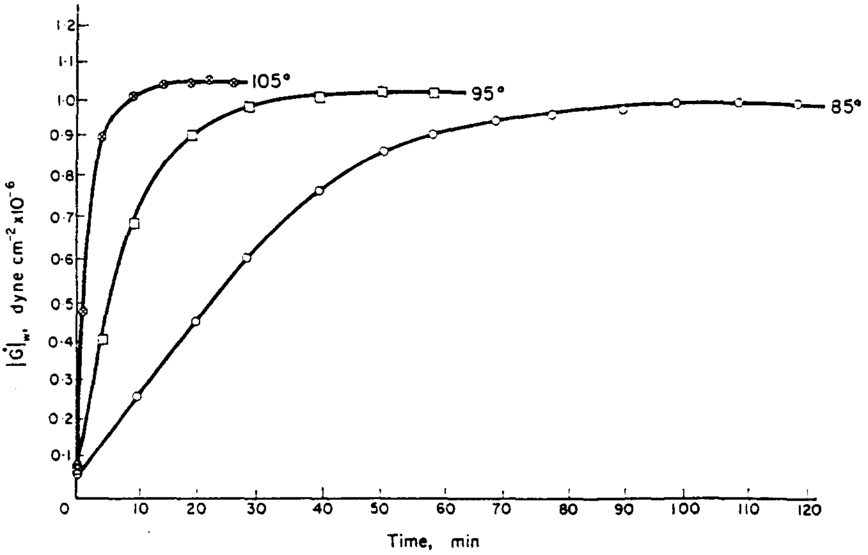

FIG. 1. Variation of $|G^*|_w$ with time and temperature of cure.

TABLE 1. COMPARISON OF $|G^*|_w$ AND $|G^*|_m$ FOR CURE TEMPERATURE 95°

Time (min)	Modulus factor (dyne cm^{-2} × 10^{-6})	
	$\lvert G^*\rvert_w$	$\lvert G^*\rvert_m$
2	0·15	0·11
5	0·40	0·36
10	0·68	0·66
20	0·92	0·90
30	0·99	1·00
40	1·02	1·03
50	1·03	1·04

4.2 *Rheogoniometer measurements on disk vulcanizates*

The rheogoniometer was also used for measurements on disk vulcanizates over the frequency range $1 \cdot 0 \times 10^0$ to $1 \cdot 0 \times 10^{-5}$ c.p.s. in order to determine the shape of the modulus/frequency curve over this range. Figure 3 shows the variation of G' with frequency. The fact that the elastic modulus factor/frequency lines have zero slope suggests that measurements are being made on a true rubbery plateau. Also shown in Fig. 3 are the maximum values of $|G^*|_m$ obtained from curing the PDMS/peroxide stock in the Monsanto rheometer. It can be seen that these values of $|G^*|_m$ lie within the "scatter" of G' points obtained from the rheogoniometer, i.e.

$$|G^*|_m \approx G.$$

However, since $|G^*| = [(G')^2 + (G'')^2]^{\frac{1}{2}}$ it appears that the elastic modulus G' would be identical with $|G^*|$ only if $G'' = 0$. Table 2 gives values which support this view for a PDMS vulcanizate fully cured in the rheogoniometer.

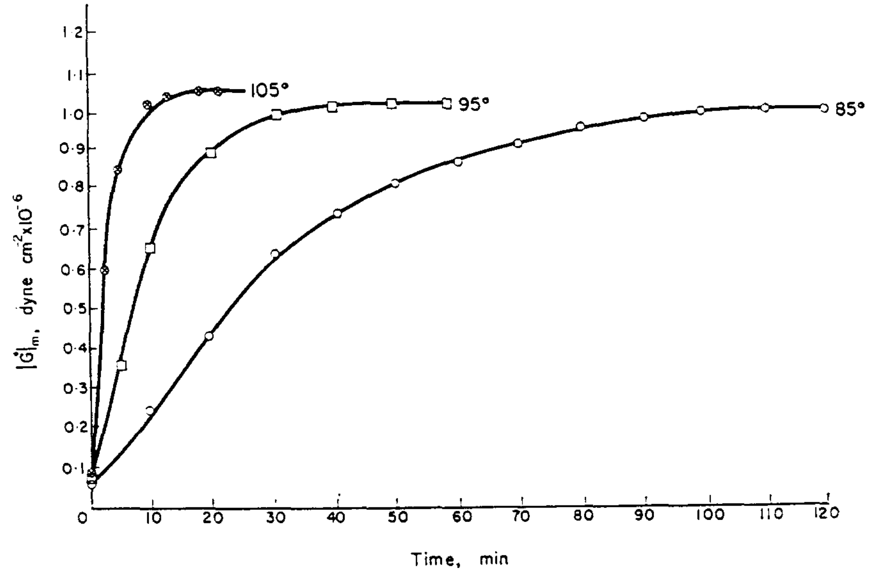

FIG. 2. Variation of $|G^*|_m$ with time and temperature of cure.

TABLE 2. VARIATION OF G', G'' AND $|G^*|_w$ WITH TIME OF CURE. TEMPERATURE OF CURE = 105°

Cure time (min)	Modulus factor (dyne cm^{-2} × 10^{-6})		
	G'	G''	$|G^*|_w$
1	0·484	0·078	0·490
3	0·824	0·052	0·826
5	0·950	0·030	0·951
7·5	1·028	0·016	1·028
10	1·045	0·007	1·045
15	1·049	0·004	1·049

We have also entered in Fig. 3 the maximum modulus factor obtained when the cure was carried out in the rheogoniometer, i.e. the modulus factor obtained when the cure was effectively completed. In the region where the data for pre-cured disks and samples cured in the Weissenberg instrument overlap, i.e. 1·0 × 10^0 to 5·0 × 10^{-2} c.p.s., no significant difference between the values of G' was detected. Since the vulcanizate discs were post-cured prior to testing, this suggests that the post-curing process has no effect on the fully cured modulus factor of these silicone rubber vulcanizates. This result agrees with that of Bobear(18) who found that a post-cure of 24 hr at 150° had no effect on the cross-link density of his PDMS vulcanizates.

4.3 *Equilibrium modulus by reticulometer*

Stress–strain data in compression for the solvent-swollen press-cured silicone rubber vulcanizates fitted a Gaussian elasticity equation as described in Section 2.3. A single parameter (G_{sc}) characterized the network elasticity, it being unnecessary to

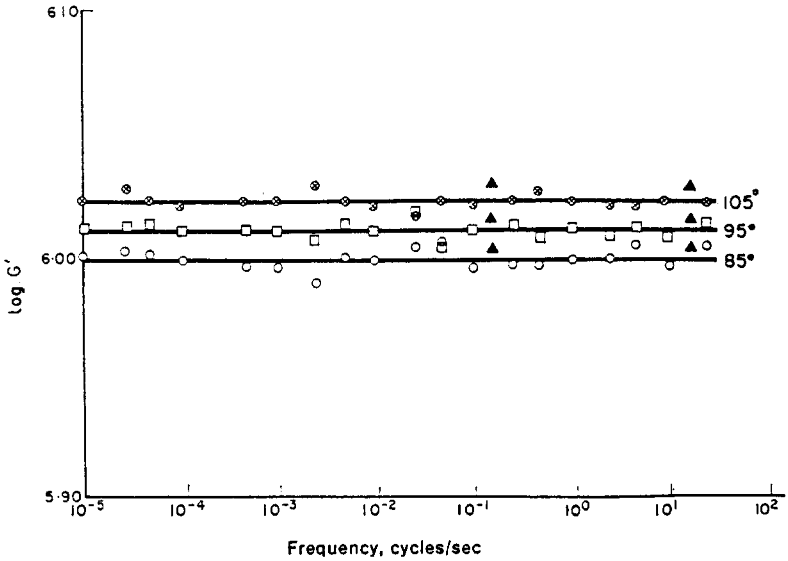

FIG. 3. Variation of G' with frequency, ⊗ measured at 105°, □ measured at 95°, ○ measured at 85°. ▲ values of $|G^*|_m$ calculated from rheometer torque measurements.

employ the two-parameter (Mooney–Rivlin) type of equation required by Mark and Flory$^{(19)}$ to describe their stress–strain measurements on swollen PDMS vulcanizates in tension.

4.4 *Comparison of "dynamic" and "equilibrium" moduli*

It remains now to show that $G' = |G^*|$ is an adequate estimate of "equilibrium modulus factor", G_{eqm}.

As the reticulometer measurements were carried out at 25°, the values of G_{sc} obtained have to be corrected to the required reference temperature by means of the relationship

$$\frac{(G_{sc})_{25^\circ}}{(G_{sc})_{x^\circ}} = \frac{(273 + 25)\, d_{25^\circ}}{(273 + x)\, d_{x^\circ}}$$

Where d_{25° and d_{x° are the densities of the sample at 25° and x^0 respectively calculated using a thermal expansion coefficient of $8 \cdot 6 \times 10^{-4}$ deg^{-1}. Table 3 shows a comparison of G_{sc} with G' and $|G^*|_m$ at the three cure temperatures.

TABLE 3. COMPARISON OF G', $|G^*|_m$ AND G_{sc} FOR SILICONE GUM VULCANIZATES

Temperature of cure	Modulus factor (dyne cm^{-2} × 10^{-6})		
	G'	$\lvert G^*\rvert_m$	G_{sc}
105°	1·05	1·06	1·10
95°	1·03	1·04	1·06
85°	1·00	1·02	0·99

It can be seen from Table 3 that very good agreement was obtained between the values of the modulus functions obtained using the three different techniques, i.e.

$$G' \approx |G^*|_m \approx G_{sc} \approx G_{eqm}.$$

5. CONCLUSIONS

The conclusions to be drawn from this programme of work with selected fully-cured PDMS vulcanizates are that the dynamic modulus factor obtained from the Monsanto rheometer can be equated with the elastic modulus obtained from the Weissenberg rheogoniometer. Further, it can be concluded that, under our conditions when measurements are made on the rubber plateau, these dynamic moduli can be equated with a swollen compression modulus factor obtained from the reticulometer,

$$\text{i.e. } G' \approx |G^*| \approx G_{sc}.$$

The good agreement between the various values suggests that rheometer and reticulometer measurements made in the rubbery plateau region may be used as estimates of equilibrium modulus factor, as has been suggested previously$^{(2)}$ for a range of natural rubber vulcanizates. However, it should be borne in mind that silicone rubbers are known to be virtually non-hysteretic and this conclusion will not necessarily apply generally to every type of elastomer vulcanizate, neither will it necessarily apply to silicone rubber networks of low crosslink density or those containing substantial quantities of non-network material. Langley and Ferry,$^{(20)}$ using creep and a torsion pendulum technique, have shown that polydimethylsiloxanes exhibit a secondary loss mechanism, at lower frequencies, which they attributed to disentanglement of free polymer chain ends. Langley and Ferry, however, were working with samples containing high sol contents (10–56 per cent by weight) and their results are not strictly

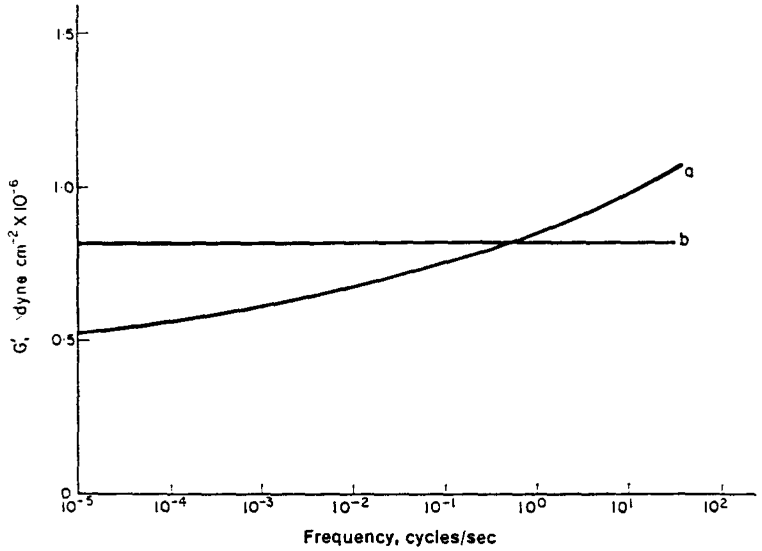

FIG. 4. Comparison of present data with those of Langley and Ferry.$^{(20)}$ (a) Data for Langley and Ferry's sample A-4 (~10% sol.) corrected for initial molecular weight. (b) Present data reduced to 25°.

comparable to ours since we are working with fully cured vulcanizates with low sol contents (less than 0·3 per cent by weight). We have, however, shown in Fig. 4 a comparison of our results with those obtained by Langley and Ferry from measurements on their sample with the highest crosslink density. We have corrected their values to account for the difference in initial molecular weight of their PDMS (500,000) as compared with ours (110,000) using the Flory⁽²¹⁾ expression

$$G = (\mathrm{d}RT/M_c)\,(1-2M_c/M)$$

where M_c is the molecular weight between crosslinks, and
M is the initial molecular weight of the polymer.

We have also corrected our results to 25°, the reference temperature used by Langley and Ferry.

Further work is in progress using the Weissenberg rheogoniometer to make measurements on silicone rubber networks of crosslink densities and sol contents comparable to those used by Langley and Ferry.

Acknowledgements—The authors thank Dr. D. R. Thomas of Midland Silicones Ltd. and Mr. L. Luckhurst of Laporte Industries Ltd. for generously supplying the samples of polydimethylsiloxane and 2,4-dichlorobenzoyl peroxide respectively.

REFERENCES

(1) A. Y. Coran, *Rubb. Chem. Technol.* 37, 689 (1964).
(2) R. B. Redding and D. A. Smith, *Sci. commun. IUPAC Macromol. Conf., Toronto, Sept. 1968*, Preprint A10; *J. Polym. Sci.* Part C, in press.
(3) H. W. Greensmith and A. A. Watson, *J. Rubb. Res. Inst., Malaya* 22, 120 (1964).
(4) L. I. Laud and J. E. Stuckey, *J. Inst. Rubb. Ind.* 3, 29 (1969).
(5) *Weissenberg Rheogoniometer Instruction Manual*, Model R.16, Sussex, England.
(6) K. Walters and R. A. Kemp, *Rheologica Acta* 7(1), 1 (1968).
(7) H. Markovitz, *J. appl. Phys.* 23, 1070 (1952).
(8) K. Walters, *Quart. J. Mech. appl. Maths.* 13, 325, 444 (1960).
(9) K. Walters and R. A. Kemp, *Deformation of Flow of High Polymer Systems*, p. 237. MacMillan, London (1967).
(10) *Monsanto Oscillating Disk Rheometer Operation and Service Manual.* Monsanto Company, Akron, Ohio, U.S.A.
(11) R. W. Wise, Monsanto Company, Akron, Ohio, U.S.A., private communication.
(12) D. A. Smith, *J. Polym. Sci.* C16, 525 (1967).
(13) F. de Candia and A. Ciferri, *Makromol. Chem.* 134, 335 (1970).
(14) T. Moore, unpublished work.
(15) E. F. Cluff, E. K. Gladding and R. Pariser, *J. Polym. Sci.* 45, 341 (1960).
(16) L. D. Loan, *Soc. Chem. Ind. Monograph* 17, 24 (1963).
(17) A. H. Khan Khadim and D. A. Smith, *Polymer* 10, 712 (1969).
(18) W. J. Bobear, *J. Polym. Sci.* A2, 299 (1966).
(19) J. E. Mark and P. J. Flory, *J. appl. Phys.* 37, 4635 (1966).
(20) N. R. Langley and J. D. Ferry, *Macromol.* 1(14), 363 (1968).
(21) P. J. Flory, *Principles of Polymer Chemistry*, p. 460. Cornell (1963).

Résumé—Les valeurs du facteur de module du polydiméthylsiloxanne peroxydé ont été obtenues en utilisant un Rhéogoniomètre Weissenberg, un rhéomètre à disque oscillant Monsanto et un réticulomètre (méthode de compression à l'état gonflé).

Pour des échantillons complètement réticulés, les valeurs des modules visqueux sont extrêmement petites et celles des modules élastiques sont indépendantes de la fréquence dans le domaine 2,5 × 10^1 à 1 × 10^{-5} cycles par seconde pour des températures comprises entre 85 et 105°. Les valeurs du module élastique obtenu avec les deux méthodes dynamiques sont en bon accord avec celles mesurées à 25° par la méthode "en équilibre", à condition que les valeurs soient rapportées à la même température de référence.

Ces résultats permettent de dire que les réseaux des caoutchoucs silicone complètement réticulés présentent un plateau d'élasticité étendu à l'intérieur duquel ils obéissent à la théorie élastique Gaussienne et ne présentent virtuellement pas d'hystérésis.

Sommario—Mediante impiego del reogoniometro di Weissenberg, del reometro a disco oscillante di Monsanto, e del reticolometro (metodo di compressione per dilatazione) si sono ottenuti dei valori del fattore di rigidità per strutture reticolari di polidimetilsiloxano/perossido.

A vulcanizzazione completa, i valori del modulo di viscosità sono trascurabilmente piccoli e quelli del modulo di elasticità sono indipendenti dalla frequenza nella gamma di $2,5 \times 10^{1}$ a 1×10^{-5} Hz e a temperature comprese tra 85 e 105°. I valori di modulo di elasticità ottenuti impiegando i due netodi dinamici concordano con quelli misurati mediante il metodo "equilibrio" a 25°, sempre che i valori vengano corretti alla medesima temperatura di riferimento.

Tali risultati sono in favore del punto di vista che le strutture reticolari di gomma al silicone completamente vulcanizzata mostrano un esteso plateau nei limiti del quale esse sono conformi alla teoria elastica gaussiana e praticamente non presentano alcuna isteresi.

Zusammenfassung—Werte für den Modul von Polydimethylsiloxan/Peroxid Netzwerken wurden mitdem Weissenberg Rheogoniometer, dem Monsanto "oscillating disk" Rheometer und dem Reticulo meter (Quell-Kompressionsmethode) erhalten.

Bei voller Vulkanisation sind die Werte des viskosen Moduls unbedeutend niedrig und die Werte für den Elastizitätsmodul sind unabhängig von der Frequenz im Bereich von $2,5 \times 10^{-1}$ bis 1×10^{-5} Cyclen pro Sekunde bei Temperaturen zwischen 85 und 105°. Die mit den beiden dynamischen Methoden erhaltenen Werte des Elastizitätsmoduls stimmen gut überein mit den durch die "Gleichgewichts" Methode bei 25° bestimmten Werten, vorausgesetzt daß eine Korrektur auf die gleiche Referenz-temperatur ausgeführt wird.

Diese Ergebnisse stützen die Ansicht, daß vollständig ausvulkanisierte Siliconkautschuk Netzwerke ein vergrössertes kautschuk-artiges Plateau zeigen, innerhalb dessen sie der Gauss'schen Elastizitätstheorie gehorchen und praktisch keine Hysteres zeigen.