Experiments on the small-strain behaviour of crosslinked natural rubber: 1. Torsion

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The torsional behaviour of 1, 3 and 5 phr peroxide crosslinked natural rubber has been characterized over a range of strains from near the undistorted state ($\gamma \approx 0.017$) to $\gamma \approx 1.0$. Isochronal measurements of both torque and normal force were used to calculate values of the derivatives of the strain energy function W with respect to the first and second stretch invariants I_1 and I_2. In the course of our work we found that, contrary to many reports in the literature, $\partial W/\partial I_1$ was affected significantly by the amount of crosslinking. Finally for the 1 phr peroxide crosslinked rubber it was found that, while ageing for 14 months at ambient conditions did not significantly affect the small-strain torsional modulus, $G = 2(\partial W/\partial I_1 + \partial W/\partial I_2)$, it did significantly affect the individual derivatives $\partial W/\partial I_1$ and $\partial W/\partial I_2$.

Keywords Ageing; normal force; rubber; small-strain; strain energy function; torsion

INTRODUCTION

During the past decade there have been many studies of the behaviour of crosslinked rubbers at small deformations. In several of the reported studies[1-5], either sheet biaxial or torsional experiments were carried out to determine values of the derivatives of the strain energy function in shear. Of interest was the observation that $\partial W/\partial I_2$ (the derivative of the strain energy function with respect to the second stretch invariant) went through a maximum with decreasing strain and that there was evidence to suggest that at small deformations the value of $\partial W/\partial I_2$ became negative. Such results have been reported by Zapas[1] for crosslinked butyl rubber, Penn and Kearsley[2] and Kearsley and Zapas[3] for peroxide crosslinked natural rubber, Kawabata *et al.*[4,5] for peroxide crosslinked and sulphur crosslinked natural rubbers and Becker[6] for crosslinked natural rubber.

In this work we investigated the behaviour of peroxide crosslinked natural rubber at deformations near the undistorted state going to torsional strains lower than those reported previously (i.e. $\gamma < 0.02$ for this study *versus* $\gamma \gtrsim 0.05$ for the other studies). In the course of our work we examined the effects of the degree of crosslinking and of ageing on the derivatives of the strain energy function. Our experiments were carried out by applying a torsion and measuring both the torque and normal force. The strain energy function derivatives, $\partial W/\partial I_1$ and $\partial W/\partial I_2$ (at $I_1 = I_2$) were determined from the torque and normal force data using the approach developed by Penn and Kearsley[2].

In the sections that follow we discuss our methods and results and compare them with results reported in the literature. The salient results are summarized here: (a) we did not find that $\partial W/\partial I_2$ becomes negative with decreasing strain; (b) the small-strain torsional modulus, $G = 2(\partial W/\partial I_1 + \partial W/\partial I_2)$, is relatively unaffected by ageing of the rubber while the individual strain energy function derivatives, $\partial W/\partial I_1$ and $\partial W/\partial I_2$, are affected significantly; (c) $\partial W/\partial I_2$ is relatively independent of crosslinking while $\partial W/\partial I_1$ increases with increasing crosslinking; (d) at low degrees of crosslinking, $\partial W/\partial I_2$ is nearly as large as $\partial W/\partial I_1$ for freshly moulded samples.

The general design of the experiments was based on previous work in which it was shown that various scaling laws can be applied for the analysis of the data. In the next section we describe the analysis used to determine the strain energy function derivatives. In the subsequent section the experimental work is described and then we present the data and discuss the results.

THEORETICAL CONSIDERATIONS

Introduction

The lack of long-time stability of our experimental apparatus made it impossible to obtain accurate equilibrium data for the normal force response of natural rubber in torsion. We therefore obtained isochronal data at short times for single-step stress relaxation experiments and treated these data in the same fashion as if they were equilibrium data. Such treatment is justified from work by Rivlin[7] in which he showed that in certain strain histories time-dependent behaviour can be treated in the same fashion (by using isochronal data) as elastic behaviour. This is true for histories approaching a single step in strain, where the material being at rest up to time $\tau = 0$ is subjected to a strain and held at that deformation up to time $\tau = t$. For direct comparison with the finite elasticity theory we can introduce a function $\hat{W}(I_1, I_2, t)$ which is not a strain energy function, but which for isochronal data from single-step deformation histories can be treated as the strain energy function $W(I_1, I_2)$ where I_1 and I_2 are the first and second stretch invariants. (For simplicity we

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will write $\hat{W}=\hat{W}(I_1, I_2, t)$ throughout this paper.) Then we can determine $\hat{W}_1=\partial\hat{W}/\partial I_1$ and $\hat{W}_2=\partial\hat{W}/\partial I_2$, the derivatives of $\hat{W}$ with respect to I_1 and I_2, in a fashion similar to that by which one determines $\partial W/\partial I_1$ and $\partial W/\partial I_2$ for an elastic solid.

Torsion of a cylinder

We now consider torsion of a right circular cylinder with radius R where a twist per unit length, Ψ, is applied at time $\tau=0$ and the torque and normal forces are measured at times $\tau=t$ after the application of the step in strain. The torque $T(t)$ and total normal force (compressive) $N(t)$ are given by the following expressions[8]:

$$T(t)=4\pi\Psi\int_0^R(\hat{W}_1+\hat{W}_2)r^3\,\mathrm{d}r \qquad (1)$$

$$N(t)=-2\pi\Psi^2\int_0^R(\hat{W}_1+2\hat{W}_2)r^3\,\mathrm{d}r \qquad (2)$$

We can then obtain algebraic expressions for $\hat{W}_1$ and $\hat{W}_2$ by applying the scaling law for torsion derived by Penn and Kearsley[2]:

$$\hat{W}_1+\hat{W}_2=\frac{1}{4\pi\Psi R^4}(3T+\Psi T_\Psi) \qquad (3)$$

$$\hat{W}_1+2\hat{W}_2=\frac{-1}{\pi\Psi^2R^4}(N+\Psi^2N_{\Psi^2}) \qquad (4)$$

where T_Ψ is the derivative of torque with respect to twist Ψ, and N_{Ψ^2} is the derivative of normal force with respect to the square of the twist Ψ^2. Equations (3) and (4) can be solved simultaneously to obtain $\hat{W}_1$ and $\hat{W}_2$. These are values of $\hat{W}_1$ and $\hat{W}_2$ obtained where $I_1=I_2=3+\Psi^2R^2$.

For purposes of data analysis it will be useful to use values of reduced torque and reduced normal force to examine variability in the data and non-linearity of material behaviour. The reduced torque is defined as $T/\pi\Psi R^4$ and the reduced normal force is defined as $2N/\pi\Psi^2R^4$. It can be seen from equations (3) and (4) that reduced torque is equal to $\hat{W}_1+\hat{W}_2$ when the product ΨT_Ψ is equal to T and reduced normal force is $-(\hat{W}_1+2\hat{W}_2)$ when the product $\Psi^2N_{\Psi^2}$ is equal to N.

EXPERIMENTAL

Sample preparation

Samples of natural rubber (National Bureau of Standards Standard Reference Material SRM-385) were crosslinked at 149°C for 2 h using 1, 3 and 5 parts per hundred parts of rubber (phr) dicumyl peroxide. The use of dicumyl peroxide as a 'quantitative' crosslinking agent for natural rubber has been discussed extensively in a recent article by Wood[9]. Our selection of these moulding conditions assures virtually complete reaction of the peroxide.

The samples were machined to final dimensions by adhesively bonding to a lathe fixture and removing material using a high-speed grinding wheel. Fixturing was developed so that specimens could be machined in the lathe and bonded to fixtures which were suitable for mounting in the testing machines. The procedure assured us that the specimen ends would be reasonably flat and perpendicular to the cylinder sides. In addition it provided a ready method of centering the specimens in the testing fixtures. A cyanoacrylate adhesive was used for bonding the samples to the fixtures.

Table 1 presents the sample designations, amount of peroxide used, sample geometry and the molecular weight between crosslinks, as calculated using the procedure of Wood[9]. Samples that are designated as unaged were tested within one week of moulding. One sample was aged at ambient laboratory conditions for 14 months after unaged testing and then retested.

Torsion testing

Torsional tests were carried out using a Rheometrics Dynamic Mechanical Spectrometer* (RDMS). Single-step torsional strain histories were applied to the samples and the torque and normal force responses were recorded continuously with time. The tests were conducted by deforming the sample to a given twist Ψ_1, for 2 min. The twist was then removed and the sample maintained at zero deformation for a minimum of 4 min. The sample was then twisted to a deformation $-\Psi_1$ for 2 min and returned to zero for a minimum of 4 min. A deformation of $-\Psi_2$ ($|\Psi_2|>|\Psi_1|$) was then applied for 2 min and the sample returned to zero deformation for a minimum of 4 min. This procedure was followed until the maximum deformation was obtained. The materials showed very little time dependence in their responses, even at the lowest crosslink density (1 phr peroxide). In *Figure 1* are plotted stress relaxation curves for samples A, B and C. The torque and normal force data as functions of deformation (ΨR) are reported as isochronal values at 45 s.

The angles of twist applied to the samples ranged from 0.0087 to 1.44 rad. The sample deformations corresponding to these twists varied with the exact sample geometries. The range of deformations (based on the outer

Table 1 Description of samples of dicumyl peroxide crosslinked natural rubber

Sample designation	Peroxide content (phr)	Cylinder geometry Diameter (cm)	Height (cm)	Average molecular weight between crosslinks*
A (unaged)	1	1.219	0.734	19610
B (unaged)	3	1.229	0.945	5030
C (unaged)	5	1.214	0.902	2890
D (aged)	1	1.267	1.245	19610

* Calculated from formula given by Wood[9]

$$\tfrac{1}{2}M_c^{-1}=36.986(f_p-0.31)\times10^{-6}$$

M_c is the molecular weight between crosslinks and f_p is the parts per hundred peroxide by mass per 100 parts of rubber. This assumes that each dicumyl peroxide molecule reacts to form one crosslink

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* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for the purpose.

diameter of the sample cylinder) was from approximately $\gamma = 0.017$ to $\gamma = 1.0$. (This corresponds to $I_1 = I_2 = 3.00029$ to $I_1 = I_2 = 4.0$.) All tests were performed at 23° ± 1°C.

The accuracy of the experiments was dependent on angular resolution ($\approx \pm 0.0005$ rad). torque sensitivity (0.1 g cm) and normal force sensitivity (≈ 0.1 g). The actual normal force measurements were somewhat less accurate than 0.1 g due to the fact that the transducer used on the RDMS is sensitive to small thermal gradients and there was some drift in the normal force response at the lowest normal force values measured. The specimen dimensions were measured using a caliper accurate to 0.0025 cm.

RESULTS AND DISCUSSION

In *Figures 2–4* are plotted values obtained at 45 s of the logarithms of torque ($T/\pi R^3$) and normal force ($2N/\pi R^2$) *versus* logarithm of strain (ΨR) for the 1, 3 and 5 phr dicumyl peroxide crosslinked natural rubbers (samples A, B and C). The torque and normal force respectively follow first and second power dependences on deformation up to values of ΨR of approximately 0.15–0.20. At larger deformations we observe small non-linearity in behaviour.

In *Figures 5–7* are plotted reduced torque ($T/\pi\Psi R^4$) *versus* $\log(\Psi R)$ and in *Figures 8–10* are plotted reduced normal force ($2N/\pi\Psi^2 R^4$) *versus* $\log(\Psi R)$. It is evident from these plots that the material behaviour cannot be described by a Mooney[10] strain energy function (i.e. $T/\pi\Psi R^4$ and $2N/\pi\Psi^2 R^4$ constant with deformation).

The choice of a linear, expanded scale for reduced torque and normal force in *Figures 5–10* shows the variability in the data. The data reproducibility is quite good for the torque even at the smallest strain ($\leqslant \pm 2.5\%$). The normal force variability is small at strains above about 0.10 ($\leqslant \pm 3\%$) while at smaller strains the variability increases. The differences in torque and normal force variabilities are due to the fact that torque measurements are relatively insensitive to sample misalignment, the flatness of the cylindridal sample ends, and how parallel the machine fixtures are while the normal forces are sensitive to such experimental variables.

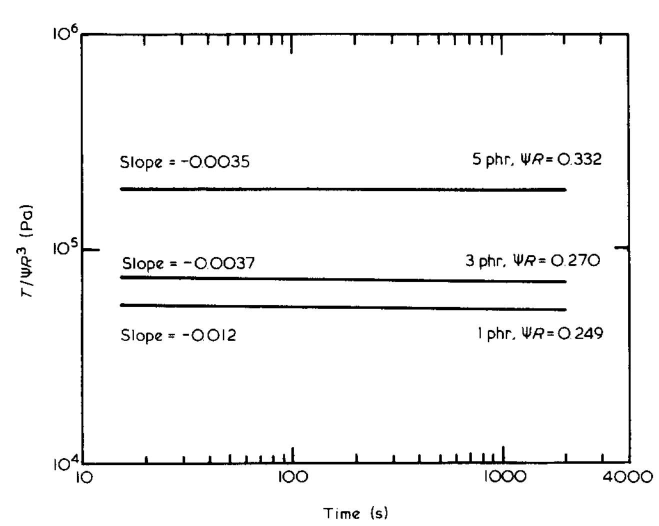

Figure 1 Stress relaxation of 1, 3 and 5 phr dicumyl peroxide crosslinked natural rubber in torsion. Slope values represent relaxation rate per logarithmic decade of time. ΨR is the deformation at the outer surface of the cylindrical samples. $T = 23°C$

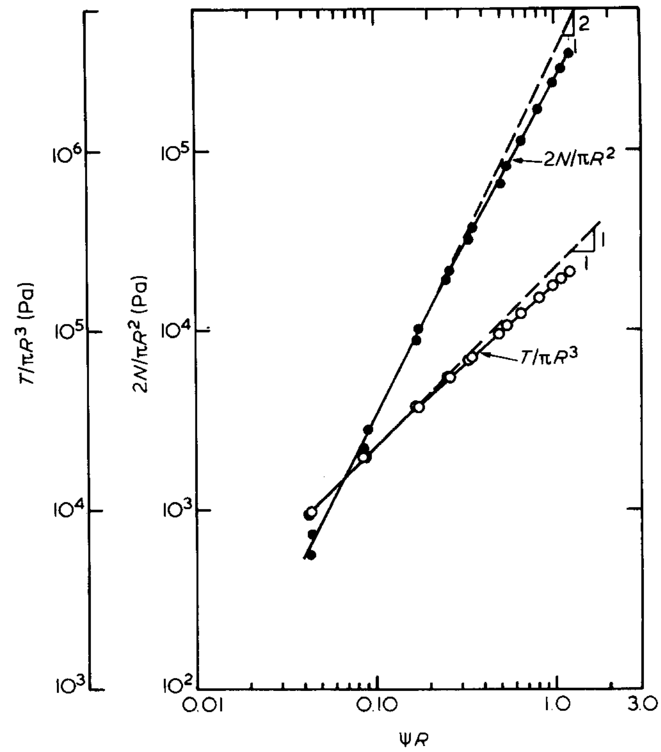

Figure 2 Torque ($T/\pi R^3$) and normal force ($2N/\pi R^2$) vs. deformation (ΨR) for natural rubber crosslinked with 1 phr dicumyl peroxide, sample A. Values are data obtained 45 s after the deformation was applied to the samples. $T = 23°C$

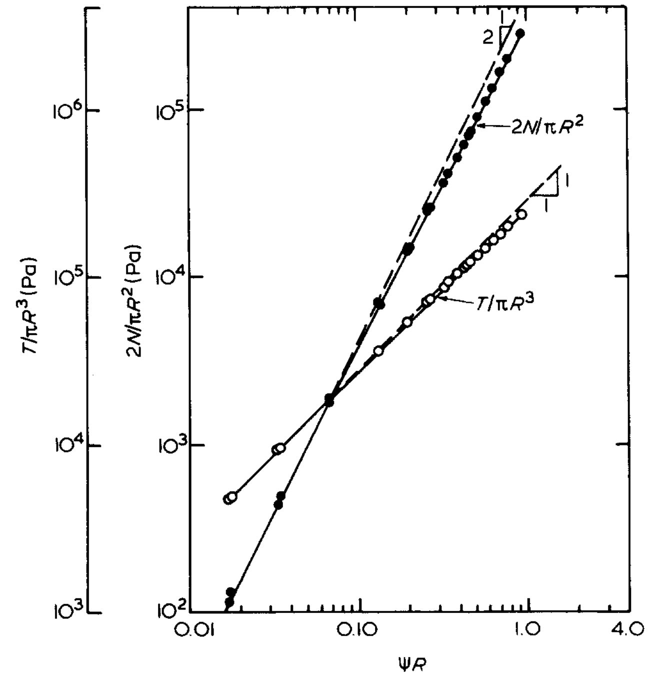

Figure 3 Torque ($T/\pi R^3$) and normal force ($2N/\pi R^2$) vs. deformation (ΨR) for natural rubber crosslinked with 3 phr dicumyl peroxide, sample B. Values are data obtained 45 s after the deformation was applied to the samples. $T = 23°C$

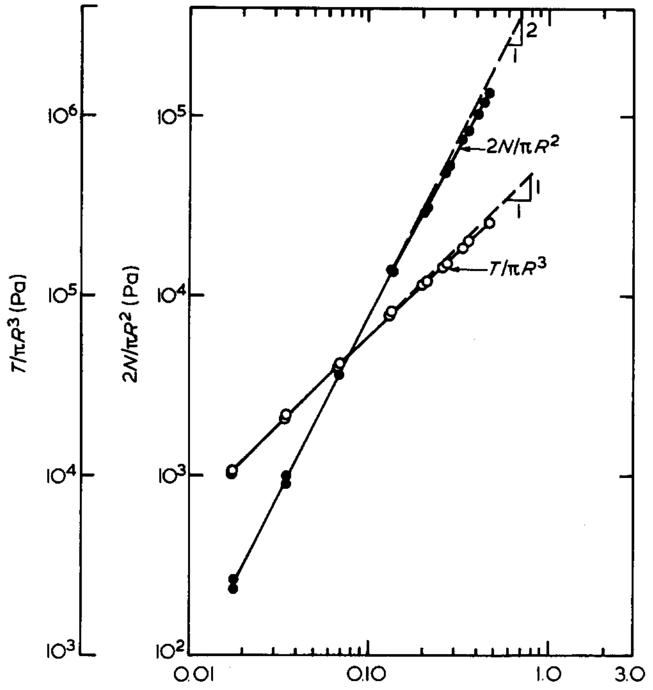

Figure 4 Torque ($T/\pi R^3$) and normal force ($2N/\pi R^2$) vs. deformation (ΨR) for natural rubber crosslinked with 5 phr dicumyl peroxide, sample C. Values are data obtained 45 s after the deformation was applied to the samples. $T = 23°C$

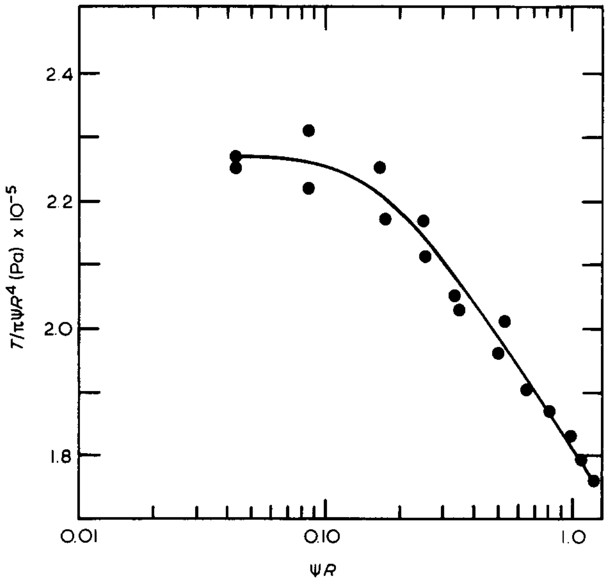

Figure 5 Reduced torque ($T/\pi\Psi R^4$) vs. deformation (ΨR) for natural rubber crosslinked with 1 phr dicumyl peroxide, sample A. Values are data obtained 45 s after the deformation was applied to the samples. $T = 23°C$. Deviations from a constant value correspond to deviations from 'Mooney' behaviour

Using the data for the small-strain region where the slope of the plots in *Figures 1–3* are constant, we can readily calculate the small-strain values for $\hat{W}_1$ and $\hat{W}_2$. The results are presented in *Table 2*. There are three interesting comments which can be made about the data in *Table 2*. First, $\hat{W}_1$ and $\hat{W}_2$ are nearly equal for the 1 phr and 3 phr rubbers ($\hat{W}_2 \simeq 0.3\hat{W}_1$ for the 5 phr rubber). This is unusual in that literature values of $\hat{W}_2$ for natural rubber[2–4] are usually markedly less than $\hat{W}_1$. Also in *Table 2* we see that for these three samples $\hat{W}_2$ increases only slightly with crosslinking while $\hat{W}_1$ increases dramatically. Finally, we observe that in no instance is $\hat{W}_2$ negative. In fact, our data for these samples give this result even at the extremes of the raw data, for strains of 0.017 which is a lower strain than reported by other workers who have measured negative values of $\hat{W}_2$.

The results discussed so far relate only to the three samples (A, B, C) moulded as cylinders 1.27 cm in diameter by 1.27 cm high and tested shortly after they were moulded. There is apparently a dependence of the material response on moulding conditions and time between moulding and testing. This will be discussed below.

Sample D was moulded in the same geometry and under the same conditions as samples A, B and C. It was cured with 1 phr dicumyl peroxide. Sample D was tested one week after moulding and again 14 months after moulding. It was stored at ambient conditions in the laboratory, i.e. 23° ± 1°C. The sample was exposed to the fluorescent light illuminating the laboratory as well as to relative humidity variations of between 35% and 70% in the course of a year. *Table 3* compares the values of $\hat{W}_1 + \hat{W}_2$, $\hat{W}_1$, and $\hat{W}_2$ obtained for sample D at the two different testing times. As can be seen, the values of $\hat{W}_1$

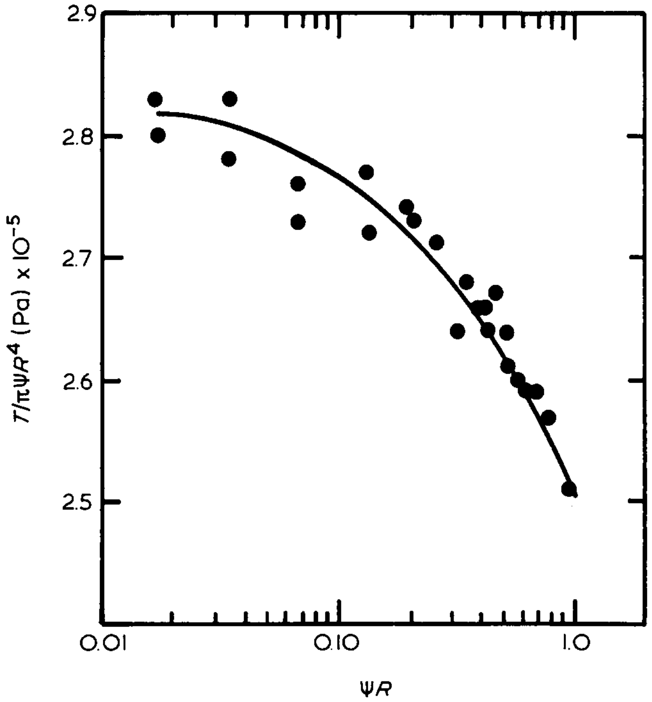

Figure 6 Reduced torque ($T/\pi\Psi R^4$) vs. deformation (ΨR) for natural rubber crosslinked with 3 phr dicumyl peroxide, sample B. Values are data obtained 45 s after the deformation was applied to the samples. $T = 23°C$. Deviations from a constant value correspond to deviations from 'Mooney' behaviour

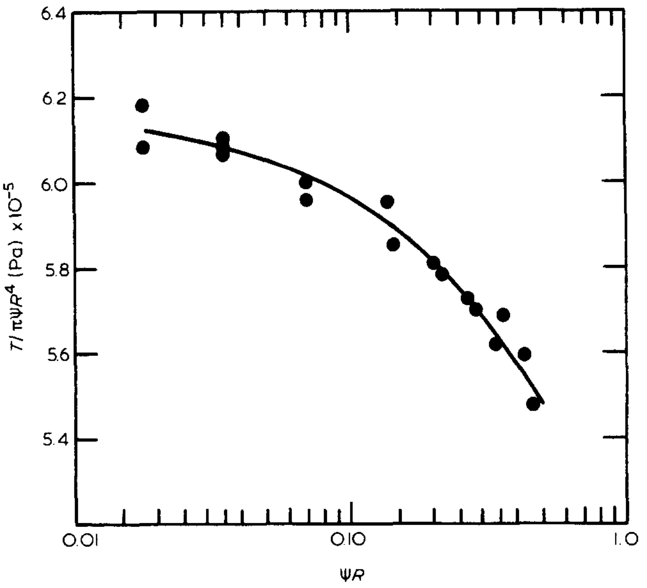

Figure 7 Reduced torque ($T/\pi\Psi R^4$) vs. deformation (ΨR) for natural rubber crosslinked with 5 phr dicumyl peroxide, sample C. Values are data obtained 45 s after the deformation was applied to the samples. T=23°C. Deviations from a constant value correspond to deviations from 'Mooney' behaviour

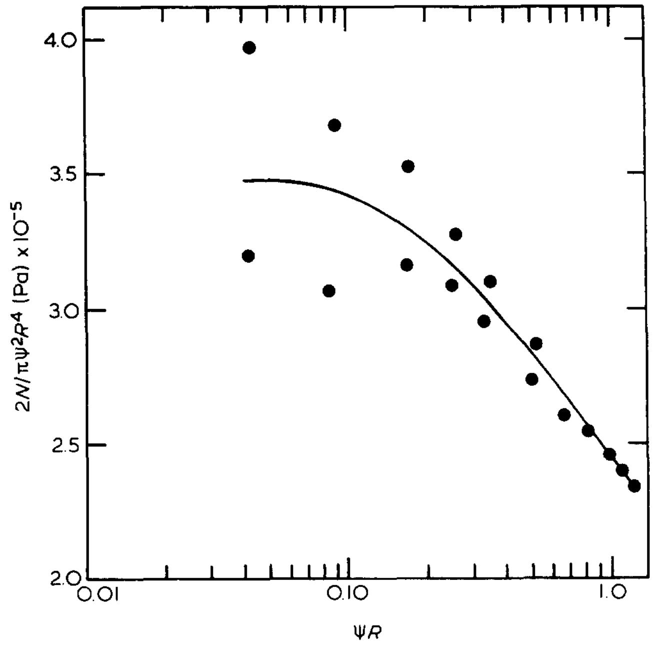

Figure 8 Reduced normal force ($2N/\pi\Psi^2R^4$) vs. deformation (ΨR) for natural rubber crosslinked with 1 phr dicumyl peroxide, sample A. Values are data obtained 45 s after the deformation was applied to the samples. T=23°C. Deviations from a constant value correspond to deviations from 'Mooney' behaviour

$+\hat{W}_2$ for the two conditions are not greatly different, although the values of $\hat{W}_1$ and $\hat{W}_2$ are quite different. $\hat{W}_1$ is larger for the sample tested shortly after moulding while $\hat{W}_2$ is smaller. In the case of the sample tested shortly after moulding, $\hat{W}_2 \approx 0.8\hat{W}_1$, while when the same sample was tested after 14 months, $\hat{W}_2 \approx 0.25\hat{W}_1$. We feel that these results would not be significantly different if the data had been obtained at much longer times since the samples show so little time dependence. The differences between the aged and unaged samples suggest that the method of

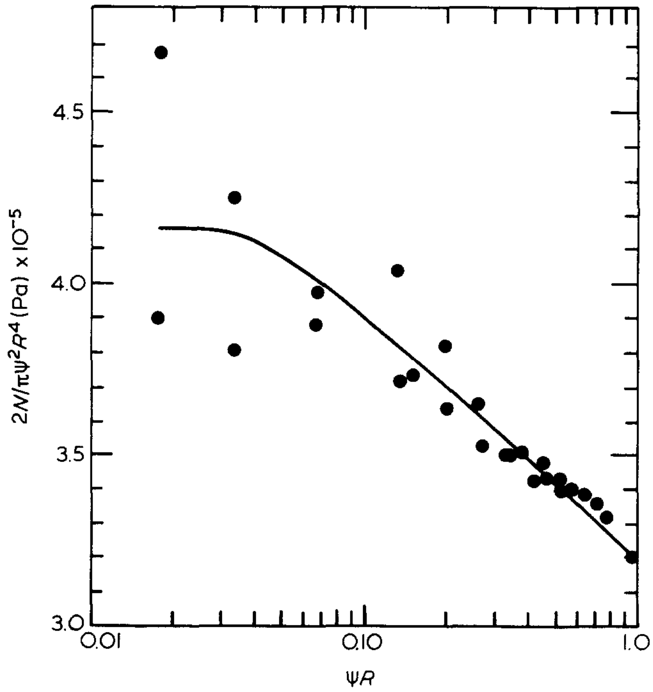

Figure 9 Reduced normal force ($2N/\pi\Psi^2R^4$) vs. deformation (ΨR) for natural rubber crosslinked with 3 phr dicumyl peroxide, sample B. Values are data obtained 45 s after the deformation was applied to the samples. T=23°C. Deviations from a constant value correspond to deviations from 'Mooney' behaviour

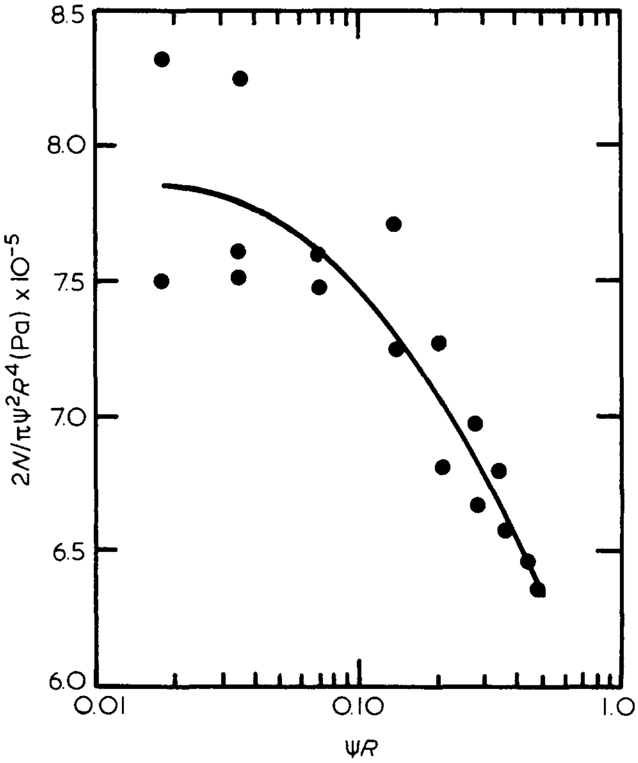

Figure 10 Reduced normal force ($2N/\pi\Psi^2R^4$) vs. deformation (ΨR) for natural rubber crosslinked with 5 phr dicumyl peroxide, sample C. Values are data obtained 45 s after the deformation was applied to the samples. T=23°C. Deviations from a constant value correspond to deviation from 'Mooney' behaviour

Table 2 Values of the derivatives of the strain energy function at 45 s for dicumyl peroxide crosslinked natural rubber

Sample	$I_1=I_2$ (ΨR)	$\hat{W}_1$ (MPa)	$\hat{W}_2$ (MPa)	$\hat{W}_1+\hat{W}_2$ (MPa)	$\hat{W}_1+2\hat{W}_2$ (MPa)
A	3.0018(0.0424)	0.108	0.120	0.228	0.348
B	3.00029(0.0170)	0.148	0.134	0.282	0.416
C	3.00031(0.0175)	0.467	0.145	0.612	0.757

Table 3 Comparison of the derivatives of the strain energy function for aged and freshly moulded natural rubber crosslinked with 1 phr dicumyl peroxide

Sample	$I_1=I_2$ (ΨR)	$\hat{W}_1$ (MPa)	$\hat{W}_2$ (MPa)	$\hat{W}_1+\hat{W}_2$ (MPa)	$\hat{W}_1+2\hat{W}_2$ (MPa)
A	3.0018(0.0424)	0.108	0.120	0.228	0.348
D (freshly moulded)	3.014(0.118)	0.112	0.110	0.222	0.332
D (aged)	3.014(0.118)	0.182	0.036	0.218	0.254

sample preparation (i.e. moulding and curing conditions) can affect the results. In searching the literature one finds considerable differences among preparation procedures for samples used for the measurement of the derivatives of the strain energy function of natural rubber. In the following paragraphs we compare some of the work in the literature with that of our own. In *Table 4* are presented abbreviated results for $\hat{W}_1$, $\hat{W}_2$, $\hat{W}_1+\hat{W}_2$ and $\hat{W}_1+2\hat{W}_2$ in the small deformation region along $I_1=I_2$ (i.e. pure shear).

There is an interesting aspect to the data reported in *Table 4*. For all of the rubbers tested (except our own 3 and 5 phr natural rubbers), the values of $\hat{W}_1+\hat{W}_2$ (half the shear modulus, G) are approximately 0.20 MPa. This is in spite of the fact that the amount of crosslinking agent (if one considers only the peroxide cured natural rubbers) varies from 1 phr to 4 phr. This is contrary to results reported by Wood[11] from many literature sources for which $G=2(\hat{W}_1+\hat{W}_2)$ is reported to vary nearly linearly with amount of decomposed peroxide in the rubber. For $G=0.4$ MPa, the amount of peroxide should be approximately 1.16 phr, and for $G=0.7$ MPa one would need 2.8 phr peroxide. The anomaly reported here might be attributed to a number of things. First, the values reported by Wood are nominal equilibrium values. The time dependence of the rubbers described in *Table 4* is quite small (less than 1.2% decrease in $\hat{W}_1+\hat{W}_2$ per decade of time), however, and the anomaly is greater than can be accounted for by time-dependent effects. Perhaps a more important factor is the actual amount of dicumyl peroxide which decomposes. For Kawabata's[5] 4 phr peroxide cured rubber, the cure conditions were 145°C for 30 min. This results in less than 40% decomposition of the peroxide (based on Wood's[9] half-life equation for peroxide decomposition as a function of temperature). Thus Kawabata's rubber should behave as if it were cured with approximately 1.6 phr peroxide.

In the case of the Kearsley and Zapas data[3], there appears to be a different problem. Both the rubber cured with 2 phr and that cured with 4 phr peroxide give the

Table 4 Values of the derivatives of the strain energy function for crosslinked rubbers measured at small deformations

Rubber	$I_1=I_2$	Time	$\hat{W}_1$ (MPa)	$\hat{W}_2$ (MPa)	$\hat{W}_1+\hat{W}_2$ (MPa)	$\hat{W}_1+2\hat{W}_2$ (MPa)	Reference
2 phr sulphur cured NR	3.0046	5 min	0.2102	−0.0230	0.1872	0.1642	Kawabata[4]
	3.0051	5 min	0.2379	−0.0465	0.1914	0.1449	
	3.0062	5 min	0.2510	−0.0579	0.1931	0.1352	
4 phr peroxide cured NR	3.03	10 min	0.254	−0.029	0.225	0.196	Kawabata[5]
	3.04	10 min	0.230	−0.005	0.225	0.220	
2 and 4 phr peroxide cured NR	3.00239	15 min	0.2484	−0.0148	0.2336	0.2188	Kearsley and Zapas[3]
	3.00240	15 min	0.2540	−0.0204	0.2336	0.2132	
	3.00958	15 min	0.2061	+0.0289	0.2350	0.2639	
NR, unknown crosslinker	3.003	10 min	0.223	−0.0109	0.2121	0.2012	Becker[6]
Sulphur cured butyl rubber (creep data)	3.1050	3 h	0.215	−0.010	0.205	0.195	Zapas[1]
	3.1125	20 h	0.191	+0.07	0.198	0.205	
1 phr peroxide cured NR, aged	3.014	45 s	0.182	+0.036	0.218	0.254	This work
1 phr peroxide cured NR	3.0018	45 s	0.108	+0.120	0.228	0.348	This work
3 phr peroxide cured NR	3.00029	45 s	0.148	+0.134	0.282	0.416	This work
5 phr peroxide cured NR	3.00031	45 s	0.467	+0.145	0.612	0.757	This work

same values for the derivatives of the strain energy function. The rubber was cured at 126°C for 16 h which is long enough to assure a 99.5% conversion of the peroxide. However, the rubber was also post-cured for 1 h at 170°C. The long time at 126°C and the 1 h at 170°C could have resulted in oxidation of the rubber. It is well known[12,13] that natural rubber oxidizes at temperatures above ≈ 100°C and long exposures to higher temperatures could cause reversion of the rubber.

In the case of our sample preparation we note that the modulus values obtained for the 3 phr natural rubber sample are slightly low when compared with those reported in Wood's article[11], while the 1 phr and 5 phr rubbers have slightly high values. The deviations however are within the variability reported by Wood.

Thus, it appears that processing variables must be considered when comparing results for rubbers which are nominally the same.

Yet these factors alone do not account for the fact that in our tests we did not obtain negative values of $\hat{W}_2$ for any of the samples tested, while in the work to which we are comparing our results, negative value of $\hat{W}_2$ were obtained. We tested most of our samples within one week of moulding. Since the value of $\hat{W}_2$ appeared to decrease with increasing time after moulding (aged sample), there is the possibility that the samples are changing with time. This would be consistent if one considered the aged sample to have 'relaxed' the residual stresses induced during moulding. This would also be consistent with the thought that a homogeneous material is produced as the material relaxes over time. Penn and Kearsley[2] chose a cure at 126°C for 16 h to assure a uniform material. The other experiments (Kawabata, Becker and Zapas) were carried out on thin sheets of material rather than on cylinders. Material inhomogeneity due to curing would be a small problem with these samples. Why material inhomogeneity would produce anomalously high normal forces, and therefore give rise to high values of $\hat{W}_2$, is not known. The reasons for these discrepancies certainly should be investigated further.

SUMMARY

Experiments in torsion where the torque and normal force were monitored continuously with time were carried out on samples of natural rubber crosslinked with 1, 3 and 5 phr dicumyl peroxide. It was found that, while the shear modulus increased as expected with amount of crosslinking agent, the individual derivatives of the strain energy function did not; $\partial\hat{W}/\partial I_2$ increased only slightly with amount of peroxide, while $\partial\hat{W}/\partial I_1$ increased dramatically. Also we found that at small strains, $\partial\hat{W}/\partial I_2$ did not become negative for any of the samples tested in contrast to results reported in the literature[1-5]. This is in spite of the fact that our experiments were carried to smaller strains than have been reported previously.

For the freshly moulded samples we found that $\partial\hat{W}/\partial I_2 \approx \partial\hat{W}/\partial I_1$ for the 1 and 3 phr peroxide cured natural rubbers. For the 1 phr natural rubber it was found that ageing of the sample at ambient conditions for 14 months resulted in a decrease in $\partial\hat{W}/\partial I_2$ so that it was equal to $\approx 0.2\partial\hat{W}/\partial I_1$.

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