Experiments on the small-strain behaviour of crosslinked natural rubber: 2. Extension and compression

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Experiments were carried out to characterize the small-strain tension and compression behaviour of dicumyl peroxide crosslinked natural rubber. Strains that were smaller by an order of magnitude than any reported previously on natural rubber were achieved. Our results support the contention that the compression and extension moduli of natural rubber are different. A new finding is reported: that is, the moduli in tension and compression do not become constant but rather they increase significantly as zero deformation is approached.

Keywords Compression; extension; modulus; reduced stress; rubber elasticity; small-strain

INTRODUCTION

The study of the behaviour of crosslinked rubber at deformations near the undeformed configuration is of fundamental importance to the understanding of the rubbery state. It has been generally accepted that the stress–strain curve for rubber has a continuous slope through zero deformation (going from tension to compression)[1], i.e. the tension and compression moduli are the same. Certainly this is true in classical rubber elasticity theory[2]. Experimental results to support the continuity of the modulus at zero deformation have been presented by Treloar[3], Sheppard and Clapson[4] and Wolf[5]. However, VanderHoff and Glynn[6] and Blokland[7] offer data which suggest that the infinitesimal moduli in tension and compression may be different.

In this paper we report experiments carried out at strains which are smaller by an order of magnitude than any reported previously, i.e. closer to the undeformed configuration. Our results not only support the contention that the compression and extension moduli may be different but we also report a new result, namely that the moduli in tension and compression do not become constant as zero deformation is approached but rather they increase significantly.

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 phr dicumyl peroxide. The samples were compression moulded as cylinders either 1.27 cm in diameter by 1.27 cm length or 2.2 cm in diameter by 33 cm length.

The samples were machined to final dimensions by adhesively bonding them to a lathe fixture and then removing material using a high-speed grinding wheel. A method 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 fixtures. A cyanoacrylate adhesive was used for bonding the samples to the fixtures. *Table 1* presents the sample designations, amount of peroxide used in moulding and the sample geometries.

Extension and compression testing

Extension and compression tests were carried out on either the Rheometrics Dynamic Mechanical Spectrometer* (RDMS) or the Imass Dynastat*. Single-step strain histories were applied to the samples and the axial (tensile or compressive) forces were recorded continuously with time. The tests were carried out in one of two ways. Procedure I was used for testing samples A, B and C. A strain ε_1 was applied to the sample for 2 min. The deformation was then returned to zero for a minimum of 4 min. Then the next larger strain ε_2 was applied to the sample for 2 min followed by 4 min at zero deformation. This procedure was followed until the maximum deformation (at which machine load capacity was exceeded) was reached. For sample A tensile tests were carried out first, while for samples B and C compressive tests were carried out first. Sample D was tested in the same fashion except that replicate tests were carried out by reversing the procedure in going from the maximum deformation to the minimum. Sample D was tested in compression prior to being tested in extension.

* 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

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Table 1 Description of samples of dicumyl peroxide crosslinked natural rubber

Sample designation	Peroxide content (phr)	Cylinder geometry	
		Diameter (cm)	Height (cm)
A	1	1.219	0.734
B	3	1.229	0.945
C	5	1.214	0.902
D	5	2.029	5.732
E	5	1.181	0.993

Sample E as well as sample D subsequent to testing by procedure I were tested using procedure II. In procedure II the tests were performed by applying a tensile strain ε_1 to the sample for 2 min and returning the sample to zero deformation for a minimum of 4 min. Then a compressive strain $-\varepsilon_1$ was applied to the sample for 2 min and the sample was returned to zero deformation for a minimum of 4 min. The sample was then deformed to a strain $-\varepsilon_2$ ($\varepsilon_2 > \varepsilon_1$) for 2 min and returned to zero for a minimum of 4 min. Then the strain ε_2 was applied to the sample. This procedure was followed until the maximum deformation was obtained. Replicate tests were carried out in a similar fashion where the deformation was increased from zero and also where the amount of deformation was decreased from a maximum back towards zero.

The zero strain position was set by applying a force equal to the weight of the sample plus one fixture to balance the weight on the load cells since the samples were bonded at both ends. All data reported are isochronal values at 45 s.

The deformation applied to the samples ranged from ± 0.005 mm to 1 mm on the RDMS and from ± 0.0015 mm to 1 mm on the Dynastat. The corresponding strains vary with sample dimensions, but the strain range for all tests was from $\varepsilon = \pm 1 \times 10^{-4}$ to 3×10^{-2}. All tests on the RDMS were conducted at $23° \pm 1°$C. Those on the Dynastat were carried out at $24° \pm 1°$C.

The experimental accuracy depends on the resolution of the displacement measurement (± 0.0002 mm for the RDMS; ± 0.00005 mm for the Dynastat) and the sensitivities of the force transducers (± 0.1 g). The force measurements are somewhat less accurate on the RDMS due to problems with zero drift on the load cell. Drift of the zero in the Dynastat load cell was not observable over the period of 10 h during which this instrument was used. The specimen dimensions were measured with a caliper accurate to 0.0025 cm.

THEORETICAL CONSIDERATIONS

Data analysis

The lack of long-time stability in the RDMS experimental apparatus made it impossible to obtain accurate equilibrium data for the extension and compression behaviour of natural rubber. 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[8] in which it was shown that for 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 elasticity theory, then, 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 $W(I_1, I_2)$. I_1 and I_2 are the first and second stretch invariants.

Then, for deformations in simple extension and simple compression, the stress difference $\sigma_{11} - \sigma_{22}$ is written as:

$$\sigma_{11} - \sigma_{22} = 2\left(\lambda^2 - \frac{1}{\lambda}\right)\left(\hat{W}_1 + \frac{1}{\lambda}\hat{W}_2\right) \quad (1)$$

where λ is the stretch and the subscripts on $\hat{W}_i$ refer to differentiation of $\hat{W}$ with respect to the first and second stretch invariants I_1 and I_2. A common method of data representation used with rubbery materials is the so-called Mooney–Rivlin plot in which reduced stress σ_R is plotted *versus* $1/\lambda$. The reduced stress is defined, using equation (1), as:

$$p_R = \frac{\sigma_{11} - \sigma_{22}}{\lambda^2 - 1/\lambda} = 2\left(\hat{W}_1 + \frac{1}{\lambda}\hat{W}_2\right) \quad (2)$$

At small deformations, since $\lambda = 1 + \varepsilon$

$$p_R \sim \frac{E}{3} = \frac{\sigma_{11} - \sigma_{22}}{3\varepsilon} \quad (3)$$

where E is the Young's modulus and ε is the strain defined as $(L - L_0)/L_0$, where L is the deformed length and L_0 the length of the sample at zero deformation.

Representation of the data on a reduced stress plot provides a sensitive measure of the deviations of the elastic properties from constant values. In fact, such a representation shows deviations of material behaviour from classical rubber elasticity theory[2] or so-called neo-Hookean behaviour[9].* Therefore, in part of this work we will present results based on plots of reduced stress *versus* ε at very small values of ε.

The bonded cylinder

Our experiments were carried out (with the exception of sample D) using cylinders of rubber having low aspect ratios. Since the ends of the cylinders were bonded to the test fixtures, a non-homogeneous stress distribution results when the sample is deformed in either tension or compression. The result is that if one determines the strain in the sample by measuring the displacement of the sample ends (as we did in this study), the apparent modulus as calculated from the ratio of stress to strain is higher than that which would be obtained were the cylinder not constrained at the ends.

The boundary value problem of a cylinder with fixed ends loaded in tension or compression has been treated by

* Such a presentation has been criticized for magnifying errors near the undeformed state[5]. Wolf[5], for example, stated that a 0.1% error in the stretch λ would result in a 10.5% error in the reduced stress if $\lambda = 1.01$. However, since what one actually measures in a small-strain experiment is the change in length of the sample, $\Delta L = L - L_0$ and $\lambda = 1 + \Delta L/L_0 = 1 + \varepsilon$, then, in Wolf's example, $\varepsilon = 0.01$. A 0.1% error in λ then represents a 10% error in ε, which is approximately the same as the error in the reduced stress. In an experiment where the error in ε is 0.1% the error in the reduced stress is also only 0.1%.

numerous authors either analytically[10–13] or numerically[11]. Since the problem is solved using linear infinitesimal elasticity, the solutions all give the result that the apparent modulus to actual modulus ratio, $K = E_a/E$, while depending on sample geometry, is independent of deformation. In this work we will use the values of K determined from the finite difference analysis of Messner[11].

RESULTS AND DISCUSSION

In *Table 2* are summarized some results from stress relaxation tests carried out on the peroxide crosslinked natural rubbers used in this study. As can be seen, there is very little time dependence for these rubbers, as measured by the stress decay per logarithmic decade of time. We remark, furthermore, that within experimental accuracy there was no dependence of the relaxation rate on the magnitude of the deformation.

In *Figures 1–3* are depicted stress–strain diagrams for samples A, B and C (1, 3 and 5 phr dicumyl peroxide). What is evident in these figures is that at small strains the apparent moduli in tension and compression are not equal. Note, too, that with the exception of sample A the compression stress–strain curves appear linear over the range of strains tested while the tensile stress–strain plots show considerable curvature over the same strain range. The correction factors for the modulus, due to the end constraints based on Messner's[11] finite difference analysis, are presented on the figures and in *Table 3*. In order to be assured that Messner's finite difference results were reasonable, we compared the corrected modulus values with modulus values calculated from torsional modulus values obtained on the same samples[14]. As can be seen in *Table 4* the agreement is reasonable.

Table 2 Rate of stress relaxation for dicumyl peroxide crosslinked natural rubber

Sample	Dicumyl peroxide (phr)	Rate of relaxation*
A	1	–0.011
B	3	–0.0041
C	5	–0.0036
D	5	–0.0016
E	5	0

* Rate of stress decay per logarithmic decade of time

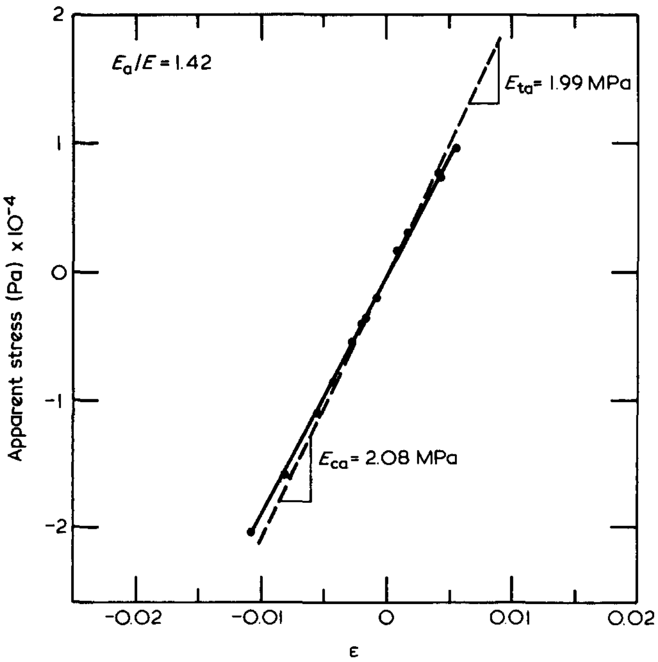

Figure 1 Apparent stress vs. strain for natural rubber crosslinked with 1 phr dicumyl peroxide, sample A. E_a/E determined from Messner's finite difference analysis[11]

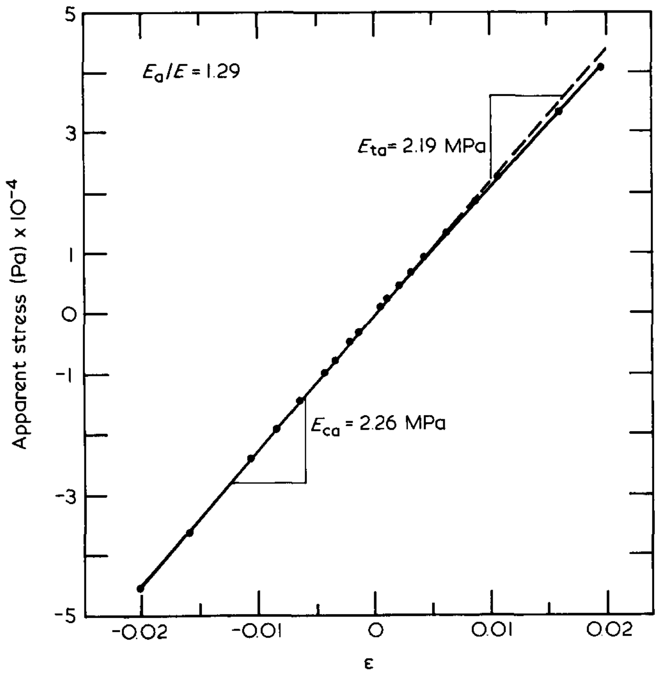

Figure 2 Apparent stress vs. strain for natural rubber crosslinked with 3 phr dicumyl peroxide, sample B

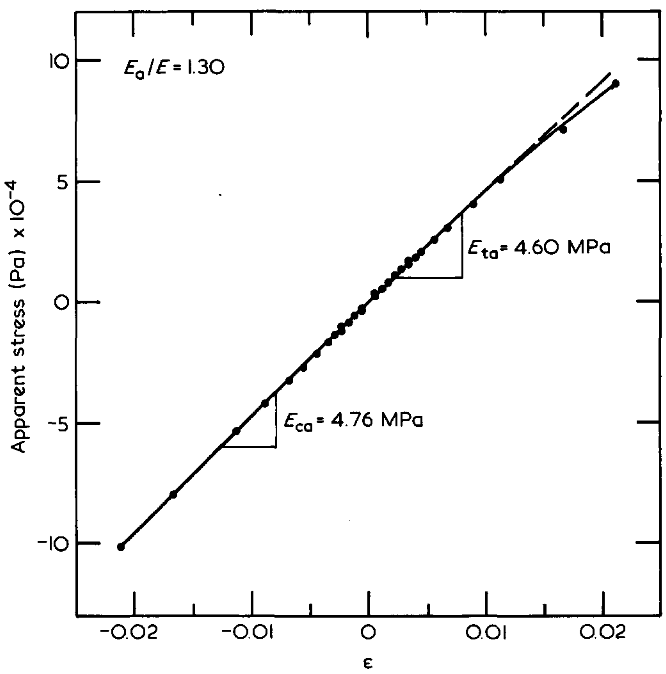

Figure 3 Apparent stress vs. strain for natural rubber crosslinked with 5 phr dicumyl peroxide, sample C

One aspect of presenting data as stress–strain plots is that small deviations from a straight line are not readily apparent, particularly at small deformations. One representation of the data which shows deviations of the material modulus from a constant value is a Mooney–Rivlin plot. In *Figures 4–6* plots of reduced stress *versus* strain are shown for the same data presented in *Figures 1–3*. The data are presented with $+\varepsilon$ to the left of zero and $-\varepsilon$ to the right, so that the plots take on the form of a conventional Mooney–Rivlin plot. The interesting result which can be seen in these plots is that, as the undeformed state is approached, the reduced stress increases significantly for all of the samples. (This result was unexpected.) In addition, these data also show that the reduced stress (modulus) in compression is greater than the reduced stress (modulus) in tension, if we extrapolate the data outside of the area where the reduced stress (modulus) increases rapidly. This is depicted by the short broken lines in the drawings.

We did not expect to find the modulus of the crosslinked natural rubber to increase as the undeformed configuration (zero strain) was approached. Since the data obtained on samples A–C were limited, we undertook to carry out further experiments to verify that the modulus indeed increases near the undistorted state. First, we moulded a sample with a greater aspect ratio and larger cross-sectional area (sample D). These actions had three

Table 3 Correction factor* for elastic modulus for finite length cylinders

Sample designation	Diameter/length	Correction factor*, E_a/E
A	1.661	1.42
B	1.301	1.29
C	1.347	1.30
D	0.354	<1.02
E	1.189	1.22

* Determined from Messner's[11] reported values which were based on a finite difference solution to the linear elastic boundary value problem for a cylinder with constrained ends. Correction factors were obtained assuming material incompressibility, i.e. Poisson's ratio = 0.50

Table 4 Comparison of elastic modulus, for extension and compression data on natural rubber with that calculated from torsion

Sample	*E*, extension (MPa)	*E*, compression (MPa)	*E* = 3*G** (MPa)
A	1.40	1.46	1.37
B	1.69	1.75	1.69
C	3.54	3.66	3.67

* Data from ref. 14

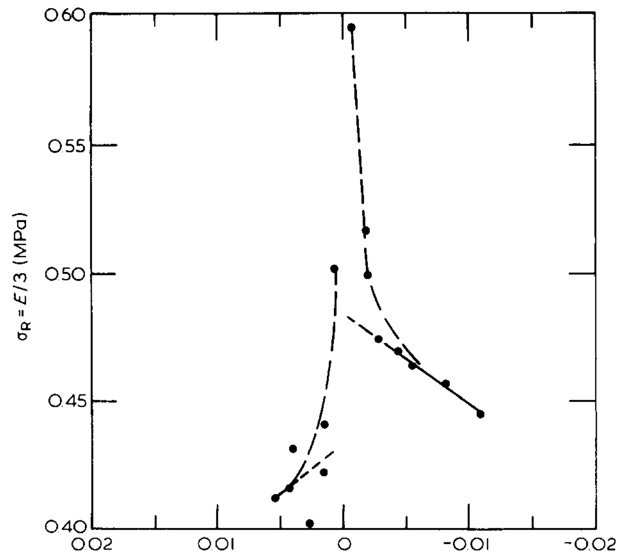

Figure 4 Reduced stress vs. strain for natural rubber crosslinked with 1 phr dicumyl peroxide, sample A. Broken lines represent linear extrapolation of data away from undistorted state

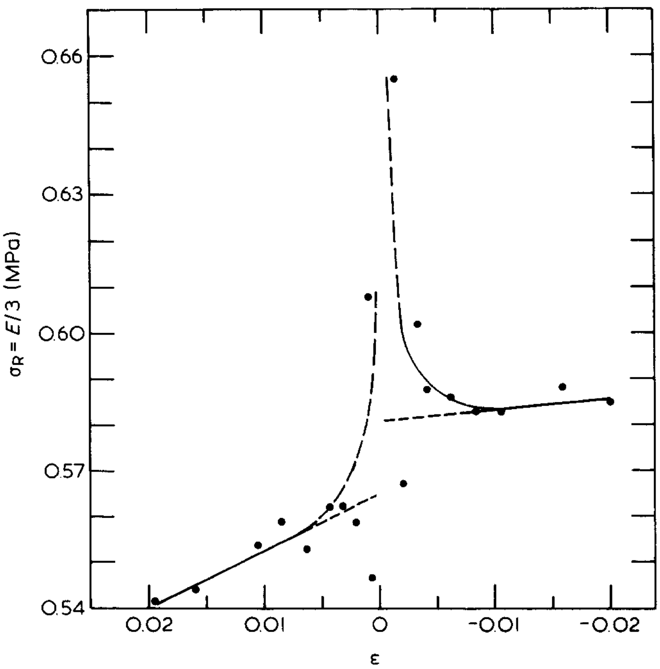

Figure 5 Reduced stress vs. strain for natural rubber crosslinked with 3 phr dicumyl peroxide, sample B

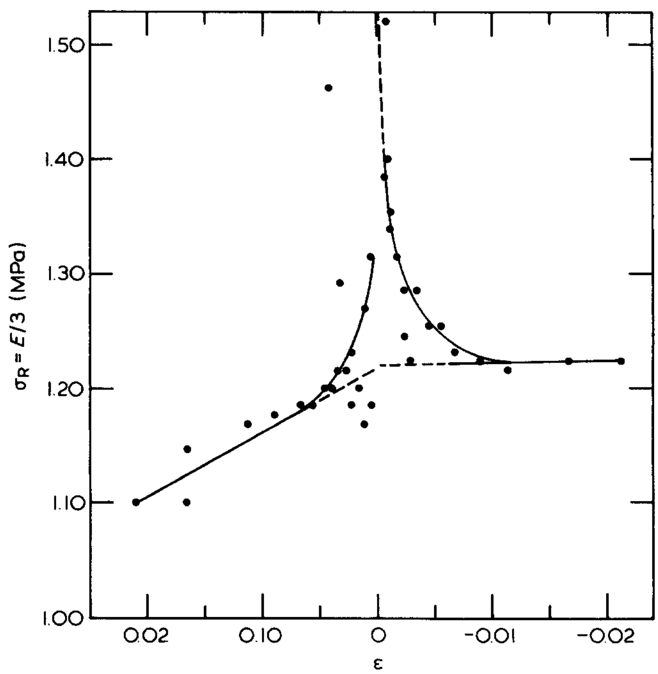

Figure 6 Reduced stress vs. strain for natural rubber crosslinked with 5 phr dicumyl peroxide, sample C

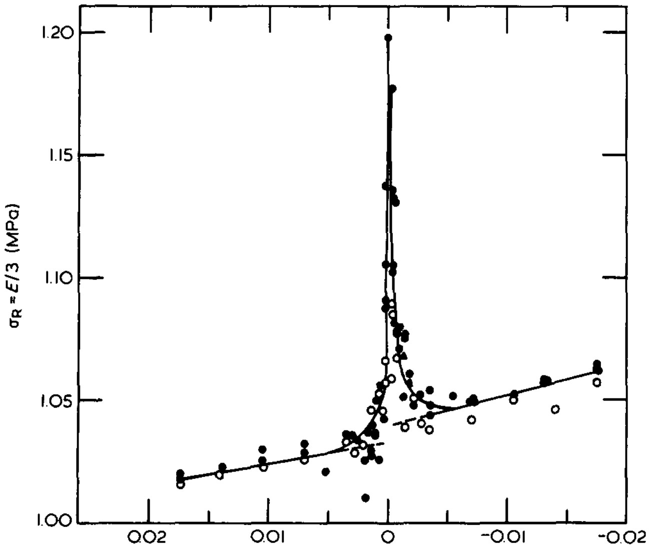

Figure 7 Reduced stress vs. strain for natural rubber crosslinked with 5 phr dicumyl peroxide, sample D. Filled symbols are for tests carried out using procedure I and open symbols for tests carried out using procedure II

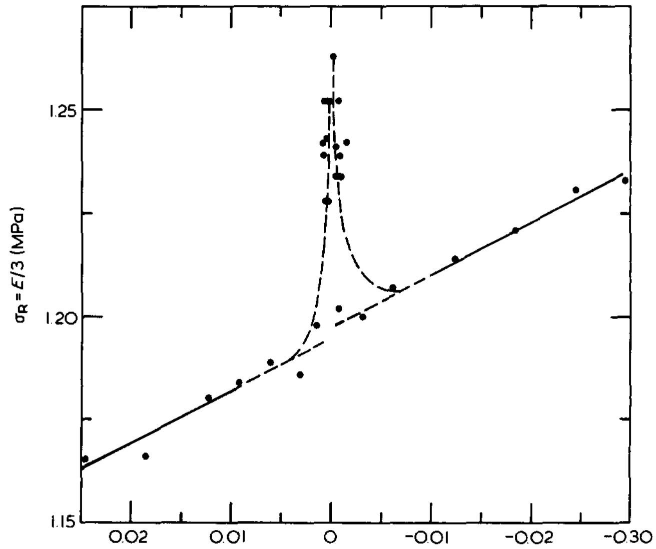

Figure 8 Reduced stress vs. strain for natural rubber crosslinked with 5 phr dicumyl peroxide, sample E

effects to improve the experimental accuracy. One was to increase the force required to achieve a given strain by increasing the cross-sectional area of the sample. Another was to increase the displacement required to achieve a given strain by increasing the sample length. Finally, by increasing the sample aspect ratio, any end effect would be made much smaller. As for this latter, although there is little reason to believe that constraining the cylinder ends could create an increase in apparent modulus as the undeformed state is approached, we felt that any such precautions as could be taken should be.

The second thing that we did was to mould a small sample (E) and make arrangements to test the sample on a different piece of mechanical testing equipment in order to assure ourselves that an unknown systematic error in the RDMS machine was not giving us an anomalous result. For this reason we conducted tests using a Dynastat testing machine. The configuration of the Dynastat is completely different from that of the RDMS and we felt that it would be highly unlikely that both the RDMS and the Dynastat would give the same spurious results. The only precaution we were unable to take was that of testing the same sample on the two test machines due to the fact that the samples fractured upon removal from the test fixtures.

In *Figures 7* and *8* the results for samples D and E are depicted in the form of reduced stress *versus* strain plots. As can be seen, as the undistorted configuration is approached, the reduced stress (modulus) increases for both materials. The broken lines also show that the tension and compression moduli of the rubbers are different at strains above approximately 10^{-3}.

The results presented above were quite unexpected. The data show that the compressive modulus is greater than the extensional modulus at strains $\gtrsim 10^{-3}$ and that as the undistorted state is approached both the tension and compression moduli increase. Explanations of this phenomenon are difficult to make. E. A. Kearsley of this laboratory has suggested that this may be due to the compressibility of the material becoming important at zero deformation[15]. It is also conceivable that the non-uniform deformation resulting from the cylinder ends being constrained could give this result. If, however, the high modulus values which occur near zero deformation are due to the constrained ends, it implies that in this boundary value problem the solution for a non-linear elastic material (rubber) does not converge to the linear elastic solution.

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REFERENCES

1 Wood, L. A. *J. Res. NBS* 1977, **82**, 57–63
2 Treloar, L. R. G. 'The Physics of Rubber Elasticity', 3rd Edn, Clarendon Press, Oxford, 1975
3 Treloar, L. R. G. *Trans. Faraday Soc.* 1944, **40**, 59–70; *Rubber Chem. Technol.* 1944, **17**, 813–825
4 Sheppard, J. R. and Clapson, W. J. *Ind. Eng. Chem.* 1932, **24**, 782; *Rubber Chem. Technol.* 1933, **6**, 126–150
5 Wolf, F. P. *Polymer* 1972, **13**, 347–354
6 VanderHoff, B. M. E. and Glynn, P. A. R. *J. Macromol. Sci. Chem. A* 1969, 3 (5), 991–1004
7 Blokland, R. 'Elasticity and Structure of Polyurethane Networks', Rotterdam University Press, Gordon and Breach, New York, 1968
8 Rivlin, R. S. *Q. Appl. Math.* 1956, **14**, 83–89
9 Rivlin, R. S. and Saunders, D. W. *Phil. Trans. R. Soc. London A* 1951, **243**, 251
10 Filon, L. N. G. *Phil. Trans. R. Soc. London A* 1902, **198**, 147–233
11 Messner, A. M. 'Stress Distributions in Poker-Chip Tensile Specimens', Aerojet-General Technical Paper, 127-SRP, September 1963
12 Gent, A. N. and Lindley, P. B. *Proc. Inst. Mech. Eng.* 1959, **173**, 111–122
13 Pickett, G. *J. Appl. Mech.*, A-176 to A-182, September 1944
14 McKenna, G. B. and Zapas, L. J. *Polymer* 1983, **24**, 1495 (preceding paper)
15 Kearsley, E. A. personal communication, June 1981