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Comparison of Stress-Strain Relations of Polybutadiene Vulcanizates in Compression and in Extension

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SUMMARY

According to elementary statistical theory of rubber elasticity, the modulus of rigidity $\tau/(\lambda - \lambda^{-2})$ is constant. The phenomenological theory predicts that this modulus is in first approximation equal to the sum of a constant ($2C_1$) and a deformation-dependent term, $2C_2$. The dependence on elongation of experimental modulus data of many elastomers agrees more or less with the C_2 term. Several attempts have been made to explain this dependence on the basis of molecular phenomena or by refinements of the statistical theory of elasticity. At present there is no consensus of opinion on the origin or interpretation of the deformation-dependent term. Almost all of the data on this dependence have been generated in extension experiments.

In this report accurate data are presented on the modulus of rigidity and its dependence on degree of deformation in compression. Because of its high ratio C_2/C_1 in extension, the polymer chosen for these measurements is cis-1,4 polybutadiene cross-linked quantitatively with decamethylene dismethylazodicarboxylate. It is found that at very small deformations the relation between compressive force and compression is best represented by a constant modulus of ridigity. This initial modulus is linearly related to the chemical cross-link concentration, as is the modulus in extension. However, the two relations differ. The modulus in compression is higher than that in extension for strongly vulcanized rubber and lower at low cross-link concentrations. Complex curves are obtained in Mooney-Rivlin plots to which no meaningful C_2 values can be assigned. In general, the modulus of rigidity increases somewhat with compression. At compression ratios approaching those at which the samples fail, the modulus increases more rapidly with compression. This phenomenon is comparable to the familiar upturn in the extension Mooney-Rivlin plot. The upturn in compression occurs at rather small deformations.

These observations are discussed in terms of the differences between changes in network topology on compression and those on elongation.

INTRODUCTION

According to elementary statistical theory of rubber elasticity the stress per undeformed cross sections τ is given by

$$\frac{\tau}{\lambda - \lambda^{-2}} = k[\nu]RT \tag{1}$$

Here λ is the extension or compression ratio (l deformed/l undeformed), $[\nu]$ is the concentration of elastically effective network chains, and k is a constant with a value of the order of unity. At small deformations the ratio in the left-hand side of Eq. (1) is equal to the shear modulus. For convenience this ratio will be referred to as the modulus of rigidity at any deformation.

It is well known that the experimental results obtained on elongation can be represented better by the relation

$$\frac{\tau}{\lambda - \lambda^{-2}} = 2C_1 + 2C_2\,\lambda^{-1} \tag{2}$$

than by Eq. (1). Here C_1 and C_2 are constants. Many refinements of Eq. (1) have been proposed to account for the dependence of the modulus of rigidity on the extension ratio. Over the last few years this subject has received renewed attention, and a number of reviews have been published recently [1-3].

Equation (2) is a simple form of the phenomenological relation between stress and strain developed from considerations of symmetry applied to an isotropic, incompressible, elastic continuum [4, 5]. This relation is called the Mooney-Rivlin equation (MR), and a graph of the modulus of rigidity versus the reciprocal deformation ratio is referred to as a Mooney-Rivlin plot.

It has been shown that neither relation (1) nor the MR equation satisfactorily describes the stress-strain behavior over the full range of elongations to which elastomers can be subjected without failure. At high extensions the assumptions underlying Eq. (1) are not valid. At small elongations up to 10–30% strain the modulus of rigidity is independent of deformation in accordance with Eq. (1) [3, 6]. In the region of about 70 to 300–500% elongation the MR equation best fits the experimental data, and approximate values of C_2 can be assigned to this elongation region. This parameter C_2 may be viewed as a measure of the deviation from the statistical theory. Its value is remarkably high for cis-1,4 polybutadiene [6], namely, about 3 and 20 times the C_2 values of cross-linked natural rubber and polydimethylsiloxane, respectively.

Because of this unexpectedly large deviation from the statistical theory for networks of very flexible polybutadiene chains ($T_g = -108°C$), it was considered worthwhile to conduct deformation experiments in compression on the same elastomer. Since the polymer is virtually incompressible in bulk, uniaxial compression is equivalent to biaxial extension.

EXPERIMENTAL

Polymer

The polybutadiene sample used is characterized by the following data: cis-1,4 content 92.8%; intrinsic viscosity in toluene at 30°C 3.57 dl/g; number average molecular weight 3.0×10^5 (calculated from the molecular weight distribution obtained by elution from a Baker-Williams column). This elastomer is the same as polybutadiene A used in the stress elongation measurement reported previously [6].

Vulcanization Procedure

The polybutadiene was cross-linked with decamethylene dismethylazodicarboxylate (DMDADC). This agent is believed to react quantitatively [7]. The melting point of the compound used was 38–39°C. It was kept at liquid nitrogen temperatures to prevent degradation. Because of the high reactivity of the curing agent it was dissolved in the polymer at -20°C by mixing precooled, etheral solutions of elastomer and DMDADC. The mixed solution was poured onto cold mercury. The solvent was evaporated at -20°C with dry nitrogen first at atmospheric pressure (3–4 days) and then at about 300 mm Hg pressure (2 days). Thus, sheets of polymer-agent mix about 1.5 mm thick were obtained. No cross-linking reaction had taken place during this preparation; the sheets were soluble in benzene. The vulcanization reaction was allowed to proceed by slowly warming to room temperature over a period of 2 days.

The chain concentration $[\nu]^*$ of the elastomer sheets was calculated from the stoichiometry of the vulcanization reaction with the aid of a relation reported in Ref. [8]. The asterisk indicates that in this calculation corrections for chain ends and sol content were applied. The swelling ratios in benzene and hexane were also determined. They fitted the curves of volume fraction of polymer in both solvents versus calculated chain concentration obtained for the samples previously prepared and described [6] except for the sheet with the lowest chain concentration. The DMDADC used to vulcanize this film had been stored at -10°C and appeared to have lost some activity. The chain concentration reported for this sheet was taken from the swelling ratios and the curves mentioned.

Samples

For the compression measurements, three or four disks 16 mm in diameter were punched out from the various polymer sheets. They were stacked to form a cylinder about 5–6 mm high. For the extension measurements, samples shaped like common commercial rubber bands were died out. Their circumference and width were 127 and 1.7 mm, respectively.

Apparatus

The apparatus used and the procedures followed to determine the properties of the elastomers in extension were the same as described before [6].

The instrument used to obtain the data in uniaxial compression is similar to the one described by Forster [9]. The essential parts are two stainless-steel plates, one fixed and the other movable by a screw mechanism. Each plate is perforated by 30 holes 0.1 mm in diameter leading to a chamber filled with silicone oil [Fluid 200, Dow Corning Silicones Ltd., viscosity 20 centistokes)]. The holes are evenly distributed over a circular area slightly smaller than the cross section of the samples.

The sample is placed between the perforated areas of the plates and compressed by moving one of the plates. Silicone oil is then forced under pressure through the holes, seeping evenly from between the sample surfaces and the compressing plates. This effectively eliminates friction between the elastomer and the plates, allowing uniform lateral expansion of the sample. The distance between the plates is measured with a precision of 0.002 mm by means of a dial micrometer.

The pressure in the oil chamber is regulated with gas from a cylinder of compressed nitrogen. The oil pressure is measured with a closed, helium-filled mercury manometer 340 cm high. With this instrument, pressures up to 15 atm can be recorded with a precision of about 2.5% at the lowest pressures recorded and rapidly increasing to negligible errors at high pressures.

Procedure

For compression measurements, the pressure in the oil chamber was raised quickly until oil started to seep from between sample and plates. A valve in the line admitting gas from the compressed nitrogen cylinder to the oil chamber was then closed. Seepage of oil continued, at first rapidly for about half a minute, due to the small excess of pressure imposed, and then slowly because of stress relaxation in the sample. Several pressure readings were taken during the relaxation process, including values at 2 and 10 min after the onset of oil seepage.

A strain cycle was followed identical to the stress cycle of the extension measurements reported earlier (Fig. 3 of Ref. [6] with "compression" instead of "force" as the ordinate variable). After each compression measurement lasting 10 min the sample was allowed to recover at atmospheric pressure for a period of 10 min. The strain cycle included repeated series of six measurements each at small compressions below maximum values varying from 5 to 8%. These series were used to determine the zero compression thickness (rest height) of the samples very accurately. The initial compression moduli were calculated from these series. It is believed that this strain cycle allows fast initial relaxation to take place and that it eliminates to a large extent the influence of long-time, slow relaxation processes.

Measurements continued until failure of the sample (highly cross-linked rubbers) or until the maximum safe pressure of the manometer was attained.

Results

Few accurate data have been published on uniaxial compression of elastomers. Three reports on the behavior of natural rubber are mentioned here. Treloar [10], Rivlin and Saunders [11], and Forster [9] found that the modulus of rigidity is independent of the degree of compression, in accordance with Eq. (1). The vulcanizates used by these authors had moduli of about 4, 4, and 6 kg/cm^2, respectively. In order to test our instrument and check the experimental procedure, a natural rubber sample was prepared by curing with DMDADC to a chain concentration of about 0.03 mole/liter. The results of the compression measurements of this specimen are shown in Fig. 1. In conformity with the earlier report on extension data, the reciprocal of the compression ratio is plotted along the abscissa as suggested by the MR equation. It is seen from Fig. 1 that the results confirm the independence of the modulus of rigidity on compression ratio up to very high deformations for this weakly cross-linked material.†

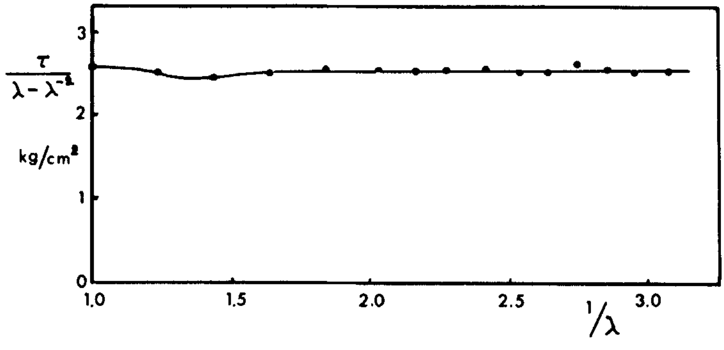

Fig. 1. Mooney-Rivlin plot for natural rubber in compression.

For the polybutadiene samples, however, the compression behavior is completely different. The MR plots markedly differ from the one shown for natural rubber. The results are depicted in Fig. 2. Several features are noteworthy.

(A) The curves deviate appreciably from the relations predicted by the statistical theory, Eq. (1), or by the phenomenological theory, Eq. (2). These differences are more complex than the deviations observed from these theories in elongation experiments. In compression, the deviations from the statistical theory are considerably smaller than those for extension. The shapes of the various lines preclude the assignment of meaningful MR C_2 values in contrast to the curves for elongation, which show linear sections albeit over limited regions of $1/\lambda$.

(B) The curves in Fig. 2 are similar in shape. The modulus of rigidity increases in the region of the lowest observable compression ratios, i.e., near the end of the curves. A corresponding increase in the modulus is observed in extension, where these upturns at high elongations are generally attributed

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†Preliminary results for more densely vulcanized natural rubber indicate a dependence of the modulus on compression at low and high deformations.

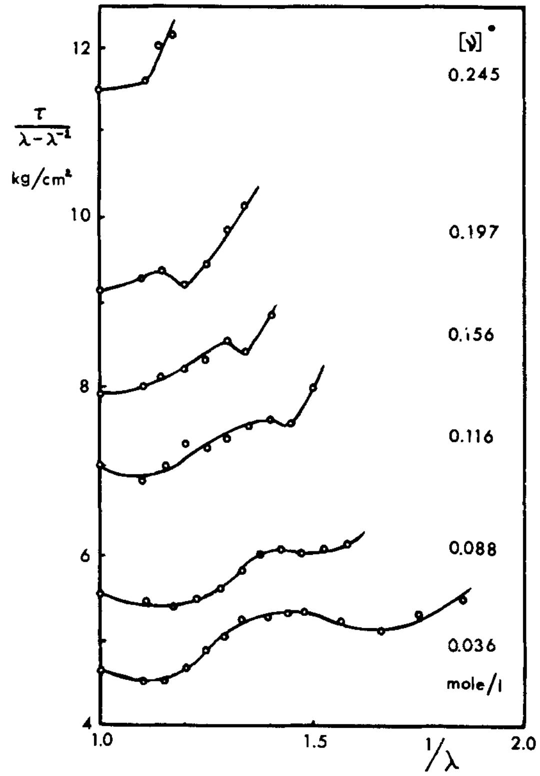

Fig. 2. Mooney-Rivlin plot for cis-1,4 polybutadiene in compression.

to a fraction of the network chains approaching their contour lengths. A similar phenomenon may be expected in compression. Because the networks are extended in two directions, the upturns occur at relatively low values of $1/\lambda$.

(C) A maximum and a minimum in the modulus values occur at compressions smaller than those corresponding to the upturns at the end of the curves. In Fig. 3, $1/\lambda_{max}$ and $1/\lambda_{min}$ are plotted versus the chain concentration of the vulcanizates. A consistent pattern is observed which lends credit to the belief that these extreme values reflect real phenomena and are not spurious results.

(D) All modulus values plotted are those calculated from pressure readings after 2 min of relaxation. Curves corresponding to 10-min relaxation times are very similar in shape to those shown. The 10-min values are

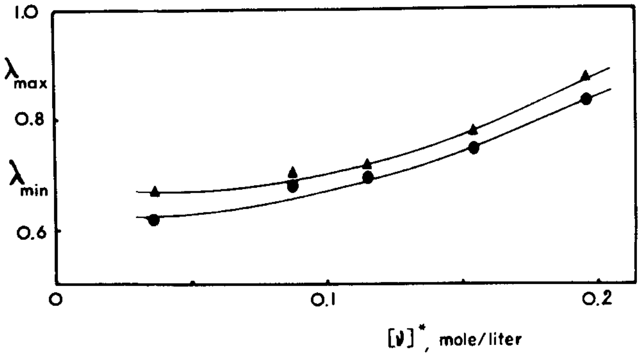

Fig. 3. Extension ratios λ_{max} and λ_{min} as a function of chain concentration.

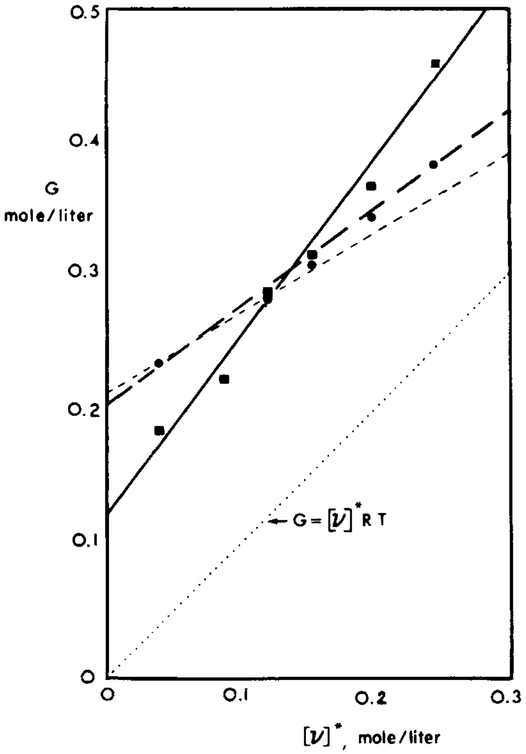

Fig. 4. Shear modulus as a function of chain concentrations. ■, in compression; ●, in extension;- - -, in extension from Ref. [6].

between 3 and 8% smaller than the 2-min values. For two vulcanizates (0.088 and 0.197 mole/liter) the initial modulus was measured with relaxation times of 10 min between subsequent compression increments instead of 2 min. The 10-min initial moduli were, respectively, 6.3 and 6.4% lower than the corresponding 2-min values.

(E) The initial shear modulus increases with network chain concentration. This dependence is shown in Fig. 4 together with the corresponding relation between shear modulus from extension measurements and chain density. The latter dependence agrees reasonably with the previously reported relation [6], which was derived from measurements on a different set of samples prepared from the same materials according to the same procedures as applied here. For easy comparison with chain concentrations, the modulus values have been expressed in units of RT(T = 298°K) and, therefore, have the dimensions of concentrations.

Table 1. Average Values of Standard Deviations from Least-Squares Lines in Percentage Elongation or Compression

Stress-strain relation	A	B	C	Ref.
Extension	0.034	0.025	0.024	[6]
Extension	—	—	0.025	This report
Compression	0.163	0.073	0.071	This report

The numerical results for the initial moduli are very sensitive to the value of the sample rest height or rest length. This dimension varies with the type of stress-strain relation used to extrapolate height or length to zero stress. Average values of the standard deviations from least-squares lines are listed in Table 1 for the following stress-strain relations assumed:

$$\text{A: } \tau \propto (\lambda - 1) \qquad \text{B: } \tau_a \propto (\lambda - 1) \qquad \text{C: } \tau \propto (\lambda - \lambda^{-2}).$$

Here τ_a is the force/cross section of the deformed specimen.

These values show that a high degree of accuracy has been achieved in compression, although the results are not quite as precise as those obtained in extension. As in the elongation experiments, the stress-strain relations B or C fit the data best. The rest heights of the samples used for further calculations of the data for the MR plots were computed using relation C.

DISCUSSION

With the present state of knowledge of network topology no detailed molecular interpretation can be offered for the complex shape of the MR curves. However, a few characteristics of these curves deserve comment.

The upturns at the ends of the curves reported here are not as steep as in the corresponding curves for elongation, and they occur at lower degrees of deformation in compression as compared with extension. These differences, which are possibly related, may result from fewer modes of adjustment of the forces acting on the cross-links or physical entanglements being available in two-dimensional extension than in uniaxial elongation.

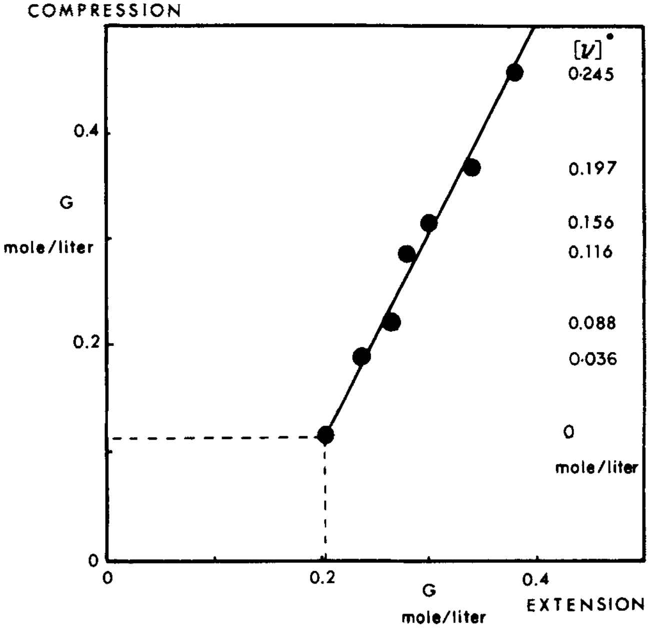

Fig. 5. Shear modulus in compression compared with shear modulus in extension.

A remarkable feature of the results reported here is the difference between initial shear moduli determined in compression and those measured in extension. In Fig. 5 a graphic comparison is made between the values of these two sets of moduli. The results shown include a set of values for $[\nu]^* = 0$. These data were obtained by extrapolation to the ordinate axis of the lines in Fig. 4 representing the relation between modulus and chain concentration. This extrapolation is physically unrealistic (no cross-linking; therefore, no equilibrium modulus; the polymer flows). However, extrapolation allows one to assign a value for the initial modulus at $[\nu]^* = 0$ to what is interpreted to be the concentration of all physical entanglements present in the uncured polymer. All or a fraction of these interloopings of chains are entrapped by the chemical cross-linking reaction and thus form a permanent feature of the vulcanizate networks.

If it is assumed that the elementary statistical theory is essentially correct, one would expect the concentration of elastically effective chains, and hence the initial modulus, to equal the sum of a constant (associated with entanglement concentration) and the concentration of chains calculated from, and proportional to, the amount of cross-linking agent. Figure 5 clearly shows that the type of deformation is another factor affecting the modulus. The apparently effective entanglement concentration at $[\nu]^* = 0$ from extension measurements seems to be about double that from compression experiments. It must be kept in mind that these concentrations have been obtained from the results of *deformed* networks. However, the degree of deformation was very small $[\pm(\lambda - 1)_{\max} < 5\text{-}8\%]$. It appears that on deformation, entanglements soon become effective, i.e., the interloopings appear to be so tight that even at small deformations the entanglement "points" act as cross-links due to the local friction preventing sliding of chains past one another.

The results displayed in Figs. 4 and 5 show that there is a discontinuity in modulus at $\lambda = 1$ where the type of deformation changes from extension to compression. The ratio $G_{\text{comp}}/G_{\text{ext}}$ varies from 0.6 to 1.4. Prins [12] also found differences between these two moduli. For polyurethanes at cross-link concentrations comparable to those of our samples, the above ratio is 1.8.

Among the many modifications and refinements of the statistical theory of elasticity put forward, there is one that predicts a discontinuity in modulus at $\lambda = 1$. Dobson and Gordon [13] have pointed out that the excluded volume effect allows more scope for lengthening of chain end-to-end vectors than for shortening them. The fraction $f(\lambda)$ of network chains whose vectors shorten on increasing the applied stress suffers a discontinuity at $\lambda = 1$. It can be calculated, from the expressions† for $f(\lambda)$ derived by these authors, that in extension $f(\lambda \to 1) = 0.58$ and in compression $f(\lambda \to 1) = 0.42$. It follows that at constant volume *more* end-

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†The conditions in Eqs. (20) and (21) of Ref. [13] should read $\lambda > 1$ and $\lambda < 1$, respectively.

to-end vectors *shorten* on slight extension than on slight compression of the sample. The combined effect of a higher resistance to shortening of chains than to their extension and the presence of a higher fraction of shortening chains on small elongations leads one to expect that the extension modulus should be higher than the compression modulus. The data presented here show that this is the case only at small cross-link concentrations. Therefore, either this explanation is not valid or other phenomena come into play for more densely cured samples.

One such phenomenon worth considering is that of engagement of entanglements of deformation. The probability of engagement depends on the direction of the end-to-end vectors of the entangled chains relative to the direction of deformation. If the movement of cross-links is approximately affine, the direction of deformation determines the deformed lengths of the end-to-end vectors of individual chains. The closer the direction of the end-to-end vector of a chain in the undeformed state approaches the direction of *extension*, the higher is the elongation of this vector on deformation, and the higher is the probability of entanglement engagement by or with this chain. When the end-to-end vector of the undeformed chain is perpendicular to the extension direction, the vector shortens on deformation and the probability of entanglement engagement is minimal.

The degree of orientation toward the direction of extension is shown in Fig. 6. The curves calculated from formulae reported by Treloar [14] represent the distribution of relative numbers of chain vectors N with angles θ with respect to the direction of *deformation* as a function of the angle Φ between chain vectors and the direction of *extension* both for 10% elongation ($\lambda = 1.1$; $\Phi = \theta$) and 10% compression ($\lambda = 0.9$; $\Phi = 90^\circ - \theta$). The curves in Fig. 6 show that the vector distribution in extension is much more concentrated around small values of Φ than that for compression. This is in agreement with the data shown in Fig. 5 at small chain concentrations where the modulus in extension is larger than the compression modulus.

Apart from the difference in the orientation distributions of chain vectors between elongated and compressed samples, there is a difference in the mode of movement of one chain end with respect to the other in the extension direction between elongating samples and those undergoing compression. In elongations, the distance between neighboring cross-link points on a single chain parallel to the extension direction increases proportional to λ in that *one* direction. However, on compression, the distance between points of chains in planes at right angles to

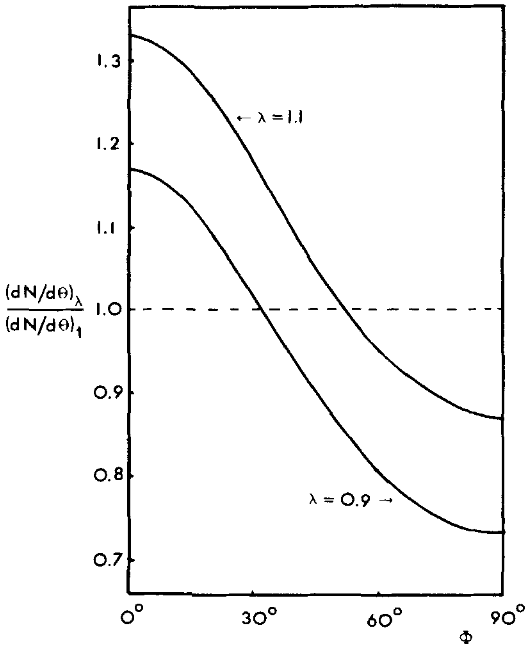

Fig. 6. Orientation distribution. N, relative number of chains; θ, angle between chain vector and direction of deformation; Φ, angle between chain vector and direction of extension.

the compressive force increases in *two* mutual perpendicular directions. It is speculatively suggested that this difference in the mode of movement of cross-link points with respect to one another also affects the probability of entanglement engagement; the probability being higher in compression than on extension. This effect probably becomes more important with decreasing size of the network chains and could account for the observation that the compression modulus increases faster with cross-link concentration than does the elongation modulus, as the data in Fig. 5 demonstrate.

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