# Orientation hardening of PVC

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True stress–strain relations for PVC under plane strain compression and under uniform extension in tension have been determined. In each case true stresses increase with strain as orientation hardening sets in. Attempts have been made to relate the orientation hardening process to three types of function: (1) a first order reaction process; (2) a power law function (after Bahadur); (3) Rivlin–Mooney stored energy relationships. Of these (1) fits the results only up to moderate extensions, (2) and (3) both give good linear graphs.

When a tough thermoplastic material is extended in a tensile test, the stress first rises in an approximately linear way, and then a point is generally reached when a shear band is formed which leads to 'necking'[1–3]. Because this process generates complex stress systems and localized heating in the neck[4,5], it is not easy to obtain a true stress–true strain relation in tension to characterize the deformation process. As a consequence it is difficult to measure the contribution of orientation hardening[6,3] to the post-yield behaviour. Only with the plasticized cellulose esters has it been possible to find relatively rigid materials which extend uniformly under tension[7], and these materials are not very typical thermoplastics.

Recently, however, we have been able to obtain PVC not only in a rather rigid condition but also in a state in which, at low or moderate strain rates, it is capable of uniform deformation in a tensile test. This may be achieved either by quenching a commercial rigid PVC sheet in iced water[8] or by the use of a small amount of plasticizer[9] together with tensile testing at low strain rates. In these cases it is possible to obtain meaningful true stress–true strain curves in tension which may then be compared with those obtained by other stress systems. Two examples of engineering curves for uniform tensile strain are given in *Figure 1*. Details of the material and methods used are given in the next section.

## EXPERIMENTAL

### *Materials*

*Rigid PVC.* The rigid PVC sheet used was a commercial grade described as Darvic 025 and manufactured by ICI Ltd. It was in the form of clear sheets of approximate thicknesses 1.0, 3.0 and 5.0 mm containing no plasticizer but including small amounts of stabilizer and lubricant. It had a relative density of 1.39, a glass transition temperature (d.s.c., 10°C/min) of 67°C, and ICI reported a Fikentscher[10] *K*-value of 55. It was isotropic in the plane of the sheet.

*Low plasticized PVC.* This plasticized PVC material in the form of sheets was specially prepared by Bakelite Xylonite Ltd. It is less plasticized than Velbex, the general commercial material. Its composition is made up of 17 parts/100 resin of DAP (dialphanyl phthalate) plasticizer, 1 part/100 resin of epoxy stabilizer and 1 part/100 resin of a liquid barium/cadium/zinc stabilizer system. It had a thickness of about 1.7 mm.

### *Tensile tests*

The uniaxial tensile test is the most widely used test for elucidation of mechanical properties of polymers. The tensile tests were carried out in an Instron Tester (floor model TT–BM) which directly plotted out the resultant load–elongation curve. This curve can be easily transformed into an engineering stress–strain curve.

In a normal tensile test the occurrence of necking leads to different values of stress and strain in different parts of the test-piece. However, in the case where the specimen continues to deform uniformly even after yield there is no basic difficulty in carrying out a precise stress–strain analysis. In tension, the definition of the engineering stress ($\sigma$) and engineering strain ($e$) are:

$$\sigma = F/A_0$$

and

$$e = (l - l_0)/l_0$$

also $\lambda$, the extension ratio, $= l/l_0$, where $A_0$ and $l_0$ are the

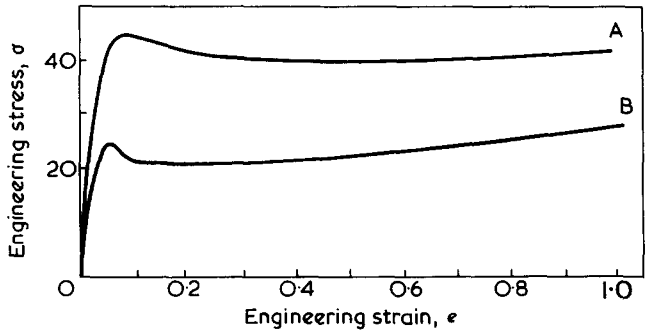

*Figure 1* Engineering stress–strain curve for PVC under uniform extension. A, Rigid quenched material (strain rate 0.5 $h^{-1}$); B, low plasticized material (strain rate 0.5 $h^{-1}$). Engineering stress ($\sigma$) vs. engineering strain ($e$) The slight fall in stress at yield is sufficient to induce necking

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original cross-sectional area and original length of the specimen, and $F$ and $l$ are the force and length of the same sample during deformation, respectively.

For true stresses ($S$) and true strains ($\epsilon$) assuming constant volume:

$$S = F/A = F/A_0 \times l/l_0 = \sigma(1 + e)$$

$$\epsilon = \int_{l_0}^{l} dl/l = \ln l/l_0 = \ln(l + e) = \ln\lambda$$

The true stress–true strain curves for a uniformly extending specimen can thus be obtained.

The tensile yield and drawing stresses for quenched PVC in tension increased with increasing time on keeping the test specimen at room temperature. Thus, as time goes on, the quenched material tends to revert to its original state to produce a structure of higher yield strength. The yield stress increases more rapidly than the drawing stress, which is not much affected probably because, as has been demonstrated with polycarbonate resin, a substantial amount of yielding has occurred and the initial structure is destroyed[11]. This reversion phenomenon could complicate the interpretation of the results obtained. However, as the time span of the longest experiment was less than 3 h and the engineering drawing stress does not vary by a meaningful experimental quantity over this time period, no correction to the tensile stress–strain data for quenched PVC was necessary. Another limitation to the use of quenched PVC is that the material only shows uniform extension in tension at moderate strain rates. Uniform extension is exhibited at strain rates less than 1 $h^{-1}$, diffuse necking occurs at strain rates between 1 and 50 $h^{-1}$, and thermal instability (necking rupture) sets in at strain rates greater than 100 $h^{-1}$.

Thus the two conflicting experimental complications mentioned above lead to the use of a very narrowly defined set of experimental strain rate conditions under which a detailed, uncomplicated study of post-yield stress–strain data can be obtained.

### *Plane strain compression*[12]

This system produces a definable strain system and area under load from which the true stress–true strain characteristics of polymers at high strains can be derived. Test specimens in the form of flat, rectangular sheets with parallel edges are compressed between two parallel flat polished dies. The dies are lubricated with 'Rocol', an invisible lubricant of a fluorocarbon telomer, to give minimal friction.

During the test, the Instron automatically traces a load–extension curve. To measure strain during loading, the readings of the dial gauges, which measure the relative displacement of the top and bottom dies were photographed against time using a pip-marker synchronized with the chart. Thus direct readings of load and specimen deflection were obtained. As the area of a test specimen under load should remain constant during the deformation, the distinction between nominal and true stresses should be unnecessary, but the large elastic strains in polymeric materials cause the ends of the deformed rectangular section of material to be bulged outwards, i.e. produces an increase up to 6% of the effective area on which the load acts. This 6% increase in effective area over which the load acts is associated with a maximum compressive strain of 0.75. It represents a minor limitation of the technique used and the effect was assumed to increase linearly with strain after the appearance of the minimum load on the plotted load–extension curve.

### *Measurements of yield stress*

Before discussing the behaviour of these polymers under post-yield conditions it would first be useful to record briefly the results obtained at yield. We measured yield stress as a function of strain rate under both modes of deformation, and the results can be used to assess the type of yield criterion to which the material is responding, according to the treatment of Bowden and Jukes[13]. These workers considered three yield criteria as applied to ideal plastic materials. These criteria result from a combination of the Von Mises and Tresca yield criteria with two forms of pressure dependence as given by Coulomb[14] and Schofield–Wroth[15]. One of the three criteria used is known as the modified Von Mises criterion which is given by:

$$(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 = 6K^2$$

where $K = C + \mu P$ and $P = -(\sigma_1 + \sigma_2 + \sigma_3)/3$; $C$ is the 'cohesion' and $\mu$ the 'coefficient of friction'.

The second criterion is known as the Mohr–Coulomb criterion. Mohr hypothesized that failure occurs when the shear stress on any plane in a material reaches a limiting value that is a function of the normal stress $\sigma_n$ on that plane. This is a generalization of the work of Coulomb who proposed:

$$\text{Maximum shear stress, } K = C - \mu\sigma_n$$

The third criterion is known as the modified Tresca criterion. It states that yielding occurs when the maximum shear stress exceeds a critical value. Combination with the pressure dependence criterion of Schofield and Wroth gives the modified Tresca criterion as:

$$\text{Maximum shear stress} = C + \mu P = K$$

Bowden and Jukes[13] related these three criteria under different stress fields to the coefficient of friction, $\mu$, which defines the sensitivity of yield stress to hydrostatic pressure. They found that $\mu = 0.11$ for Darvic rigid PVC at a strain rate of 7.3 $h^{-1}$. At this strain rate we estimated a yield stress of 71.0 $MN/m^2$ for plane strain compression and 51.8 $MN/m^2$ for tension giving a ratio of 1.37 which may then be compared with those predicted by the three different yield criteria examined by Bowden and Jukes (*Table 1*). The results are of course dependent on the appropriateness of using Bowden's value of $\mu = 0.11$ in the different formulae for yield criteria.

The results which favour the Von Mises criterion accord with previous work[16–18] and suggest that, apart from the elimination of necking, quenched PVC is not behaving very differently from other conventional rigid plastics.

### *Quantitative treatment of post yield behaviour*

Plastic materials always show a variation of yield stress and post-yield stresses with strain rate. This effect has been known for a long time and may be reasonably well represented by an Eyring viscosity equation. Taking a simple model in which yield shear stress ($\tau_y$) is given as the true tensile yield stress $S_y/2$ we can write at yield:

*Table 1* Yield criteria applied to quenched PVC ($\mu = 0.11$, ref 13)

| Criterion | Yield stress ratio (Plane strain compression/ simple tension ) |  | Experimental ratio |
|---|---|---|---|
|  | Formula | Ratio |  |
| Von Mises | $\frac{2(3^{1/2} + \mu)}{3(1 - \mu)}$ | 1.38 | 1.37 |
| Tresca | $\frac{3 + 2\mu}{3(1 - \mu)}$ | 1.21 | 1.37 |
| Mohr–Coulomb | $\frac{(1 + \mu^2)^{1/2} + \mu}{(1 + \mu^2)^{1/2} - \mu}$ | 1.24 | 1.37 |

*Table 2*

| Material | Quenched rigid PVC |  | Partly plasticized PVC |
|---|---|---|---|
| Activation (Eyring) volume, $V$(nm)$^3$ | Uniform extension<br>9.0 | Necking<br>5.2 | Untreated, uniform extension<br>7.4 |
| K(h$^{-1}$) | $1.0 \times 10^{-11}$ | $2 \times 10^{-6}$ | $2.0 \times 10^{-5}$ |

$$\dot{\epsilon}_y = K\exp(V\tau_y)/2kT = K\exp(VS_y)/4kT$$

whereby $\dot{\epsilon}_y$ is the true strain rate at yield, $V$ is a constant called the Eyring volume and $K$ a constant of proportionality. Under tension we obtained the results in *Table 2*.

The unquenched rigid material gave $V = 4.7$ nm$^3$ and $K = 5 \times 10^{-9}$ h$^{-1}$ in the necking mode.

From the complete stress–strain curves in tension we may obtain true stress–true strain curves of the type shown in *Figure 2a* and these constitute the basic data for studying the orientation hardening process. Following previous work[19,20], in which the slope of the log(rate of strain)–stress curve was found independent of the strain, it is possible to treat the effect of strain as a separate orientation hardening function. Three different ways of treating this process will now be considered.

The orientation hardening effect may also be compared for plane strain compression (*PSC*) and tension by correcting the crude result obtained in compression by the factor of 1.37 (above) and by extrapolating the strain rates to the same value as that used in tension (see *Figure 2b*).

### *Method I: first order reaction model*

According to this model the post-yield plastic deformation process (as distinct from the largely elastic deformation before yield) is associated with the exhaustion of deformable links. Since the number of such links present is limited, the plastic deformation should be bounded by a final ultimate deformation $\epsilon_\infty$ which can never be exceeded even at long times and high stresses. This treatment has been shown to behave in a generally similar way to that predicted by a model based on rubber elasticity theory at high strains (Langevin approximation[21]), which also requires there to be an absolute limit on the ultimate network strain.

In the theory of rubber elasticity this limit is related to the number of statistical units between crosslinks and, with thermoplastics, the entanglements between chains have been assumed to act in a similar manner to crosslinks.

In the simplied treatment used here the true Hookean strain assumed to be given by $S_y/E_y$ where $E_y$ is the Young's modulus given by the initial slope of the stress–strain curve is subtracted to give the plastic viscous strain $\epsilon_v$ and $S_y$ is the true yield stress. Then:

$$\frac{\mathrm{d}\ln(1 + \epsilon_v)}{\mathrm{d}t} = \dot{\epsilon}_v = K\exp(VS/4kT)F(\epsilon)$$

where according to the proposed treatment $F(\epsilon)$, the orientation hardening function, is given by: $\epsilon_\infty - \epsilon_v/\epsilon_\infty$.

A plot of the experimental values of $F(\epsilon)$ against $\epsilon_v$ is given in *Figure 3* for plasticized and quenched PVC in tension. It will be seen that the $F(\epsilon)$ falls in a linear way with $\epsilon_v$ only in the first part of the curve and that at higher strains significant strain rates are observed when zero rates would be predicted by the model. Thus, although the model may be used to describe behaviour at moderate strains, it does not perform very well at the highest strains, an observation which has already been noted in the previous work[7]. On the other hand, the curves which are obtained may be regarded as defining the function $F(\epsilon)$. Clearly in the real material the number of deformable links does not fall to zero in accordance with the simple linear model proposed which, for example, takes no account of the distribution of chain lengths between entanglements.

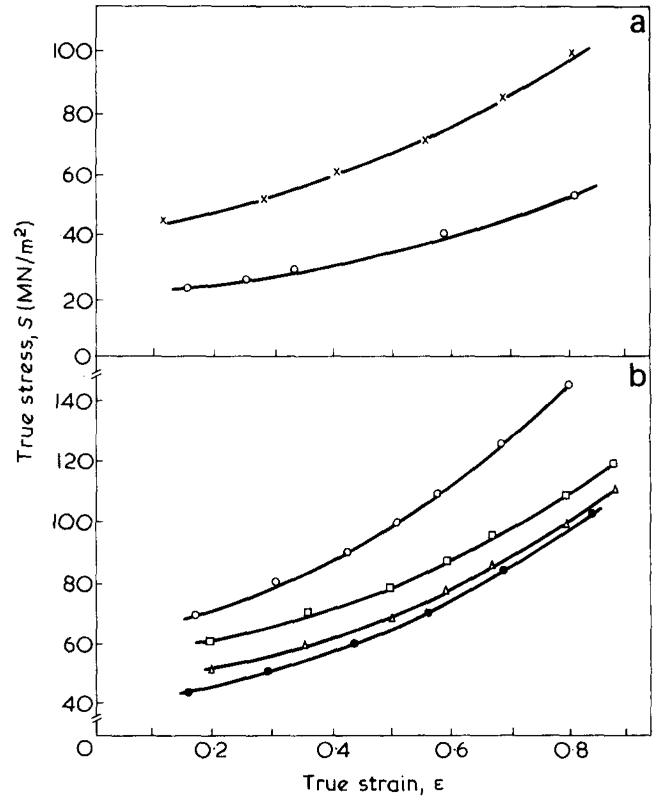

*Figure 2* (a) True stress–true strain curves for quenched and low plasticized PVC in tension. x, Rigid quenched; ○, low plasticized. True stress ($S$) vs. true strain ($\epsilon$). (b) Measurements in plain strain compression compared with unixial tension. True stress ($S$) vs. true strain ($\epsilon$). ○, Uncorrected experimental plain strain compression curve; □, as above corrected by factor of 1.37; △, same corrected to strain rate 0.5 h$^{-1}$; ●, experimental tensile curve at initial strain rate of 0.5 h$^{-1}$

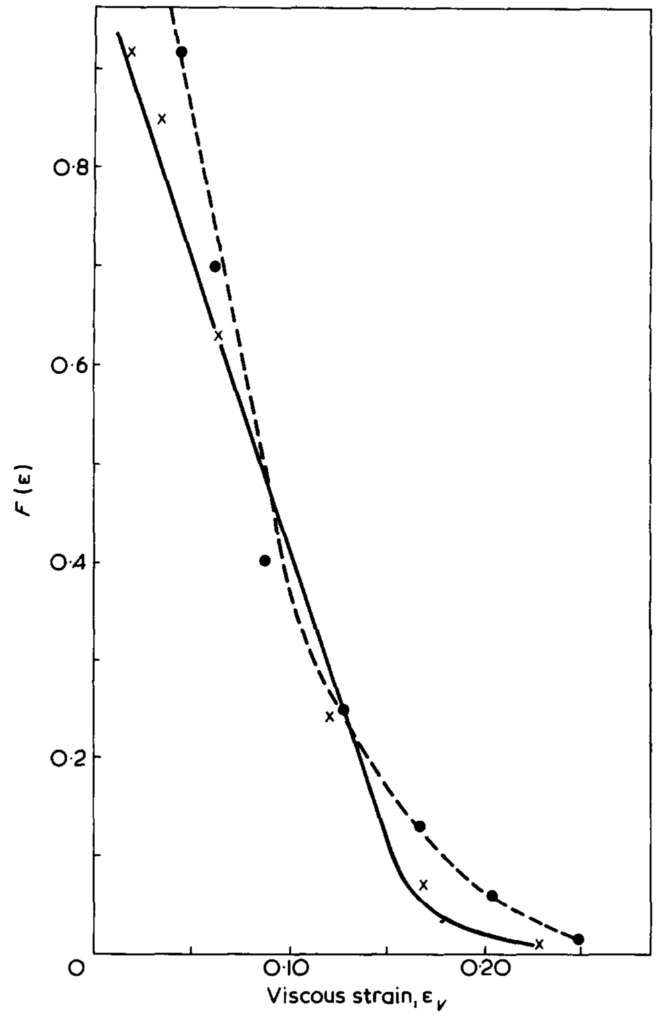

*Figure 3* Application of 1st order rate model to the orientation hardening of PVC in tension. x, Rigid quenched; O, low plasticized. $F(\epsilon)$ vs. viscous strain = $\epsilon_v = (\epsilon - \epsilon_h)$ where $\epsilon_h$ is the reversible 'Hookean' strain

In this treatment the Hookean strain is subtracted from the total strain since the model is theoretically' assumed to apply only to the plastic part of the deformation.

### *Method II: empirical equation of Bahadur*[22]

This equation has no pretensions to theoretical significance but follows much experience in the metals field. It uses a straightforward logarithmic relation of the type:

$$S = S_0 e^{m\epsilon}$$

where $S_0$ and $m$ are constants. Hence:

$$\ln S = \ln S_0 + m\epsilon$$

Further, since the equation is linear in $\epsilon$ and is applied only at relatively high extensions (e.g. above 0.2) the awkward requirement to correct for Hookean deformations is avoided. Typical curves for quenched and plasticized PVC in tension are given in *Figure 4,* from which it is clear that the Bahadur treatment can be applied successfully to our results.

### *Method III: application of Rivlin–Mooney equation for orientation hardening*

The post-yield region of the true stress–true strain curves for quenched PVC in unaxial tension and plane strain compression were next investigated in terms of an analogous rubber elasticity strain. This covers purely the orientation hardening function while the viscous part is represented by the intercept. With a rubber, where the viscosity is small, stress–strain plots of this type normally pass through the origin.

The Rivlin–Mooney[23,24] treatment of rubber elasticity considers the importance of the stored energy function. This function must be symmetrical in $\lambda_1$, $\lambda_2$ and $\lambda_3$ if the material is considered to be isotropic. Also, as the stored energy is unaltered by a change of sign of two of the lambda values (corresponding to a rotation of the deformed body through 180°), the stored energy must depend only on the even powers of $\lambda$. The stored energy can be expressed in terms of the strain invariants:

$$I_\lambda = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$$

$$II_\lambda = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_1^2\lambda_3^2$$

$$III_\lambda = \lambda_1^2\lambda_2^2\lambda_3^2$$

For an incompressible material then $III_\lambda = 1$ and thus:

$$II_\lambda = \frac{1}{\lambda_1^2} + \frac{1}{\lambda_2^2} + \frac{1}{\lambda_3^2}$$

When the stored energy function is known, the stress–strain relationship for any type of deformation mode can be determined.

For simple uniaxial tension:

$$\lambda_1 = \lambda \quad \text{and} \quad \lambda_2 = \lambda_3 = \frac{1}{\lambda^{1/2}}$$

Thus:

$$II_\lambda = 2\lambda + \frac{1}{\lambda^2}$$

and

$$I_\lambda = \lambda^2 + \frac{2}{\lambda}$$

The stored energy function, $W$, is given by:

$$W = W_I + W_{II}$$

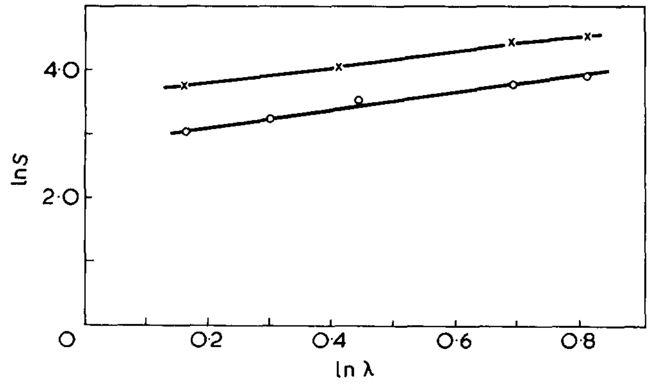

*Figure 4* Use of Bahadur equation (22) for large strain extension. $\ln S$ vs. $\ln\lambda(=\epsilon)$; Strain rate 0.5 $h^{-1}$. x, Quenched; O, low plasticized

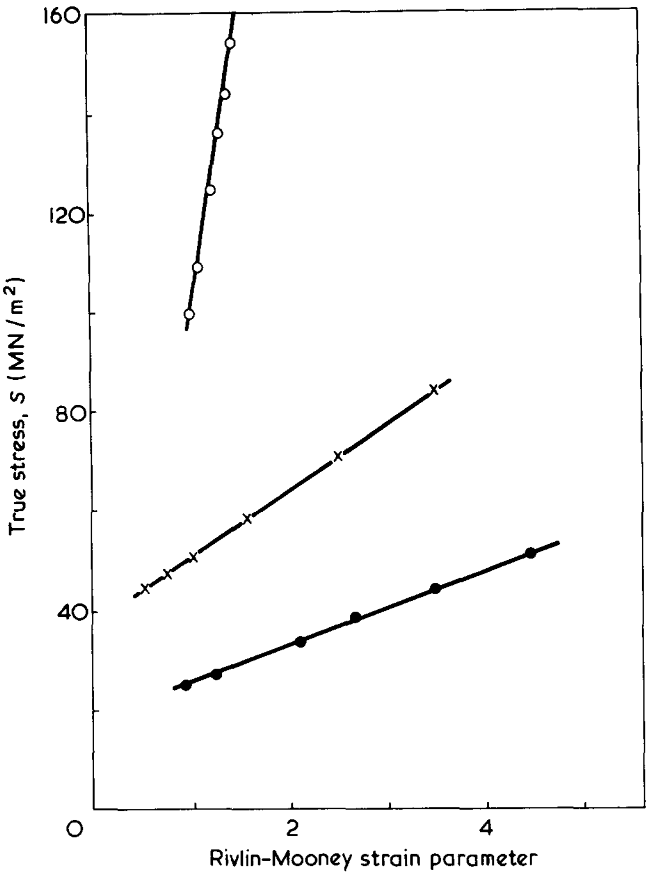

***Figure 5*** Use of the Rivlin–Mooney equation for the orientation hardening of PVC. True stress is plotted against the Rivlin–Mooney strain parameter (see text). ○, Rigid quenched PVC in plane strain compression; x, rigid PVC in tension; ●, plasticized PVC in tension. (At lower parameter values all plots show non-linearity)

where

$$W_{\mathrm{I}} = K_{\mathrm{I}}(\mathrm{I}_\lambda - 3) = K_{\mathrm{I}}\left(\lambda^2 + \frac{2}{\lambda} - 3\right)$$

and

$$W_{\mathrm{II}} = K_{\mathrm{II}}(\mathrm{II}_\lambda - 3) = K_{\mathrm{II}}\left(2\lambda + \frac{1}{\lambda^2} - 3\right)$$

(The quantity –3 is introduced in order that $W$ shall vanish in the unstrained state). Thus:

$$W = K_{\mathrm{I}}\left(\lambda^2 + \frac{2}{\lambda} - 3\right) + K_{\mathrm{II}}\left(2\lambda + \frac{1}{\lambda^2} - 3\right)$$

If $\sigma$ is the applied force/unit area of unstrained cross-section then $\sigma = \mathrm{d}W/\mathrm{d}\lambda$ and thus:

$$\sigma = 2K_{\mathrm{I}}\left(\lambda - \frac{1}{\lambda^2}\right) + 2K_{\mathrm{II}}\left(1 - \frac{1}{\lambda^3}\right)$$

In terms of true stresses:

$$S = \sigma\lambda = 2K_{\mathrm{I}}\left(\lambda^2 - \frac{1}{\lambda}\right) + 2K_{\mathrm{II}}\left(\lambda - \frac{1}{\lambda^2}\right)$$

For plane strain compression:

$$\lambda_1 = \lambda, \lambda_2 = \frac{1}{\lambda} \quad \text{and} \quad \lambda_3 = 1$$

Thus:

$$\mathrm{I}_\lambda = \mathrm{II}_\lambda = \lambda^2 + \frac{1}{\lambda^2} + 1$$

Therefore

$$W = (K_{\mathrm{I}} + K_{\mathrm{II}})\left(\lambda^2 + \frac{1}{\lambda^2} - 2\right)$$

In terms of true stresses:

$$S = 2(K_{\mathrm{I}} + K_{\mathrm{II}})\left(\lambda - \frac{1}{\lambda^3}\right)$$

We then applied these equations to our own results.

In tension it would be necessary to know both $K_{\mathrm{I}}$ and $K_{\mathrm{II}}$ in order to plot the Rivlin–Mooney relations correctly. However, the quantity $[\lambda^2 - (1/\lambda)]$ always exceeds $[\lambda - (1/\lambda^2)]$ in our experiments and becomes increasingly greater at high strains. Further, the results of rubber elasticity studies (ref 21 pp. 125–127) show that $2K_{\mathrm{I}} \sim 1.0$ and $2K_{\mathrm{II}} \sim 0.1$ for tension. We therefore made the approximation of using only $[\lambda^2 - (1/\lambda)]$ for tension and this gave a satisfactory linear plot (*Figure 5*).

In plane strain compression, a plot of true stress against the strain parameter $[\lambda - (1/\lambda^3)]$ also resulted in a linear graph. The tensile and compressive graphs both show non-linearity at the lower strain parameters in the region of slight strain softening. Both types of plots are shown in *Figure 5* for quenched PVC and plasticized PVC.

## CONCLUSIONS

Three different types of orientation hardening function have been evaluated in relation to true stress–strain measurements with quenched PVC and in certain cases with slightly plasticized PVC.

Of these relationships the Bahadur power law model and the Rivlin–Mooney relations are the most satisfactory. The first order rate model (and by implication also the Langevin rubber elasticity model) is satisfactory only at moderate elongations. Both the other relations fit the experimental data. The power law equations, though of interest for their analogy with metals, are purely empirical. However this limitation does not apply to the Rivlin–Mooney relations which are related to the basic stored energy functions for rubber-like systems. We believe that the further investigation of this type of treatment would be of value.

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