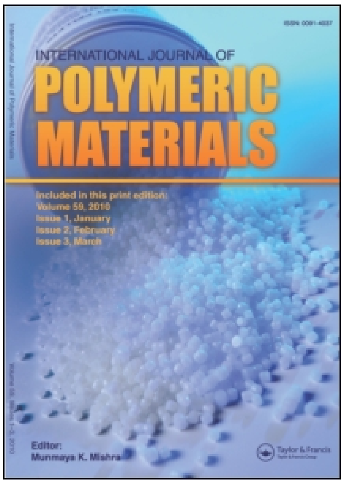

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The Elastic Constants of a Swollen Vulcanizate

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The Elastic Constants of a Swollen Vulcanizate

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For certain other purposes, it has been found necessary to determine the stress–elongation ratio curve of a vulcanizate swollen to equilibrium in a solvent, and to estimate the lateral deformation as a function of the longitudinal stretch. The true stress in a highly elastic body at large extension ratios is very different from the nominal stress, based on the original cross-section, because the lateral dimensions become very markedly different from their initial values. In a swollen elastomer in equilibrium with the swelling solvent, the situation is complicated by the fact that under hydrostatic tension or compression, the vulcanizate will absorb or reject solvent and this will affect both the length and cross-section under load.

Our considerations are based on an earlier paper derived by one of us.[1] An error has been found in Eq. (9b) of that paper, in which two subscripts were switched, and the expression for the stress developed in a tensile specimen of swollen vulcanizate at equilibrium with its swelling solvent should read:

$$\sigma_{11} = (\lambda_1{}^2 v_2/v_{20} - \lambda_1{}^{-1}) C_{\mathrm{dry}} v_2{}^{1/3} \tag{1}$$

We may replace C_{dry} by its value and obtain

$$\frac{\sigma_{11}}{RT} = \frac{\gamma}{M_c} (\lambda_1{}^2 v_2/v_{20} - \lambda_1{}^{-1}) v_2{}^{1/3} \tag{2}$$

Here σ_{11} is the true stress due to a longitudinal extension ratio λ_1, γ is the density, M_c the average molecular weight between crosslinks of the vulcanizate, v_2 the volume ratio of dry elastomer in the swollen vulcanizate, and v_{20} the value of v_2 for isotropic pressure (p) of zero. If the stress tensor is divided into its deviatoric and isotropic components, we have

$$\sigma_{11} = 3p \tag{3}$$

Simultaneously, Flory's[2] relationship holds, so that

$$\frac{\sigma_{11}}{RT} = \frac{3p}{RT} = 3\left(\frac{\gamma}{M_c}\right)\left(\frac{\nu_2}{2} - \nu_2^{1/3}\right) - \frac{3}{V}[ln(1-\nu_2)+\nu_2+\mu\nu_2^2] \tag{4}$$

Equations (2) and (4) may be easily solved for σ_{11} and λ_1 in terms of ν_2. Where the stress is referred to the original cross-section, we have

$$\frac{f_{11}}{RT} = \frac{1}{\lambda_1\nu_2^{1/3}}\left(\frac{\sigma_{11}}{RT}\right) = \frac{\gamma}{M_c}(\lambda_1\nu_2/\nu_{20} - \lambda_1^{-2}) \tag{5}$$

These results are plotted in Figure 1, and compared, on the same axes, to the behaviour expected of an elastomer of the same modulus at zero stretch but for which no exchange of solvent with its surroundings takes place.

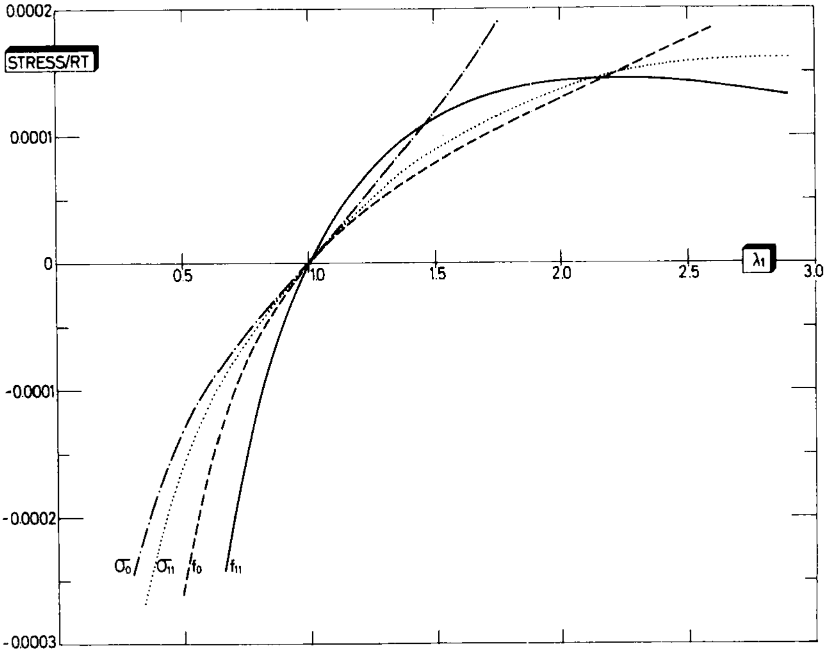

FIGURE 1 Uniaxial stress–elongation ratio curves for SBR vulcanizate (M_c = 6135) swollen in benzene. σ_{11} and f_{11} are based on the actual and original cross-sections respectively for straining during which the solvent absorbed is always in equilibrium with surrounding solvent. Subscripts 0 are for the situation in which the absorbed solvent remains constant at the unstrained level.

The parameter corresponding to Poisson's ratio is given by

$$m_{12} = \frac{\sqrt{(\nu_{20}/\nu_2\lambda_1)} - 1}{\lambda_1 - 1} \tag{6}$$

and is plotted in Figure 2, where it is compared to the behaviour of an incompressible elastic solid, for which $m = -\dfrac{\lambda_1^{-1/2} - 1}{\lambda_1 - 1}$.

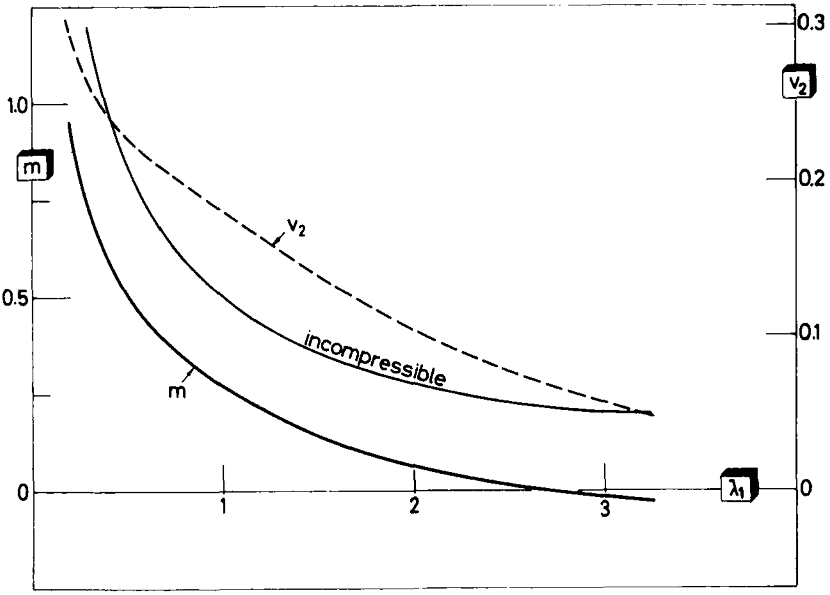

FIGURE 2 "Poisson's ratio" (m_{12}) for swollen SBR vulcanizate, and volume fraction of polymer in strained specimen at equilibrium. "Poisson's ratio" for an incompressible solid is also shown.

DISCUSSION

As the sample is pulled, it is subjected to a hydrostatic isotropic tension which allows the absorption of increasing quantities of solvent. This effect is well demonstrated by the comparison of σ_{11} and σ_0, or of f_{11} and f_0 in Figure 1.

For incompressible materials, if the stress is referred to the initial cross-section rather than the actual cross-section, a lower value is obtained (compare f_0 with σ_0). In the case of the swollen vulcanizate, however, the expansion of the cross-section and the softening do not follow the same laws, and the comparison of the curves for σ_{11} and f_{11} is not as simple. It will be seen that, if such distortions were at all possible, f_{11} actually passes through a maximum. This would indicate a type of instability which, to our knowledge, has never been observed.

All calculations were based on the system $V_1 = 87$, $\gamma = 0.96$, $\nu_{20} = 0.18$, $M_c = 6135$ and $\mu = 0.37$.

References

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2. P. J. Flory, *Principles of Polymer Chemistry*, p. 578, Cornell U.P. (1953).