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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 crosssection, 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.<sup>1</sup> 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:

$$\sigma_{11} = (\lambda_1^2 \nu_2 / \nu_{20} - \lambda_1^{-1}) C_{dry} \nu_2^{1/3}$$
(1)

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

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

Here  $\sigma_{11}$  is the true stress due to a longitudinal extension ratio  $\lambda_1$ ,  $\gamma$  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<sup>2</sup> relationship holds, so that

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

Equations (2) and (4) may be easily solved for  $\sigma_{11}$  and  $\lambda_1$  in terms of  $\nu_2$ .

Where the stress is referred to the original cross-section, we have

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

30

The parameter corresponding to Poisson's ratio is given by

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

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



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  $\sigma_{11}$  and  $\sigma_0$ , or of  $f_{11}$  and  $f_0$  in Figure 1.

For incompressible materials, if the stress is referred to the initial crosssection rather than the actual cross-section, a lower value is obtained (compare  $f_0$  with  $\sigma_0$ ). 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  $\sigma_{11}$  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  $V_1 = 87$ ,  $\gamma = 0.96$ ,  $v_{20} = 0.18$ ,  $M_c = 6135$  and  $\mu = 0.37$ .

### References

- 1. Z. Rigbi, Int. J. Eng. Sci. 7, 1163 (1969).
- 2. P. J. Flory, Principles of Polymer Chemistry, p. 578, Cornell U.P. (1953).