$\overline{r_{fp}^2}$	Mean square end-to-end distance of the chains of component p in the free state
$\overline{r_{fr}^2}$	Mean square end-to-end distance of freely rotating chains
$\overline{r_\Theta^2}$	Mean square end-to-end distance of unperturbed chains
A	Cross-sectional area of swollen rubber
E	Young's modulus of swollen rubber
E_0	Young's modulus of unswollen rubber
L	Length of swollen rubber
L_1	Unstrained length of swollen rubber
M_n	Number-average molecular weight
M_v	Viscosity-average molecular weight
N_p	Number of chains of component p
P_p	Degree of polymerization between cross-links of pth component
PAA	Poly(acrylic acid)
PVA	Poly(vinyl alcohol)
ΔS	Entropy of deformation of the swollen network due to external strain
ΔS_0	Entropy of deformation due to swelling
$\Delta S_0'$	Entropy of deformation due to both swelling and external strain
$\Delta S_p'$	Entropy of deformation of component p due to both swelling and external strain
V	Volume of swollen rubber
V_1	Unstrained volume of swollen rubber
V_r	Volume fraction of polymer
λ_i	Extension ratio of the *i*th coordinate of the swollen network due to external strain
δ	$(\overline{r_\Theta^2}/\overline{r_{fr}^2})^{1/2}$

Volume Change Accompanying Rubber Extension

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ABSTRACT: A new equation for the volume dilation accompanying rubber extension is obtained from a reinterpretation of the kinetic theory equation for rubber elasticity. This equation is shown to describe published volume-extension data better than either that derived from simple kinetic theory or that derived from the Mooney–Rivlin equation.

Beginning with the thermodynamic identity

$$(\partial f/\partial p)_{T,L} = (\partial V/\partial L)_{T,p} \tag{1}$$

and making use of the equation of state for rubber elasticity[1]

$$F = NkT\frac{\langle r^2\rangle_0}{\langle r_f^2\rangle}[L/L_0 - (L_0/L)^2V/V_0] \tag{2}$$

one can derive the following expression for the volume change accompanying rubber extension[2,3] (provided that $\langle r_f^2\rangle$ is considered independent of volume).

$$\Delta V/V_0 = KNkT(\langle r^2\rangle_0/\langle r_f^2\rangle)[1 - \alpha^{-1}] \tag{3}$$

In eq 1, f is the force required to maintain the network at length L. In eq 2, $F = f/A_0$, where A_0 is the unstretched cross-sectional area; L_0 and V_0 are the length and volume at zero force and zero pressure; V is the volume at length L; N is the number of network chains per unit volume of the unstretched sample; k is Boltzmann's constant; T is the absolute temperature; $\langle r^2\rangle_0$ is the mean-square end-to-end distance of the network chains at volume V_0 and length L_0; and $\langle r_f^2\rangle$ is the mean-square end-to-end distance the network chains would assume, at length L and volume V, if the cross-links were removed. In eq 3, K is the isothermal compressibility and $\alpha = L/L_0$.

Recent work by Christensen and Hoeve[4] indicates that eq 3 predicts $\Delta V/V_0$ well for α close to unity, but at higher extensions greatly underestimates $\Delta V/V_0$. To obtain eq 3, it is assumed that $\langle r_f^2\rangle$ is independent of the sample volume; however, if we allow $\langle r_f^2\rangle$ to depend on V (since it is in fact evaluated in the stretched state of length L and volume V) we obtain from eq 1 and 2

$$\Delta V/V_0 = KNkT\int_1^\alpha \frac{\langle r^2\rangle_0}{\langle r_f^2\rangle}\left[\frac{\gamma(\alpha^3 - 1) + 1}{\alpha^2}\right]d\alpha \tag{4}$$

where $\gamma = (d \ln \langle r_f^2\rangle/d \ln V)_{T,L}$. Assuming γ to be independent of α, we obtain

$$\Delta V/V_0 = KNkT[1 - (1/\alpha) + (\gamma/2)(\alpha^2 - 3 + 2/\alpha)] \tag{5}$$

The differential form of this equation was given in ref 1. The volume-extension data of Christensen and Hoeve for three nautral rubber vulcanizates are shown in Figures 1–3; from these figures it can be seen that eq 5 fits the data very well in each case. For the two unswollen vulcanizates the values of γ giving best fit are approximately the same (0.26 for the 10-min cure and 0.28 for the 40-min cure), whereas a significantly lower value of γ gives the best fit for the swollen vulcanizate (0.20 for the 15-min cure swollen 212% in xylene). γ reflects the dependence of $\langle r_f^2\rangle$ on volume or pressure; since this dependence would arise from changes in intermolecular interactions, the lower value of γ found for the swollen sample is in accordance with the fact that the importance of interactions between chains decreases with swelling.

It is of interest to determine to what extent the failure of eq 3 to describe $\Delta V/V_0$ as a function of α may be due to the failure of eq 2 to describe F as a function of α. If the sample is assumed to undergo an isotropic deformation from volume V_0 to V followed by a uniaxial extension at constant volume to length L, the treatment of Van der Hoff[5] yields the following Mooney–Rivlin-type expression in which the volume dilation is taken into account

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(5) B. M. E. Van der Hoff, *Polymer*, 6, 397 (1965).

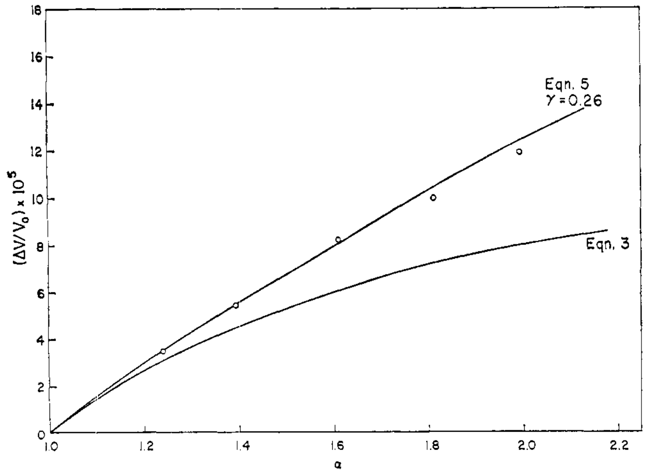

Figure 1. $\Delta V/V_0$ *vs.* α for the 10-min cured natural rubber sample of Christensen and Hoeve.

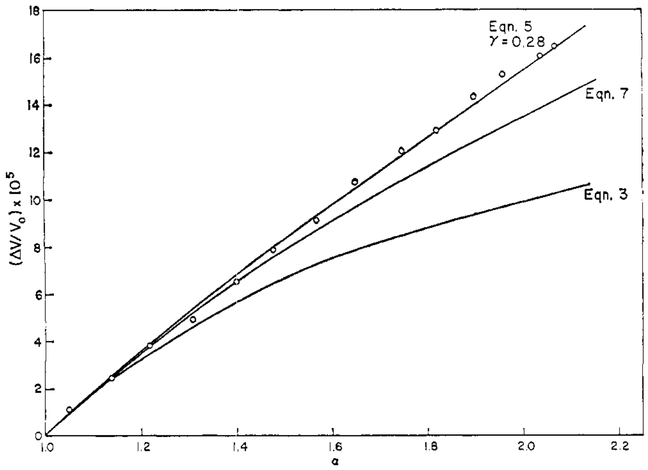

Figure 2. $\Delta V/V_0$ *vs.* α for the 40-min cured natural rubber sample of Christensen and Hoeve.

$$F = 2\left(C_1 + \frac{C_2}{\alpha}\frac{V_0}{V}\right)\left[\alpha - (1/\alpha^2)\frac{V}{V_0}\right] \qquad (6)$$

where C_1 and C_2 are the usual Mooney constants and the other terms have previously been defined. Making use of eq 1, we obtain from eq 6

$$\Delta V/V_0 = 2K\left[C_2\alpha - \frac{C_1}{\alpha} - C_2 + C_1\right] \qquad (7)$$

Values of C_1 and C_2 were obtained from the stress-strain data of Christensen and Hoeve, and these were used to calculate $\Delta V/V_0$ for two of their samples according to eq 7. The results are shown in Figures 2 and 3. It can be seen that eq 7 also underestimates the volume dilation, although it is a somewhat better approximation than eq 3 for the unswollen sample. For the swollen sample, $C_2 = 0$ and hence eq 3 and 7 give identical results. Thus the differences between the experimental $\Delta V/V_0$ and that predicted by eq 3 cannot be due solely to the failure of eq 2 to predict completely the stress-strain behavior. Indeed, the stress-strain data of the swollen network are well represented over the extension range studied by eq 2; and yet, eq 3, which follows directly from eq 2 if $\langle r_f^2\rangle$ is independent of volume, greatly underestimates the volume dilation. We feel that this is a good indication that $\langle r_f^2\rangle$ is a function of the volume of the sample.

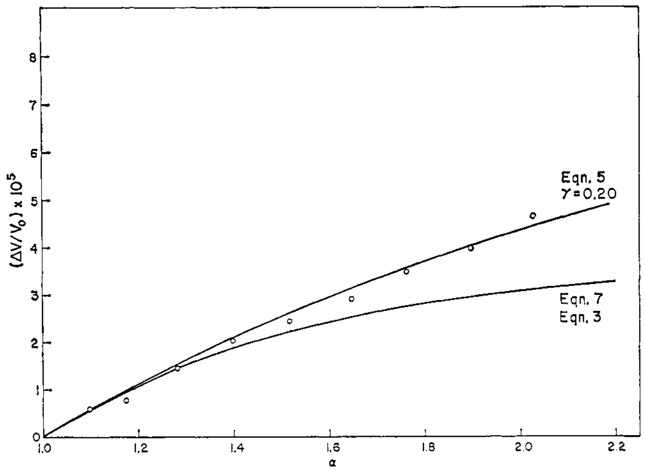

Figure 3. $\Delta V/V_0$ *vs.* α for the 15-min cured natural rubber sample of Christensen and Hoeve swollen in xylene.

Measurement of the variation of the shear modulus with pressure would provide an unambiguous method of establishing the nonzero nature of γ. According to the statistical theory the shear modulus, G, of a rubber-like network is given by

$$G = NkT(\langle r^2\rangle_0/\langle r_f^2\rangle) \qquad (8)$$

from which we obtain

$$\gamma = (\partial \ln G/\partial p)_T/K \qquad (9)$$

The present theories which assume $\langle r_f^2\rangle$ to be independent of volume and pressure would predict the shear modulus to be independent of volume and pressure also; thus any change in G with pressure would have to be attributed to change in $\langle r_f^2\rangle$.

The quantity γ must at present be regarded as an experimentally determined coefficient, much like the coefficient of expansion or the compressibility.

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