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Behavior and Properties

A Theory of Pseudo Cross-Link

4. Rubber Elasticity

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Summary

The rubber elasticity is discussed in terms of the pseudo cross-link concept. The classical equation of rubber elasticity deviates from experiments not only at large extension, but also even at small one. The former deviation is to be ascribed in most cases to the limited chain extensibility, because the steep increase of the force at large extension is varnished if the equations represented by the fractional extension derived by Guth, James or the authors is employed. The deviation at small extension is also diminished if the empirical equation of Mooney-Rivlin is used. The Mooney-Rivlin type equation can be derived on the basis of pseudo cross-link theory. The C_2-term in the Mooney-Rivlin equation is attributed to the pseudo cross-link which decreases during elongation. When the remaining pseudo cross-link is less than a critical value for viscous flow, the flow resistance partly balanced with the elastic force becomes large. The effect of viscous flow is revealed in the force in retraction as a hysteresis. Filler enhances the hysteresis.

Introduction

The theoretical equation for elasticity has already been established by several authors[1], but some discrepancy is found in actual case. At high extension the upturn of the tensile force is revealed even for non-crystallizable rubber. At moderate extension so-called Mooney-Rivlin equation[2] holds, but its meaning is not completely clear.

Many authors proposed explanations for the Mooney-Rivlin equation: For example Flory enphasized the effect of local constraints on junctions in his phantom network theory[3] or Ferry[4], Langley[5] and Dossin[6] ascribed the plateau modulus to the topological interaction or entanglement of the chain. The authors pointed out the important theoretical result that the Mooney-Rivlin equation is also valid even for the unvulcanized rubber and is explained in terms of the pseudo cross-link concept[7]. Here, the author will discuss the behavior of the vulcanized rubber in the stress-strain relation and also in the stress-strain cycle.

Theory

1. Large deformation

The elastic force f acting on the unit cross-sectional area is given as the configurational change of the chain entropy by extension, i.e., $\partial \Delta S/\partial \alpha$,

$$f = -T\partial \Delta S/\partial \alpha \qquad (1)$$

where α is an extension ratio of the specimen that is equal to that of the chain and T is the temperature. For calculation of the chain entropy the assumption of "affine" strain is adopted in general and the total entropy change ΔS is obtained by integration of that of each chain. The latter is given as a function of the configurational probability $W(x)$ of the chain having an end-to-end distance x, and therefore

$$\Delta S = \Sigma \nu W(x)\{R \ln W(\alpha x) - R \ln W(x)\} \qquad (2)$$

where ν is the number of chains existing in a unit volume. For the chain bearing n segments whose diameter is ℓ, $W(x)$ is given as a function of the fractional chain extension ratio, i.e., $x/n\ell$,

$$W(x) = \frac{n!}{[(n/2)(1 + x/n\ell)]!\,[(n/2)(1 - x/n\ell)]!} \qquad (3)$$

And under a condition that $x \ll n\ell$, it is approximated to

$$W(x) = \exp(-\beta^2 x^2) \qquad (4)$$

where β^2 is $1/2\,n\ell^2$. By using equation (4), equation (1) leads to a theoretical equation (5)

$$f = \nu k T(\alpha - 1/\alpha^2) \qquad (5)$$

However, equation (5) does not hold at high extension since the equation (4) is not satisfied. To avoid this difficulty Guth and James[8] employed an inverse Langevin function of the fractional extension, i.e., $L^{-1}(\alpha/\alpha_m)$ for the distribution function $W(\alpha)$, α_m being the ultimate extension ratio, and obtained the following equation.

$$f = (\nu k T\alpha_m/3)\{L^{-1}(\alpha/\alpha_m) - (1/\alpha^{3/2})L^{-1}(1/\alpha^{1/2}\alpha_m)\} \qquad (5)$$

Equation (6) indicates the steep increase of the force at high extension near the maximum one. The authors derived an alternative simple equation available for this purpose based on a uniform stress concept instead of the usual uniform strain concept[7]. In the former the end-to-end distance of chains is expressed as a Gaussian distribution function even after the extension, but for the chain having a large end-to-end distance the further extension is not allowed so much as that for the specimen and it is rather thermodynamically likely to assume that the chain distribution becomes more uniform in stress rather than a strain. For uniform stress distribution the entropy change of each chain is uniform and consequently the total entropy change is obtained merely by multiplying with total number of chain ν instead of integration. Equation (3) can be used to calculate total entropy change without any approximation and in this way equation (8) is obtained.

$$\Delta S = \nu\{R \ln W(\alpha x) - R \ln W(x)\} \qquad (7)$$

and

$$f = \nu kT\left\{\frac{\alpha_m}{2} \ln \frac{1 + \alpha/\alpha_m}{1 - \alpha/\alpha_m} - \frac{1}{\alpha^{3/2}} \ln \frac{1 + 1/\alpha^{1/2}\alpha_m}{1 - 1/\alpha^{1/2}\alpha_m}\right\}$$

or simply,

$$f = \nu kT\, F(\alpha) \qquad (8)$$

$$F(\alpha) = \frac{\alpha_m}{2} \ln \frac{1 + \alpha/\alpha_m}{1 - \alpha/\alpha_m} - \frac{1}{\alpha^2} \qquad (9)$$

It was found that the f—F(α) plot gives a straight line valid for up to high extension, but the straight line does not pass through the origin and an additional term f_∞ is necessary as shown in figure 1.

$$f = \nu kT\, F(\alpha) + f_\infty \qquad (10)$$

The term f_∞ was found to be ascribed to the contribution of the pseudo cross-link.

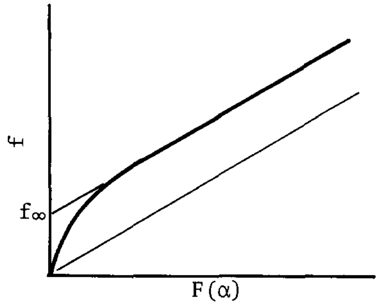

Fig. 1 Stress-strain relation

2. Mooney-Rivlin equation

For the elasticity at high extension a phenomenological equation (11) proposed by Mooney and Rivlin is widely used.

$$f = (2C_1 + 2C_2/\alpha)(\alpha - 1/\alpha^2) \qquad (11)$$

It is composed of two terms of C_1 and C_2. As the factors relating to the concentration of the cross-link, $2C_1$ is concerned mostly with the chemical cross-bond but the meaning of the C_2-term decreasing with extension is not completely clear. Moreover, equation (11) is valid only in a short limited range. As shown in figure 2 the linear relationship holds only in the range between α_1 and α_2, i.e., α of 1.4 to 3.3 or 1/α of 0.7 to 0.3. The upturn at α_2 was ascribed to the finite extensibility[9] but sometimes to the strain-induced crystallization[10]. It was found that the upturn for non-crystallizable rubber is

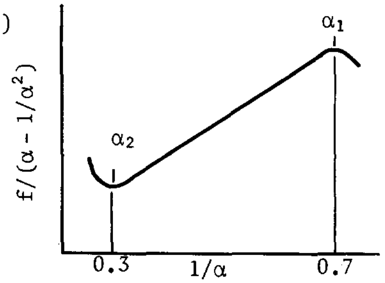

Fig. 2 Mooney-Rivlin plot having two direction points α_1 and α_2

varnished if a modified equation (12) is used.

$$f = (2C_1 + 2C_2/\alpha)F(\alpha) \qquad (12)$$

As reported in the preceding paper an equation similar to (12) was derived on the basis of the pseudo cross-link concept for the unvulcanized rubber

$$f/kT = \{(\nu_1 + \nu_e) + (\nu_0 - \nu_e)(\alpha/k')^{1/2}/\alpha\}F(\alpha) \qquad (13)$$

where ν_0 and ν_e are the fraction of the pseudo cross-link at the initial and the final stage, respectively, $\dot{\alpha}$ is the rate of extension and k_0' is the rate constant of break-down of the unit pseudo cross-link.

For the vulcanized rubber $2C_1$ is to be composed of ν_e and the chemical cross-link ν_1 and accordingly,

$$2C_1 = (\nu_1 + \nu_e)kT \qquad (14)$$

$$2C_2 = (\nu_0 - \nu_e)(\dot{\alpha}/k')^{1/2}kT \qquad (15)$$

These equations imply that the vulcanization affects mainly C_1 but not C_2. However, C_1 also involves the effect of the pseudo cross-link ν_e. As mentioned in the preceding paper the ν_e-term is attributed to the pseudo cross-link regenerated after the flow of the chain and corresponds to the viscous flow resistance. The ν_e-term may be varnished immediately after the stop of deformation. In fact, the isochronal experiment indicated that C_1-term is more rapidly relaxed than the C_2-term[11].

The C_2-term means the elastic force due to the pseudo cross-link and proportional to the fraction of the pseudo cross-link and may correlate with the molecular volume of the segment. Equation (15) is rewritten as

$$2C_2 \backsim \{(\nu_0 - \nu_e)/N\}(N_0kT/V\ ) \backsim RT/V \qquad (16)$$

where N_0 is the Avogadro's number and V is the molecular volume of the segment. the value $(\nu_0 - \nu_e)/N$ is mainly determined by the molecular interaction energy rather than the size of segment, and

$$(\nu_0 - \nu_e)/N \cong \nu_0/N = \exp(-\Delta H_0/kT + \Delta S_0/R) \qquad (17)$$

where ΔH_0 is the heat of pseudo cross-linking and ΔS_0 is its entropy equal to 2R. In fact, Boyer et al.[12] pointed out that the ratio C_2/C_1 decreases as the diameter of molecular chain increases. The C_2-term is also a function of $\dot{\alpha}$ and k_0' as shown by

$$2C_2 \backsim \left[\frac{\dot{\alpha}}{k_0' \exp(\alpha - 1/\alpha^2)}\right]^{1/2} \backsim \dot{\alpha}^n \exp(E_0^*/2RT) \qquad (18)$$

It was known that C_2 increases with the rate of extension and decreases with temperature[7]. However, sometimes C_2 is not significantly affected by the rate of extension or the temperature when $\dot{\alpha}/k_0'$ becomes to unity. Equation (12) is transformed at large extension into

$$f/kT = (2C_1 + 2C_2/\alpha)F(\alpha) \cong 2C_1F(\alpha) + 2C_2 \qquad (19)$$

However, the force at very large extension is affected by the viscous flow of the chain especially for the semi-vulcanized rubber and is to be represented as reported in the preceding paper.

$$f/kT = \{\nu_1 + \nu_e + (\nu_0 - \nu_e)/\alpha\}\, e^{-k''\phi t/3}\, F(\alpha) \qquad (20)$$

where ϕ is the fraction of pseudo cross-link ν_2, i.e., $\nu_e + (\nu_0 - \nu_e)/\alpha$.

$$\phi = \nu_2/(\nu_1 + \nu_2) \qquad (21)$$

And k'' is equal to k' when $(\nu_1 + \nu_2)$ is larger than ν_B, but otherwise

$$k'' = k'(n_B/n)^{3.5} = k'\{(\nu_1 + \nu_2)/\nu_B\}^{3.5} \qquad (22)$$

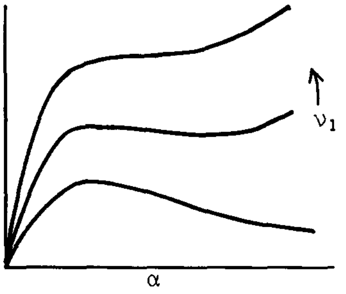

Fig. 3 f-α plot as a function of vulcanization ν_1

Equation (20) or equation (23)

$$f/kT = \{(\nu_1 + \nu_e) + (\nu_0 - \nu_e)\, e^{-k't}\} \times e^{-k''\phi t/3}\, F(\alpha) \qquad (23)$$

possesses two maxima at

$$k't = 1 \text{ and } (k' + k''\phi/3)t = 1$$

giving figure 3. In the Mooney-Rivlin equation (11) these maxima are varnished, but another departure occurs at α_1 of 1.4 in figure 2. It is ascribed to the necessary elongation of the unit chain for the break-down as mentioned in the preceding paper

$$\alpha_1 = (-\Delta H/RT)^{1/2} = 1.4 \sim 1.6$$

The upper limit may arise from the limited extensibility of the chain and sometimes from the strain-induced crystallization. For non-crystallizable rubber the upturn in the Mooney-Rivlin plot is obtained as follows. Equation (12) is expanded to give

$$(f/kT)/(\alpha - 1/\alpha^2) \cong 2(C_1 + C_2/\alpha)\{1 + (1/3)(\alpha^2/\alpha_m^2)\} \qquad (24)$$

Equation (24) indicates a maximum α_2 at a condition that $d\{f/(\alpha - 1/\alpha^2)\}/d\alpha$ is zero[13]

$$\alpha \cong \left(\frac{3C_2\alpha_m^2}{2C_1 + C_2/\alpha}\right)^{1/3} \cong \left[\frac{3\nu_0\{N/(\nu_1 + \nu_2)\}^{1/2}}{2(\nu_1 + \nu_e) + \nu_0/\alpha}\right]^{1/3} \qquad (25)$$

The upturn in the Mooney-Rivlin plot occurs at smaller extension for the rubber of larger C_1 or higher degree of vulcanization.

3. Stress-strain cycle

The rheological behavior of the vulcanized rubber is more characteristic in the stress-strain cycle than a simple extension. As is known as the Mullins effect[14] the retraction force is more or less lower than the extension force and a significant hysteresis is observed.

In the retraction the recovery of the pseudo cross-link occurs and is represented by a similar equation to equation (11) or (12). But the regeneration of the pseudo cross-link occurs in the chain extended and there may be a shift between extension and retraction. At a turn-back point B the actual extension of the chain λ is smaller than that of the specimen α and the difference between them may remain as a shift, i.e., $\Delta\alpha$.

$$\Delta\alpha = \alpha_B - \lambda_B = \alpha_B(1 - e^{-k''\phi t_B/6}) \qquad (26)$$

The exponential factor $\exp(-k''\phi t)$ is replaced by $1/\alpha$ in the Mooney-Rivlin equation and then equation (26) is transformed to

$$\Delta\alpha = \alpha_B\{1 - (1/\alpha_B)^{1/6}\} \qquad (27)$$

$\Delta\alpha$ is 1.5 or 2.3 for 6 or 8 of α_B, respectively. In the case that $(\nu_1 + \nu_2)$ is smaller than ν_B, ϕ is larger than unity and

$$k'' = k'/\phi^{3.5}$$

The elastic force involves a significant contribution of viscous flow, which is not completely revealed in the retraction, and consequently, the extension force f_1 and the retraction one f_{-1} are represented as

$$f_1 = (\nu_1 + \nu_2)\, e^{-k''\phi t/3}\, F(\alpha)\, kT \qquad (28)$$

and

$$f_{-1} = f_1 - (\nu_B\dot{\alpha}/k'')\, \alpha\, kT \qquad (29)$$

There is a significant hysteresis, as shown in figures 4 and 5.

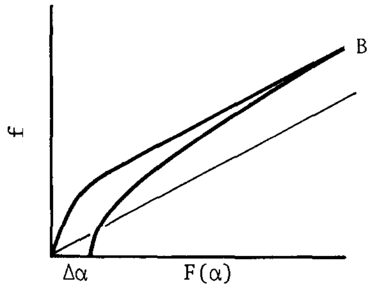

Fig. 4 Deformation without flow of chain

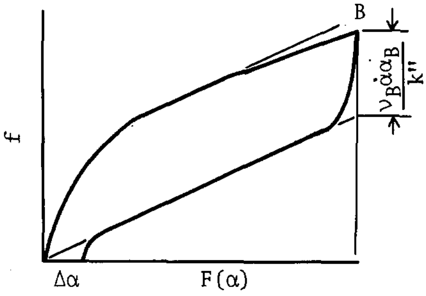

Fig. 5 Deformation with flow of chain

4. Filled rubber vulcanizate

From equation (31) in the preceding paper the equations (28) and (29) are respectively modified as equations (30) and (31) for filled rubbers; for the extension

$$f/kT = [(\nu_0 - \nu_e)/\alpha\cdot e^{-k''\phi t} + x\,(\nu_{f_0} - \nu_{fe})/\alpha\cdot e^{-k''\phi_f t}]\,F(\alpha) \qquad (30)$$

and for the retraction

$$f_{-1} = f - (\nu_2/k'' + x\,\nu_f/k''_f)\,\dot{\alpha}\alpha\, kT \qquad (31)$$

where α is taken to be $\alpha(\text{actual})/(1 - x)^{1/3}$. A similar curve to figure 5 may be applicable.

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