Polymer Bulletin 10, 336-342 (1983)

Polymer Bulletin

Theory of Pseudo Cross-Link
3. Rheological Behavior

Junji Furukawa

Department of Applied Chemistry, Aichi Institute of Technology, Yakusa-cho, Toyota, 470-03 Japan

Summary

Stress-relaxation, creep and stress-strain relations are discussed in terms of pseudo cross-link concept. The decrease of cross-links by the stress or strain leads to an equation similar to the Mooney-Rivlin equation. Viscous flow is also an important factor decreasing the cross-sectional area of the specimen and the chain-extension. Viscosity much decreases with increasing rate of extension and temperature. Filler ingredient plays roles of not only enchancing the chain strain but also providing the pseudo cross-link due to adsorption of the rubber on the filler surface.

Theory

1. Decrease of pseudo cross-link by extension

Static behavior of solid polymers such as stress-relaxation, creep and stress-strain relations can be interpreted on the basis of the pseudo cross-link concept. For the cross-linked rubber the elastic force f (dyne/cm^2) acting on the original cross-sectional area A = 1 cm^2 at an extension ratio λ is given as follows[1];

$$f = \nu kTA(\lambda - 1/\lambda^2) \quad (1)$$

where ν is the number of cross-links or the number of chains existing in a unit volume or 1 cm^3 of a specimen.

For non-vulcanized rubber ν is taken to be the number of pseudo cross-links ν_2 and is variable with the time t and represented simply by equation (2)

$$\nu = \nu_2 = \nu_e + (\nu_0 - \nu_e)\, e^{-k't} \quad (2)$$

where ν_0 is an equilibrium value at the initial stage under no stress and ν_e is that at the final stage under stress. k' is a rate constant of break down of the pseudo cross-link per second.

At the same time the decrease of pseudo cross-link is accompanied by the decrease of the cross-sectional area and chain extension. The cross-sectional area decreases from the initial area A_0 to the area A at the time

t. The chain extension ratio λ is smaller than the extension ratio of the specimen α. They are given from figure 1. The end-to-end distance of the chain, its elongation and the number of the chain along the extension direction are given by $(N/\nu_0)^{1/2}$, α and $(\nu_0/N)^{1/3}$, respectively, and the length of the specimen is equal to their product. After the change of the pseudo cross-link from ν_0 to ν, these values change respectively to $(N/\nu)^{1/2}$, λ and $(\nu/N)^{1/3}$ for the same length of the specimen, and consequently

$$(N/\nu_0)^{1/2}\alpha(\nu_0/N)^{1/3} = (N/\nu)^{1/2}\lambda(\nu/N)^{1/3}$$

or

$$A/A_0 = \lambda/\alpha = (\nu/\nu_0)^{1/6} = e^{-k't/6} \qquad (3)$$

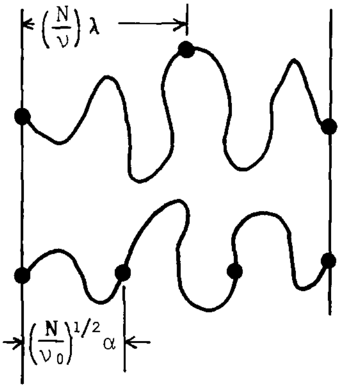

Fig.1 Relation between λ and α

Substituting equations (2) and (3) into (1), the stress is given as

$$f/kT = \{\nu_e + (\nu_0 - \nu_e)e^{-k't}\}(A/A_0)(\lambda/\alpha)(\alpha - 1/\alpha^2)$$

$$= \{\nu_e + (\nu_0 - \nu_e)e^{-k't}\}e^{-k't/3}(\alpha - 1/\alpha^2) \qquad (4)$$

It is also noticed that the rate constant k' is much affected by the force or strain which decreases the activation energy for the break down of the cross-link of size b, i.e. bE_0^* by the work done W. Namely,

$$k' \propto \exp\{-(bE_0^* - W)/RT\} \qquad (5)$$

The work done W is given by a product of the force, the cross-sectional area $(n^{1/2}\ell)^2$ and the loosen bond length $\delta\ell$ and the size of pseudo cross-link b as shown in figure 2

$$W = f\ (n^{1/2}\ell)^2\ \delta\ell \times bN_0 \qquad (6)$$

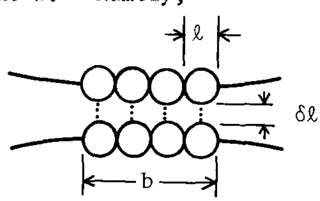

Fig. 2 Pseudo cross-link in the loosen state

where n, ℓ and N_0 are the number of segments of a chain, the diameter of a segment and Avogadro's number, respectively and δ is assumed to be 0.04 as mentioned before. Substituting the following relations

$$f = \nu kT(\lambda - 1)$$

$$n = N/\nu \quad \text{and} \quad \ell^3 = 1/N$$

it follows that

$$k' = k_0' e^{b\delta(\lambda - 1)} \cong k_0'\delta b\lambda \qquad (7)$$

where

$$k_0' = (kT/h)n_B^{-3}\, e^{-bE_0^*/RT}$$

The size b lies between 4 and 16. Equation (7) implys that k' becomes larger as the chain extension ratio λ increases.

2. Pseudo cross-links of multiple size

Since the cross-link of the size b possesses b-times larger value of the heat of formation ΔH, the entropy loss ΔS and the activation energy E^* than those of the unit link, ΔH_0, ΔS_0 and E_0^*, respectively, the fraction of the b-size cross-link ν_b/N and its relaxation time τ_b are given by equations (8) and (9), respectively.

$$\nu_b/N = \exp\{b(-\Delta H_0/RT + \Delta S_0/R)\} \qquad (8)$$

$$\tau_b = 1/k_b' = (h/kT)n_B^3 \exp(bE_0^*/RT) \qquad (9)$$

Eliminating b from equations (8) and (9), a dynamic spectrum of the cross-link ν or the elasticity E against the relaxation time τ is obtained as a function of temperature.

$$\log(E/E_A) = \log(\nu/N) = (-\Delta H/E_0^*)(1 - T/T_A)\log(\tau_A/\tau) \qquad (10)$$

where E_A and τ_A are values for the unit size cross-link A. T is an experimental temperature and T_A is a transition temperature given by $\Delta H_0/\Delta S_0$.

As mentioned previously another transition temperature T_B for the flow exists, which is equal to $1.5\,T_A$, and at near T_B, equation (10) is rewritten as

$$E/E_A = \nu/\nu_A = (\tau_A/\tau)^{1/2} \qquad (11)$$

For the multiple size network the cross-links having sizes smaller than b are relaxed during the time t equal to τ_b and the fraction of the remaining cross-link is given by equation (12).

$$\nu/\nu_0 = (\tau_0/\tau)^{1/2} = (\tau_0/t)^{1/2} \qquad (12)$$

where ν_0/N and τ_0 are the initial fraction of the cross-links and their relaxation time, respectively. τ_0 is also affected by the strain and expressed by equation (13).

$$\tau_0 = (1/k_0')\,e^{-\delta b(\lambda - 1/\lambda^2)} = 1/\delta b\lambda k_0' \qquad (13)$$

Substituting equation (13) into equation (12) and taking that the extension ratio of chain λ is equal to that of the specimen α and the rate of extension is $\dot{\alpha}$ or α/t, it follows that

$$f/f_0 = (k't)^{-1/2} = (\dot{\alpha}/\delta b k_0')^{1/2}(1/\alpha) \qquad (14)$$

Under stress the successive break down of the pseudo cross-link takes place. The force at break is assumed to be represented as a product of the fractional number of the remaining pseudo cross-link ν_2/N, the fraction of pseudo cross-link having more than the bond energy $-\Delta H$ in a total chain energy given by $\lambda^2 RT$ and the bond force constant given by $d(-\Delta H/\ell^2)/d\ell \cong -\Delta H/V_0$, V_0 being a molar volume of the segment.

$$f = (\nu_2/N)\exp\{-(-\Delta H/\lambda^2 RT)\}(-\Delta H/V_0) \qquad (15)$$

Equation (15) possesses the maximum at

$$\lambda = (-\Delta H/RT)^{1/2} \qquad (16)$$

For the unit pseudo cross-link $(CH_2)_2$, $-\Delta H$ is 1360 cal and equation (16) becomes to

$$\lambda = (1.36/0.6)^{1/2} = 1.5$$

at 0.6 Kcal of RT. This value is close to the value obtained by taking ν_0/N to 1/2.

$$\lambda = (N/\nu_0)^{1/2} = \sqrt{2} = 1.4$$

A chain composed of two or three units is assumed to be linked with a pseudo cross-link composed of two or three units as the chain of the minimum size.

3. Rheological equations

Equation (14) derives several rheological relations.

(1) Stress-strain relation —— From equations (4) and (14), equation (17) is obtained

$$f/(\alpha - 1/\alpha^2) = kT\{(\nu_0 - \nu_e)(\dot{\alpha}/\delta k_0')^{1/2}/\alpha + \nu_e\} \quad (17)$$

which corresponds to the useful phenomenological relation of Mooney and Rivlin[2], i.e.,

$$f/(\alpha - 1/\alpha^2) = 2C_1 + 2C_2/\alpha \quad (18)$$

In fact, the plots of $f/(\alpha - 1/\alpha^2)$ against $1/\alpha$ gives a straight line in various cases not only for vulcanized rubbers, but also for unvulcanized rubbers. The meaning of C_1 and C_2 have been discussed by several authors but the pseudo cross-link concept also gave a likely explanation[3]. C_1 and C_2 are given as follows

$$2C_1 = (\nu_1 + \nu_e)\,kT \quad (19)$$

and

$$2C_2 = (\nu_0 - \nu_e)(\dot{\alpha}/\delta k_0')^{1/2}\,kT \quad (20)$$

where ν_1 is the number of the chemical cross-link for the vulcanized rubber. Equation (20) suggests that C_2 increases as the rate of extension increases and k_0' or the temperature is lowered. This fact was confirmed by the authors[3]. However, C_2 becomes constant when $\dot{\alpha}/k_0'$ becomes unity, and in this case equation (17) is written as

$$f/(\alpha - 1/\alpha^2) = kT\{(\nu_0 - \nu_e)/\alpha + \nu_e\} \quad (21)$$

It is noticed that equation (18) is valid for the value of α above 1.4. For the vulcanized rubber there is an upper limit arising from the limited extensibility of the chain dependency on the degree of vulcanization. Figures 3 and 4 illustrate the profile of the stress-strain relation, where the curve a refers to equation (19) and b refers to the curve for vulcanized rubbers.

(2) Stress-relaxation —— Taking α to be a constant in equation (15), f is given as

$$f/f_0 = (1/k't)^{1/2} \quad (22)$$

which indicates that the stress decreases with $t^{1/2}$.

(3) Creep under a constant load —— Taking f to be a constant f_0, α is

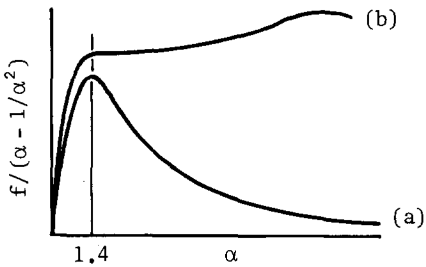

Fig. 3 Unvulcanized (a) and vulcanized rubber (b)

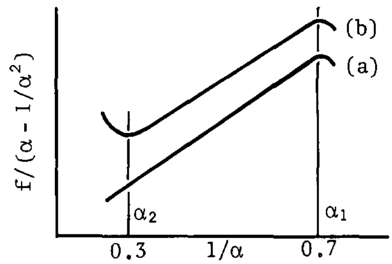

Fig. 4 Mooney-Rivlin plot for unvulcanized (a) and vulcanized rubber (b)

given as follows.

$$\alpha - 1/\alpha^2 = (f/\nu_0 kT)(k't)^{1/2} \quad (23)$$

However, if the effect of the stress on the rate constant k' is considered,

$$\frac{f_0/kT}{\alpha - 1/\alpha^2} = \left(\frac{\nu_0 - \nu_e}{\alpha}\right)\left(\frac{1}{\delta k_0'}\right)^{1/2}\left(\frac{d\alpha}{dt}\right)^{1/2} + \nu_e$$

For a small value of ν_e

$$\alpha^3/3 - 2\ln\alpha - 1/5\alpha^5 = \left\{\frac{\delta k_0'}{(\nu_0 - \nu_e)^2}\frac{f_0}{kT}\right\}t \quad (24)$$

which indicates that α increases proportionally with $t^{1/3}$.

(4) Recovery after release from load ——Taking f to be zero in equation (15), it follows that

$$d\alpha/dt = -\{\nu_e/(\nu_0 - \nu_e)\}^2\,\delta k_0'\alpha^2$$

$$1/\alpha = 1/\alpha_B + \{\nu_e/(\nu_0 - \nu_e)\}^2\,\delta k_0' t \quad (25)$$

which indicates that α decreases inversely proportionally with t, α_B being an elongation ratio at a turn-back point B.

4. Viscous flow resistance

The elastic deformation accompanied by the decrease of the pseudo cross-links involves the viscous flow of chain and it is represented as a product of the viscosity η, the rate of deformation $\dot{\alpha}$ and a factor due to the deformation α as follows. As illustrated in figure 5, the length increases from L to $L\alpha$ and the cross-sectional area decreases from L^2 to L^2/α as the specimen is elongated. The relation between the velocity gradient and the shear force is represented as

$$\frac{\Delta u}{L/\sqrt{\alpha}} = \frac{f\ (L/\ \alpha)^2}{\eta(L\alpha)(L/\sqrt{\alpha})} \quad (26)$$

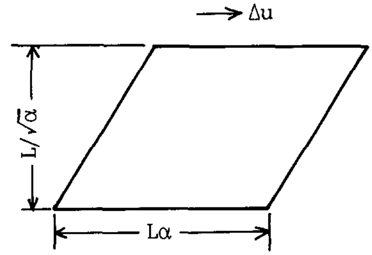

Fig. 5 Velocity gradient

Since the velocity difference Δu is equal to $L\dot{\alpha}$, the viscous force f_V becomes to

$$f_V = f/\alpha = \eta\dot{\alpha}\alpha = (\nu_2 kT/k')\dot{\alpha}\alpha \quad (27)$$

However, the viscous force induced by the extension is involved in the elastic force and is not revealed unless f_V is larger than the elastic force. In the latter case the tensile deformation results in the plastic rupture. On the contrary, the deformation in a closed vessel the continuous viscous flow occurs and the viscous force f_V is not given by equation (27) but by equation (28).

$$f_V = \eta \dot{\alpha} \qquad (28)$$

For example, the viscous flow in the capillary no correction is necessary since the length of the specimen is kept constant in the capillary.

The viscosity is affected by the deformation for two reasons: one is the acceleration of the break-down of the pseudo cross-link by the elongation of the chain and k' is increased from k_0' as pointed out in equation (13) and is represented as

$$k' = k_0 \exp\{\delta b(\lambda - 1)\} \qquad (29)$$

Another reason is the change of chain length due to the decrease of the pseudo cross-links. The average chain length n is given by

$$n = N/\nu_2 \qquad (30)$$

And n is increasing with decreasing number of the pseudo cross-link and when n becomes less than the critical length of n_B assumed to be $10^{2.4}$ as pointed out in the paper 2, k' is affected by the chain length as represented as

$$k'(n_B/n)^{3.5} = k'(\nu_2/\nu_B)^{3.5} \qquad (31)$$

where ν_B is the number of critical pseudo cross-link. The viscosity η is

$$\eta = (\nu_B kT/k')(\nu_B/\nu_2)^{3.5} \qquad (32)$$

And at the stationary state n becomes to n_0, i.e., the segmental length of the whole molecule and equation (32) becomes to

$$\eta = (\nu_B kT/k_0')(n_B/n_0)^{3.5} \exp\{-\delta b(\lambda - 1)\} \qquad (33)$$

Equation (33) is rewritten as a function of the force, i.e., $f = \eta\dot{\alpha}$ as

$$\eta = \eta_0 \exp(-\eta\dot{\alpha}/\nu_B kT) = \eta_0 \exp(-\eta\dot{\alpha}/\eta_0 k_0') \qquad (34)$$

where η_0 is the viscosity at no shear rate or

$$\eta_0 = (\nu_B kT/k_0')(n_B/n_0)^{3.5} \ n_B^3 \qquad (35)$$

Equation (34) is transformed into a simple form for the structural viscosity

$$\eta/\eta_0 = 1/(1 + \dot{\alpha}/k_0') \backsim \dot{\alpha}^{-n} \qquad (36)$$

where

$$n = 1 - \log(1 + \dot{\alpha}/k_0')/\log\dot{\alpha} \qquad (37)$$

The order of n was found to be 0.7 $\sim$ 0.9 for rubber.

5. Effect of filler

Fillers such as carbon black and clay enhance the elasticity of the polymers. The effect may be ascribed to two reasons: One is that fillers decreases the volume fraction of the polymer and as a result the actual deformation of the molecular chain becomes larger than the appearent deformation of the specimen. The second reason may be the formation of the pseudo cross-link between the filler surface and the surrounding molecular chain.

The former volume effect is calculated as follows. For the volume fraction of filler x, the tensile elongation of the specimen α is given by the sum of the tensile fraction of the polymer whose elongation is λ and that of the filler and accordingly, equation (33) holds.

$$\alpha = (1 - x)^{1/3}\lambda + x^{1/3} \cong (1 - x)^{1/3}\lambda \qquad (33)$$

Consequently, the actual extension λ is represented as

$$\lambda \cong \alpha/(1 - x)^{1/3} \qquad (34)$$

The additional pseudo cross-link due to the adsorption on the filler is given by a product of the volume fraction of fillers x and their specific number of pseudo cross-link on a unit fraction of the filler, V_f and the latter is proportional to the specific surface area, i.e., a reciprocal radius of the filler particule 1/r and the strength of adsorption given by exp $(-\Delta H_f/RT)$ where ΔH_f is an exothermic heat of adosorption.

$$x V_f \propto (1/r) \exp(-\Delta H/RT) \qquad (35)$$

Taking these effects into consideration equations (17) and (27) may be rewritten as follows

$$f/kT = \left\{\frac{\nu_0 - \nu_e}{\alpha} e^{-k'\phi t/3} + x \frac{\nu_{f0} - \nu_{fe}}{\alpha} e^{-k'\phi_f t/3}\right\} \alpha \qquad (36)$$

and

$$f_V/kT = (\nu_2/k' + x V_f/k'_f)\dot{\alpha}\,\alpha \qquad (37)$$

where the suffix f refers to the filler and α is taken to be $\alpha(\text{actual})/(1 - x)^{1/3}$.

References

1. Flory, P.J., "Principle of Polymer Chemistry", Cornell University Press 1953
2. Rivlin, R.S., Phil. Trans. Roy. Soc. London, Ser A, 241, 379(1948)
3. Furukawa, J., Okamoto, H. and Inagaki, S., Kautschuk u Gummi Kunststoffe, Heft 12, 29, 744(1976)

Accepted July 22, 1983 *S*