

Review

A New Theory on Rheological Behavior of Rubbery Material[†]

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Received April 10, 1976

INTRODUCTION

Rheological behaviors of rubbery materials have been well studied during several decades. They are of complicated function not only of polymer structure but also of experimental conditions such as temperature and deformation rate. They are demonstrated by means of a mechanical model involving spring and dashpot or an electrical model involving impedance and capacitance. However, rheological properties are so complicated that a simple model is not able to describe the retardation in creep or the relaxation of internal force and the combination of spring and dashpot is necessary for the detailed demonstration of phenomena. Accordingly, a direct relationship between chemical structure and rheological property is rather difficult to be predicted in terms of the classical rheology.

The kinetic interpretation of polymer properties was proposed by Tobolsky¹⁾ and several authors based on Eyring's non-linear viscosity equation.²⁾ This equation is applicable to a simple liquid but not to a polymer solid, because a polymer solid is very much different from the ordinary liquid; the former shows complicated viscosity having a larger dependency on molecular weight, stress and temperature than the latter.

The author³⁾ proposed already twenty years ago a hypothesis of pseudo-crosslinked structure of solid polymer. This paper provides more details according to this hypothesis.

I. ELASTICITY OF VULCANIZED RUBBER

The stress-strain relation of vulcanized rubber has been studied by several authors theoretically as well as experimentally. Theoretical Eq. (1) by Kuhn⁴⁾ and Flory⁵⁾ is widely used,

$$f = \nu kT(\alpha - 1/\alpha^2) \quad (1)$$

where f is the stress acting on the original unit area at an elongation ratio of α and ν is a number of chains equal to a number of crosslinks existing in a unit volume. Equation (1) can be derived from the entropy change ΔS caused by elongation.

[†] The paper was read at the lecture on March 19 in 1976 to mark the retirement of Professor J. Furukawa.

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$$f = -T \frac{\partial \Delta S}{\partial \alpha} \quad (2)$$

The entropy of a single chain is expressed as a logarithmic function of the number of configuration W whose end-to-end distance is r , *i.e.*,

$$W = \frac{n!}{\{(n+r/l)/2\}! \{(n-r/l)/2\}!} = \frac{1}{\frac{n}{2} \left(1 + \frac{r}{nl}\right)^{\frac{n}{2} \left(1 + \frac{r}{nl}\right)} \cdot \frac{n}{2} \left(1 - \frac{r}{nl}\right)^{\frac{n}{2} \left(1 - \frac{r}{nl}\right)}} \quad (3)$$

where n and l are a number of segments in a chain and a length of a segment, respectively. Equation (3) is simplified to Equation (4) when $r \ll n$, *i.e.*,

$$W = (\beta/\pi^{1/2})^3 \exp(-\beta^2 r^2) \quad (4)$$

where β is $3/2 nl^2$. Equation (4) is limited to use only when the elongation is small enough. The entropy of total chain is

$$S = \sum W_i k \ln W_i = k \int_{-nl}^{+nl} W \ln W dr \quad (5)$$

From an assumption that each chain is elongated by the same ratio as that of the specimen α , the total entropy becomes to

$$S(\alpha) = k \int_{-nl}^{+nl} W(l) \ln W(\alpha) dr \quad (6)$$

Consequently, the total entropy change ΔS is

$$\Delta S = S(\alpha) - S(1) = k \int_{-nl}^{+nl} W(1) \{\ln W(\alpha) - \ln W(1)\} dr \quad (7)$$

In this way, Eq. (1) is derived and therefore, Eq. (1) is valid in principle within small elongation.

At a large deformation the James-Guth equation⁶⁾ seems to be more valid than Eq. (1). It is derived from an assumption that the total entropy is expressed as an inverse Langevin function with respect to the fractional elongation, *i.e.*, r/nl ,

$$W = C \exp\{-n \mathcal{L}^{-1}(r/nl)\} \quad (8)$$

On the other hand, the Mooney-Rivlin equation⁷⁾ is applicable to the actual case,

$$f = (c_1 + c_2/\alpha)(\alpha - 1/\alpha^2) \quad (9)$$

Equation (9) is derived from Eq. (10) concerning the stored energy F due to the elongation which is composed not only of one-dimensional elongation with respect to x , y , and z components but also of two- and three-dimensional ones.

$$F = c_1(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) + c_2(\alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_x^2 - 3) + c_3(\alpha_x^2 \alpha_y^2 \alpha_z^2) \quad (10)$$

In Eq. (10) the calculation of stored energy is based on a Hookean linear function and consequently, there is no special factor favorable for the large deformation. Indeed, the c_2 -term is vanished when α becomes large. The meaning of the c_2 -term will be discussed

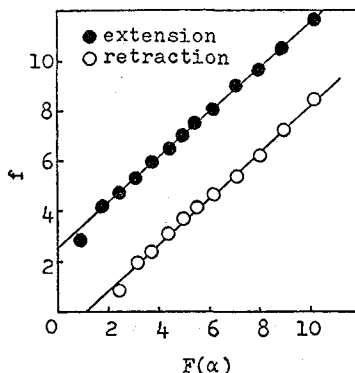


Fig. 1. Sulfur-cured SBR.

again in the latter part of this paper.

Both in Eqs. (1) and (6), a so-called principle of proportionality between elongation of each chain and that of the specimen is adopted, but at a large elongation the principle may not hold, since a chain already stretched ultimately does not allow the further elongation. It may be more natural to assume that each chain is elongated so as to uniform the stress or the entropy change. In the latter case, total entropy change is easily obtained from the entropy change having an average elongation equal to that of the specimen multiplied by the total number of chains ν , *viz.*,

$$\Delta S = \nu k \{ \ln W(\alpha) - \ln W(1) \} \quad (11)$$

Equation (11) and accordingly Eq. (2) are calculated without any approximation to give Eq. (12).

$$f = \nu k T \left\{ \frac{\alpha_m}{2} \ln \frac{1 + \alpha/\alpha_m}{1 - \alpha/\alpha_m} - \frac{1}{\alpha^{3/2}} \ln \frac{1 + 1/\alpha^{1/2} \alpha_m}{1 - 1/\alpha^{1/2} \alpha_m} \right\} = \nu k T F(\alpha) \quad (12)$$

Experiments show a good linear relationship between f and $F(\alpha)$ not only in an extension process but also in a retention one as shown in Figure 1.

However, the straight lines do not pass through the origin but an additional term b is necessary, which is almost constant but increases exponentially at a small elongation. It was found that the term b is almost proportional to the c_2 -term for various kinds of synthetic rubber with varied degree of vulcanization and b or c_2 is large for the rubber possessing polar groups. In the case of polyurethane rubber b or c_2 increases with increasing the amount of the polar urethane group, and with decreasing temperature, although the energy obtained from an Arrhenius plot is almost constant.

These results lead us to a conclusion that the c_2 -term might be correlated with a viscoelastic phenomenon, a detail of which will be discussed later.

II. ELASTICITY AND VISCOSITY OF UNVULCANIZED RUBBER

Unvulcanized rubbers exhibit also more or less elasticity in addition to viscosity in deformation and this fact suggests that the elongation of the coiled molecule occurs during the course of flow. The viscoelastic phenomenon is easily explained if the existence

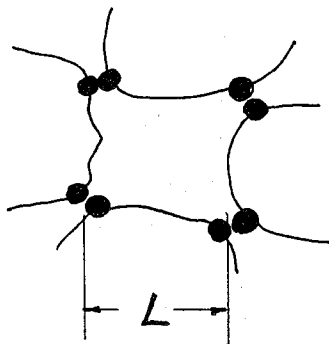


Fig. 2.

of a pseudo-crosslink is assumed. Physical entanglement of molecular chains is assumed sometimes, but the entanglement is much enhanced by intermolecular forces especially for the polymer having polar groups such as chlorine atoms and consequently a chemical entanglement is also conceivable.

Let us consider a cube of a volume of L^3 (Fig. 2) in which a single chain exists and the velocity difference Δu occurs by an applied force f between the top and the bottom of the cube, then the viscosity η is defined as

$$\frac{\Delta u}{L} = \frac{fL^2}{\eta L^2} \quad (13)$$

Δu is given by multiplying the number of breaking of crosslinks per second k' with the slippage distance $L(a-1)$, i.e.,

$$\Delta u = k' L(a-1) \quad (14)$$

f is given by

$$f = \nu k T (a-1) \quad (15)$$

Substituting Eqs. (14) and (15) to Eq. (13), η becomes to

$$\eta = \frac{\nu k T}{k'} \quad (16)$$

On the other hand, the elasticity E and the relaxation time τ are

$$E = \nu k T \quad (17)$$

$$\tau = \eta / E = 1 / k' \quad (18)$$

From Eq. (18), τ implies the time required for breaking one crosslink.

III. MELT VISCOSITY OF POLYMER SOLID

In equation (16) k' is an important factor as well as ν affecting viscosity. Similarly to Eyring's equation for liquid viscosity, k' is expressed as

$$k' = \left(\frac{kT}{h} \right) \exp \left(- \frac{\epsilon - w}{kT} \right) \quad (19)$$

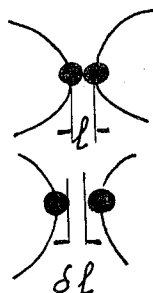


Fig. 3.

where ϵ is an activation energy for the break-down of a pseudo-crosslink decreasing by work w done by an external force. W is given by multiplying the force concentrated on a pseudo-crosslink, *i.e.*, fL^2 by the distance δl moved until breaking, l being the length of a segment and δ being a factor (Fig. 3).

$$W = fL^2 \cdot \delta l \quad (20)$$

Since the free volume of liquid is about 10% of the solid, δ may be $0.1^{1/3} \cong 0.5$. It is also obvious that n is N/ν , $l^3 N$ is 1 cm^3 , and L is $n^{1/2} l$. Accordingly,

$$k' = \left(\frac{kT}{h} \right) e^{-\epsilon/kT} e^{(\alpha-1)/2} \quad (21)$$

and

$$\eta = \left(\frac{N_0 h}{V} \right) e^{\epsilon/kT} e^{-(\alpha-1)/2} \quad (22)$$

Equation (22) shows a very large effect of the structural viscosity as compared with the ordinary liquid, because in the latter case,

$$w = fl^2 \cdot l/2 \quad (23)$$

whereas for the polymer melt

$$w = fL^2 l/2 = fnl^3/2 \quad (24)$$

In other words, w for the polymer is n times larger than that of the ordinary liquid, because the thermal motion of n segments belonging to a chain is concentrated on one crosslink.

The calculation of the number of pseudo-crosslink is carried out as follows: For the ordinary liquid the coupling and the dissociation are expressed as bimolecular and unimolecular reactions whose rate constraints are k' and k , respectively, *i.e.*,

$$\frac{d\nu}{dt} = k(N-\nu)^2 - k'\nu \quad (25)$$

At an equilibrium

$$\nu \cong N^2 k/k' = NK \quad (26)$$

where K is an equilibrium constant given with a function of an exothermic heat of crosslinking h ,

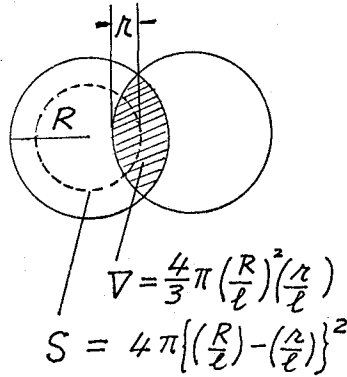


Fig. 4.

$$K = Nk/k' = e^{-h/kT}, \quad h < 0 \quad (27)$$

On the contrary, in the polymer the segment motion is much limited, since the molecular chain forms a coil and the segment moves only within a coil. Namely, the total number of collision of segments is the number of collisions of the coils times that of segments occurring in the overlapping region of two coils; the former is $(N/n_0)^2$ and the latter is

$$\left(n_0 \times \frac{n_0}{n_0^{3/2}} \right)^2 \sum V = n_0 \int_0^R \frac{4}{3} \pi \left(\frac{R}{l} \right)^2 \left(\frac{r}{l} \right) dr = \frac{\pi}{24} \left(\frac{R}{l} \right)^4 n_0 \quad (28)$$

where n_0 is the number of segments in one chain, $n_0/n_0^{3/2}$ is a concentration of segments in a coil and V is an overlapping volume. Accordingly, the total number of collision of segments is

$$\left(\frac{N}{n_0} \right)^2 \times \frac{\pi}{24} \left(\frac{R}{l} \right)^4 n_0 = \left(\frac{N}{n_0} \right)^2 \times \frac{\pi}{24} (n_0^{1/2})^4 n_0 = \frac{\pi}{24} N^2 n_0 \quad (29)$$

However, if the motion of coiled chain is very slow, the collision of coils is limited to the collision with neighboring coils (Fig. 4), *i.e.*,

$$\left(\frac{N}{n_0} \right) \cdot S = \left(\frac{N}{n_0} \right) \times 4\pi \left(\frac{R}{l} - \frac{r}{l} \right)^2 \quad (30)$$

where S is the number of sites locating over the sphere surface. Accordingly, the total number of collision of segments in this case is

$$\begin{aligned} \left(\frac{N}{n_0} \right) \sum V S \left(n_0 \frac{n_0}{n_0^{3/2}} \right)^2 &= \left(\frac{N}{n_0} \right) \frac{4}{3} \pi \left(\frac{R}{l} \right)^2 \left(\frac{r}{l} \right) \\ &\times 4\pi \left(\frac{R}{l} - \frac{r}{l} \right)^2 dr = 0.68 n_0^3 N \end{aligned} \quad (31)$$

From Eqs. (30) and (31), the number of junctions or crosslinks formed is proportional to n_0 or n_0^3 depending on the mobility of coiled chains. In other words, the melt viscosity of the polymer is proportional to n_0 or n_0^3 and this result is compatible with the experiment. There is a critical molecular weight, below and above which the first power and the third power dependency hold, respectively. The critical chain length n_c is known experimentally to be 10^3 — 10^4 and this value is obtained if the number of junctions ν becomes to the

number of chain, *i.e.*,

$$\frac{N}{n_0} = \nu_c = 0.8 n_0^3$$

or

$$n_0 = N^{1/4} = 10^4 - 10^5$$

IV. TEMPERATURE AND RATE DEPENDENCE OF VISCOSITY OF POLYMERS

It is well-known that the activation energy ϵ for viscous flow of unvulcanized rubber is about several kcal/mole at elevated temperature, but below room temperature the rubber becomes hard and ϵ becomes very large more than a hundred kcal/mole. This fact suggests that the size of flow unit increases with lowering temperature.

According to a concept of pseudo-crosslinked structure the number of junctions increases with lowering temperature and therefore, the number of molecules decreases with increasing junctions from N/n_0 to N/n , n and n_0 being chain length after and before the junction, respectively (Fig. 5-a),

$$\frac{N}{n} = \frac{N}{n_0} - \nu \quad (32)$$

or

$$n \cong n_0(1 + \nu n_0/N) \quad (33)$$

When ν reaches N/n_0 , the number-averaged molecular weight becomes infinitely large and beyond this critical junction, ν_c , the network structure is formed and the length of network chain n' decreases with increasing junction as given by (Fig. 5-b)

$$\frac{N}{n'} = \left(\frac{N}{n_0} - \nu_c \right) + (\nu - \nu_c) = \nu - \frac{N}{n_0} \quad (34)$$

The number of junctions involved in the original molecule is increased as

$$\frac{n_0}{n'} = \frac{\nu n_0}{N} - 1 \quad (35)$$

In the flow of polymer solid the viscosity is proportional to n before gel-point or n_0/n' after

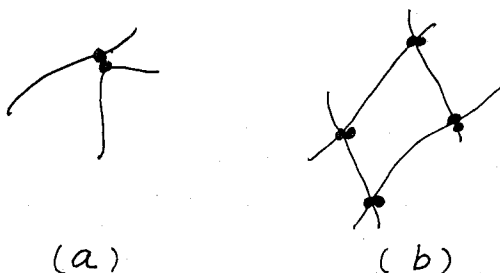


Fig. 5.

this point, since in the former case (a) the jointed molecule flows as a whole and in the latter case (b) the rate of flow is determined by the rate of break-down of crosslinks existing on a molecule. This consideration leads to the following results, *i.e.*,

$$\frac{1}{\tau_a} = k_a' = \left(\frac{kT}{h} \right) \left(1 + \frac{\nu n_0}{N} \right) \exp \left\{ - \left(\frac{\varepsilon_a}{kT} \right) \left(1 + \frac{\nu n_0}{N} \right) \right\} \quad (36)$$

and

$$\frac{1}{\tau_b} = k_b' = \left(\frac{kT}{h} \right) \left(\frac{n_0}{N} - 1 \right) \exp \left\{ - \left(\frac{\varepsilon_b}{kT} \right) \left(\frac{\nu n_0}{N} - 1 \right) \right\} \quad (37)$$

where ε_a and ε_b are the activation energies for the flow of the whole molecule and the break-down of pseudo-crosslinks, respectively. In case (a) $\nu n_0/N$ is less than unity, whereas in case (b) $\nu n_0/N$ is larger than unity and accordingly, the apparent activation energy increases much with lowering temperature and with increasing molecular weight in the latter case.

In both cases, the change in rheological behavior is given as a function of k 's and time t . If $k_a't$ or t/τ_a is less than unity, the viscous flow of molecule is negligible and instead, the material becomes elastic. In the same sense, if $k_b't$ or t/τ_b is less than unity, the observable change of break-down of pseudo-crosslinks is negligible and the material behaves as a highly crosslinked or glassy one. Accordingly, the points of $k_a't=1$ and $k_b't=1$ are regarded as phase-transition points, *i.e.*, a melt-rubbery transition temperature and T_b , rubbery-glassy one. They are given by

$$\ln \left(\frac{kT_a}{h} \right) - \frac{\varepsilon_a}{kT_a} + \ln t = 0 \quad (38)$$

and

$$\ln \left(\frac{kT_b}{h} \right) - \frac{\varepsilon_b}{kT_b} \left(\frac{n_0}{N} - 1 \right) + \ln t = 0 \quad (39)$$

Taking,

$$\frac{\nu n_0}{N} = n_0 e^{-h/kT} \cong n_0/T^\alpha \quad (40)$$

Equations (38) and (39) become to

$$\varepsilon_a/kT_a + \ln t = \text{const} \quad (41)$$

and

$$\varepsilon_b/kT_b^{\alpha+1} + \ln t = \text{const} \quad (42)$$

These equations give so-called time-temperature inversion relation, α being a value larger than zero.

V. THIXOTROPIC PHENOMENON AND MOONEY-RIVLIN EQUATION

Raw rubber exhibits a thixotropic phenomenon such as hardening during storage and softening on warming or repeated deformation. The phenomenon seems to be demon-

strated in terms of change in pseudo-crosslinks, whose formation and break-down are given by Eq. (43),

$$\frac{d\nu}{dt} = kN^2(1 - 2\nu/N) - k'\nu = \bar{k}(\nu - \nu_e) \quad (43)$$

where $\nu_e = kN/(2kN + k')$ and $k = 2kN + k'$. In this relation k and k' and equilibrium crosslinks ν_e are varied during the course of deformation but for the sake of simplicity only the change of ν_e is taken into account. ν_e , i.e., an equilibrium value under stress is smaller than the initial ν_0 , i.e., a value under no stress and ν_e is given by

$$\nu_e = \nu_0 e^{-(\alpha-1)} \quad (44)$$

From Eqs. (43) and (44),

$$\frac{d\nu}{d\alpha} = -(\bar{k}/\dot{\alpha}) (\nu - \nu_0 e^{-(\alpha-1)}) \quad (45)$$

and

$$\frac{\nu}{\nu_0} = \frac{1}{(\bar{k}/\dot{\alpha}) - 1} \left\{ \frac{(\bar{k})}{\dot{\alpha}} e^{-(\alpha-1)} - e^{-(k/\alpha)(\alpha-1)} \right\} \quad (46)$$

are obtained. Equation (46) is simplified into Eq. (44)

when $\bar{k}/\dot{\alpha} > 1$,

$$\frac{\nu}{\nu_0} = e^{-(\alpha-1)} = \frac{1}{\alpha} \quad (47)$$

and when $\bar{k}/\dot{\alpha} < 1$, Eq. (48) is applicable,

$$\frac{\nu}{\nu_0} = e^{-(\bar{k}/\dot{\alpha})(\alpha-1)} \quad (48)$$

Equation (47) implies a rapid but limited disentanglement of pseudo-crosslinks, whereas Eq. (48) implies a slow disentanglement, the latter of which depends on the rate of deformation but the former does not. In actual case, two- or multi-stage deformation or relaxation is observed and this fact is explained by the combination of rapid disentanglement and slow one.

Finally, the rapid disentanglement is also associated with the c_2 -term of Mooney-Rivlin equation on rubber elasticity. From Eq. (47) c_2/α is considered to be equal to

$$\frac{c_2}{\alpha} = \nu_0 k T e^{-(\alpha-1)} = \frac{\nu_0 k T}{\alpha} \quad (49)$$

The reason for the rapid disentanglement is not yet elucidated but the successive and cumulative formation of crosslinks during storage may be one of the reason.

CONCLUSION

A pseudo-crosslinked structure of unvulcanized and vulcanized rubber seems to be a useful concept accounting for elastic, viscous and viscoelastic phenomena. The theory can

describe the phenomena quantitatively in terms of molecular weight, heat of crosslinking, temperature and rate of deformation and accordingly, it is more useful than the classical rheology in order to obtain more detailed insight into chemical structure of rubbery material.

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