Effect of Chemical and Physical Crosslinks on Strength of Rubber and Plastics—A Theoretical Approach

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SYNOPSIS

For rupture of rubber and plastics, three types are proposed: (a) elastic, (b) plastic, and (c) brittle. For (a) the rupture takes place at the ultimate elongation of chains between crosslinks. Strength f is proportional to the number of crosslinks and also the fraction of effective chains giving the optimum degree of vulcanization ν. Both ν and f at the maximum strength decrease with increasing the bond energy D of crosslinks. The rupture in (b) occurs for filled rubbers. The maximum reinforcement with filler is expected to be attained at 20% volume fraction of filler from the pseudo-link model in which the number of links are proportional to the specific surface area, the fraction, and the adsorption ability of the filler particles. For (c) the craze occurs due to the breakdown of pseudo-crosslinks of the smallest size b, and b is 2 at the glass transition temperature. Impact strength is improved by the dispersion of rubber particles at the optimum fraction of 13% and under the small distance of neighboring particles, which is 0.4 μm and is corresponding to the relaxation distance. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In a preceding study[1] the rupture of rubber and plastics are dealt with theoretically with use of the pseudo-crosslink model. Three types of ruptures were proposed to occur, respectively, in brittle, elastic, and plastic zones depending on the rate of elongation and/or temperature.

Effects of vulcanization and fillers are enormous in elastic and plastic rupture, and they attain maxima of strength at an optimum degree of vulcanization and an optimum amount of fillers. Checking the literature, the optimum degree of vulcanization is affected by the mode of vulcanization such as sulfur cure, peroxide cure, or γ-irradiation. These results lead to a more detailed insight into the mechanism of rupture.

Effect of Bond Strength of Crosslinks

In the preceding study,[1] the rupture of vulcanized rubbers at the elastic region is caused by the scission of the main chain and is expressed as follows:

$$f = \frac{\nu}{N}\frac{D}{V}\exp\left[-\frac{2}{3}\frac{D}{(\alpha^2/2)RT}\right] \quad (1)$$

where f is the force at break, ν and N are the number of crosslinked and total segments in a unit volume of the specimen, respectively, ν/N is the fraction of crosslinks, D is the bond energy of the main chain, and V is the molar volume of a segment. The exponential factor implies a fraction of breaking chains whose elongation ratio is α. Here, $(\alpha^2/2)RT$ is the average kinetic energy of chains, D is the bond energy of the main chain, and $(2/3)D$ is an activation energy for scission. It was assumed that the scission takes place at the ultimate elongation of chains, α_m, and the elongation at break α is

$$\alpha = \alpha_m = (N/\nu)^{1/2} \quad (2)$$

The vulcanization decreases the elongation at break α, whereas it increases the strength. The strength attains a maximum at the condition that

$$\frac{2}{3}\frac{D}{(\alpha^2/2)RT} = 1 \quad \text{or} \quad \frac{\nu}{N} = \frac{3RT}{4D} \quad (3)$$

giving

$$f_{max} = \frac{3}{4e}\frac{RT}{V} \quad (4)$$

Equations (3) and (4) imply that the bond strength decreases the optimum degree of crosslinks but does not affect the maximum strength. This fact may be ascribed to the decrease of the fraction of the actual chains to be broken, since the exponential factor in Eq. (1) decreases with increasing the number of crosslinks, which is (v/N) or equal to $1/\alpha^2$, and also with increasing the bond strength D. However, the maximum strength seems to decrease actually with increasing the bond strength of crossbonds. When the contribution of the elastic force of the unbroken chains is taken into consideration, Eq. (1) is modified as

$$f = \frac{v}{N}\left[\frac{D}{V}e^{-x} + \frac{RT}{V}\alpha(1 - e^{-x})\right] \quad (5)$$

where x is $(v/N)(4D/3RT)$.

It may be assumed that the kind of crossbond is different depending on the mode of vulcanization. When the crosslink is weaker than the main chain, the bond energy of the crosslink is to be taken as D. Then, Eq. (5) becomes Eq. (1) for the small value of v/N and the large exponential factor, but for the large value of v/N the exponential factor is small and the second term dominates, and the strength becomes

$$f = \frac{v}{N}\frac{RT}{V}\alpha = \left(\frac{v}{N}\right)^{1/2}\left(\frac{RT}{V}\right) = \left(\frac{1}{\alpha}\right)\left(\frac{RT}{V}\right) \quad (6)$$

In general, the optimum degree of vulcanization and also the maximum strength both decrease with increasing bond strength as expressed as

$$f_{max} = \left(\frac{3RT}{4V}\right)\left(\frac{1}{e}\right) + \left(\frac{2RT}{4D}\right)^{1/2}\left(1 - \frac{1}{e}\right) \quad (7)$$

Equations (6) and (7) are discussed later.

In Eq. (5) the exponential factor $\exp(-x)$ is relatively large for low degree of vulcanization (v/N), whereas the factor $1 - \exp(-x)$ of the remaining chains becomes large for high values of (v/N). The total amount of links v is composed of the chemical link v_1 and the pseudo-link of the largest size v_B. Consequently, Eq. (7) is transformed as follows when v_1 is larger than v_B, the resistance of the B

chain of the largest length, where a viscous force is given by a product of the elasticity $(v_B/N)(RT/V)$, the rate of elongation $\dot{\alpha}$, the relaxation time τ_B, and the plastic deformation is α_p.

$$f = \frac{v_B}{N(RT/V)}\dot{\alpha}\tau_B\alpha_p$$

The case of the plastic rupture is described in the following section. The transition occurs at the condition that $v_1 = v_B$ as shown in Figure 1. The force at break attains a maximum and the elongation at break changes as mentioned in the preceding study.[1]

Plastic Failure of Filled Rubber

As pointed out in Eq. (5), the strength at break depends on the elastic force of the remaining chains when the number of the crosslinks increases and the latter is balanced with the viscous flow resistance of the pseudo-crosslinks. In fact, the mode of rupture changes from elastic to plastic at high degree of vulcanization. As described in the previous study, rubber vulcanizates filled with calcium carbonate or carbon black reveal the plastic failure at high degree of vulcanization and the elongation α and the strength f at break are given by
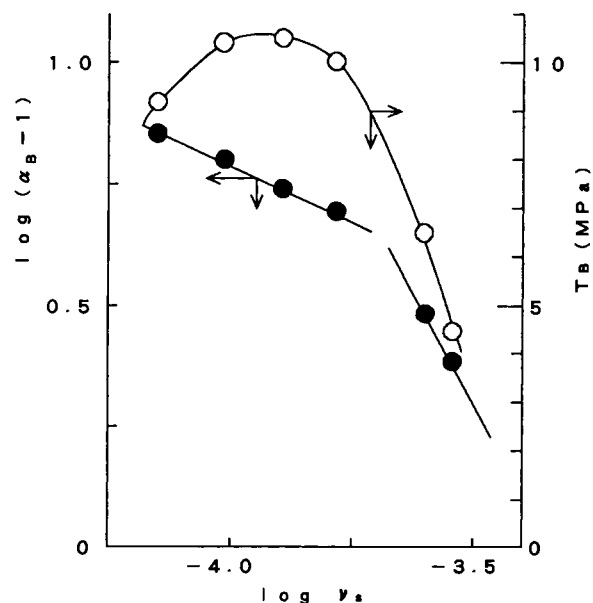

Figure 1   Transition in rupture. Data of DCP-cured NR vulcanizates: DCP, di-cumyl peroxide; DCP concentration (phr), 2, 3, 4, 5, 8, 10; α, 100 mm/min, temp. 20°C; α_B-1, elongation ratio at break; T_B, tensile strength.

$$t = 2\tau$$

or

$$\alpha = 2\dot{\alpha}\tau_f \qquad (8)$$

and

$$f = \eta_f \dot{\alpha}\alpha \qquad (9)$$

where α and $\dot{\alpha}$ are the elongation ratio and the elongation rate, respectively. τ_f is the relaxation time of the chain adsorbed on the filler surface whose number is ν_f, and η_f is the viscosity of filled rubber and τ_f, η_f and the elasticity E_f are given, respectively,[2] as

$$\tau_f = \tau_0 n_B^{2.5}(1 - a\phi_f)^{1/3} \qquad (10)$$

$$E_f = \nu_f kT = \phi_f^{2/3} N[K_f/(1 + K_f)]kT \qquad (11)$$

and

$$\eta_f = E_f \tau_f \qquad (12)$$

where τ_0 is the relaxation time of the unit segment and n_B is the chain length of the chain B of the largest size or 16^2 or 256 in the segmental unit. ϕ_f is the volume fraction of the filler and a is a factor concerning the adsorbed layer on fillers.

As a result, f becomes

$$f \sim \phi^{2/3}(1 - a\phi)^{2/3} \qquad (13)$$

giving a maximum at $\phi = \dfrac{1}{2a}$ or $\phi = 0.2$ for a of 2.5.

The plastic failure of filled rubber is explained in the preceding study where the elongation is inversely proportional to a square of the degree of vulcanization ν_1, unlike in the elastic rupture where the elongation is inversly proportional to a square root of ν_1.

The Ogunniyi's experiment[3] shows the maximum strength occurring at a constant volume fraction, i.e., 20% of added filler to which Eq. (13) is quite compatible.

Strength of Plastics

According to Eq. (7) the strength of plastics is higher than that of vulcanized rubber due to the smaller elongation at break for plastics. However, plastics are rather more vulnerable to impact deformation than rubber. The impact strength is concerned with the brittle fracture occurring at low temperature and/or high rate of deformation. In this case the pseudo-crosslinks of smallest size may be broken without its regeneration, and the craze may propagate giving rise to the crack fracture. The equation of fracture is similar to Eq. (1), but the bond energy D is replaced by the cohesion heat, bH_0 of the pseudo-crosslink of size b, and H_0 is refered to the unit link. It follows that

$$f = \frac{\nu}{N}\frac{bH_0}{V}\exp\left[-\left(\frac{4}{3}\frac{\nu}{N}\right)\left(\frac{bH_0}{RT}\right)\right] \qquad (14)$$

Since the heat H_0 is expressed with the transition temperature T_A or the glass transition one, T_g and N/ν is replaced by the chain length n_b or the square of the link size b as presented in the previous paper,[2] it follows that

$$H_0 = 2RT_A = (\tfrac{3}{2})RT_g$$

and

$$N/\nu = n_b = b^2$$

Equation (14) is transformed to

$$f = \frac{3RT_g}{2bV}\exp\left(-\frac{2T_g}{bT}\right) \qquad (15)$$

In this equation f attains a maximum at $T = T_g$ taking 2 as b and f_{max} is

$$f_{max} = \frac{3}{4}\frac{RT_g}{V}\left(\frac{1}{e}\right) \qquad (16)$$

In this case, the remaining chains whose fraction is $1 - (1/e)$ does not contribute to the impact strength because the fracture takes place locally at the tip of the craze.

According to Eq. (15) the impact strength may increase with increasing temperature. At or above T_g the strength increases with increasing T_g but decreases below T_g. In relation to the strength of polymers, fibers having crystalline structures exhibit very high strength and elasticity. The polymer forms the crystalline structure and the chains are already extended uniformly. In other words, the exponential factor becomes unity. The elastisity E and the strength f become very large as expressed as follows:

$$E = (\nu/N)E_c \qquad (17)$$

and

$$f = (\nu/N)(D/V) \qquad (18)$$

where E_c is the elasticity of the crystal. Both E and f are proportional to the density of chains in the cross-sectional area of the specimen.

Improvement of Impact Strength of Plastics by Rubber Dispersion

Reinforcement of vulcanized rubber is achieved by the ingradiation of active filler whereas the improvement of impact strength of plastic is obtained by the dispersion of rubbery particles. For the impact strength the contribution of elastic force is important according to Eq. (15). Another characteristic behavior is that the propagation of craze giving rise to crack proceeds in one direction unlike the dissipation of impact energy in the rubber dispersion, which occurs in three dimensions. From these circumstances the following condition is adopted for the fracture of the system composed of (1) rubber particles and (2) the continuous phase of plastics.

$$\phi_1^{1/3}\alpha_1 = \phi_2^{1/3}E_2\alpha_2 \qquad (19)$$

where ϕ, E, and α are the volume fraction, elasticity, and elongation ratio of each components, respectively. Here, the interface between rubber and plastics is assumed not to be rigid but to allow the slip to occur to some extent and giving the different elongation ratio, α_1 and α_2 for each phases.

The impact energy is proportional to $E\alpha^2$ and the total energy W is

$$W = \phi_1 E_1 \alpha_1^2 + \phi_2 E_2 \alpha_2^2 \qquad (20)$$

Substituting a ratio $(\alpha_1/\alpha_2)^2$ in Eqs. (19) to (20), it follows that

$$W = w_2[\phi_2 + \phi_1^{1/3}\phi_2^{2/3}(E_2/E_1)] \qquad (21)$$

Since $E_2 \gg E_1$, Eq. (21) indicates the increase of the impact strength. According to Einstein's equation of the viscosity for colloidal dispersions, a part of the solvent on the surface of the particle is immobilized, and a fraction $1 - a\phi_2$ is taken instead of ϕ_1 as the fraction of solvent, being a factor due to the adsorption. In the case of plastics, the particle is composed of rubber and the anti-impact effect is extended to the hard matrix. Similarly, Eq. (21) leads to the maximum at

$$\phi = \frac{1}{3a} \qquad (22)$$

If a is also taken to be 2.5 in this case, ϕ_1 at the maximum impact strength is 0.13, whereas it is 0.33 when a is taken to be unity. The former is adopted to the rubber particle and the latter to the glass particle, as discussed later.

DISCUSSION

The effect of the mode of vulcanization on the strength of vulcanized natural rubber was reported in literature.[4] The degree of vulcanization and the tensile strength at the maximum both seem to decrease with increasing order of the strength of the crosslinks. The order is as follows: the vulcanizate with sulfur, that with tetramethylthiuram disuifide TMT, that with peroxide, and that prepared by high-energy irradiation. The order runs parallel to the order of the bond energies (kcal/mol, i.e., 4.19 kJ/mol) of S-S (57), C-S (64), C-O (77), and C-C (85). The tensile strength increases with vulcanization, and in most cases the product of the strength times the elongation at break becomes constant. This may be accounted for by the assumption of the ultimate elongation at break.

Elasticity of filled rubber E increases with increasing the volume fraction ϕ according to the Guth–Gold equation,[5] similar to the Einstein equation for the viscosity of the colloidal solution.

$$E = E_0(1 + a\phi) \qquad (23)$$

where E_0 is the elasticity of pure rubber vulcanizate. In this case the effect is arising from the concentrated strain due to the filler or the volume effect, and the coefficient a is almost constant of 2.5. However, at large deformation it is accompanied by the slippage on the interface of fillers, and the force is given by an equation similar to Eq. (9), and in this case the effect is proportional to the number of pseudo-link ν_f on the filler surface and its relaxation time τ_f. They are expressed by Eqs. (11) and (10), respectively, depending on the nature of filler and rubber. The addition of filler increases E_f whereas it decreases τ_f; in other words they cause shifts in the log E–log τ diagram or the relaxation spectrum.

In this connection, the so-called Payne effect[6] is interesting to note. This is the effect of the amplitude of the vibration on the dynamic moduli G', G'', and tan δ for carbon-black–loaded rubber. They are expressed with a diagram similar to the relaxation

spectrum and may be concerned with the pseudo-crosslinks on the surface of carbon-black particles. They may express the distribution of pseudo-links of various bond strength for the slip by the deformation of various magnitude. Interesting is the fact that it shows the maximum of the loss modulus, or tan δ at a small amplitude, i.e., about 1–10%, and it is believed to be concerned with the carbon-black aggregate or structure. In fact, the magnitude of tan δ seems to run parallel to the adsorption ability of carbon blacks. However, the amplitude for the maximum tan δ is not specific to the sort of carbon black. It is almost constant and is not affected by the deformation cycle although the magnitude of tan δ varies. It is also independent of the molecular weight of rubber but becomes very small in the oligomer or hydrocarbon oil as the matrix. The Payne effect was found to be small for SBR and polybutadiene prepared by the living polymerization in solution, and the effect seems to be concerned with the polymer terminal, because the rubber modified by tin tetrachloride or dimethylaminobenzophenone shows very little Payne effect. Tin tetrachloride was found to react with the polymer terminal and to facilitate fixing the terminal on the surface of carbon black. On the basis of the above observation it is likely to assume that the Payne effect arises from the relaxation of terminal chains adsorbed on the surface of carbon blacks ν_f. If so, ν_f and its relaxation time τ_f are given, respectively, as by the volume V, the surface S, and the adsorption constant K_f

$$\nu_f = \frac{N}{n} \, \phi^{2/3} \, \frac{S}{V} \frac{K_f}{1 + K_f} \qquad (24)$$

and

$$\tau_f = \tau_B (1 - a\phi)^{1/3} \qquad (25)$$

In Eq. (24) n is the chain length of a whole molecule and N/n is the number of the rubber molecules or the terminal chains and K_f is an equilibrium constant of the adsorption of the terminal chains, which is not the same as that of the pseudo-link of the largest size B but may be proportional to it. The relaxation time of the terminal chain τ_B proceeds through dissociation of the pseudo-crosslink of the largest size[2] B and τ_B is expressed as a product of the relaxation time of a segment τ_0, the fraction of chains having an activation energy E_B^* and the distant length n_B of the B chains.

$$\tau_B = \tau_0 \exp(E_B^*/RT) n_B^{0.5} = \tau_0 n_B^{2.5} \qquad (26)$$

Equation (26) implies that the dissipation of strain of the largest chain is conducted by the viscous flow process. On the other hand, impact strain propagates in a linear direction by successive collision of segments through a free volume canal. Consequently, the distance for relaxation of the terminal chain, d_c, is given with a product of $n_B^{2.5}$ times the diameter of a segment l as

$$d_c = n_B^{2.5} l \qquad (27)$$

Taking $10^{2.4}$ for n_B and 1 nm for l, d_c becomes

$$d_c = 1 \text{ mm}$$

which is very close to the amplitude observed. The critical relaxation distance d_c is a universal value that is not affected by the molecular weight; but for oligomers whose chain length n is smaller than n_B or 256, the critical distance becomes smaller.

On the other hand, the magnitude of the maximum value of the loss modulus G'' and tan δ may run parallel to the adsorption ability of the polymer terminal and also the chain segment. It may be proportional to the reinforcing ability of carbon black or the rolling resistance. The modification with tin tetrachloride or dimethylaminobenzophenone were reported to have a high ability to break the carbon structure to give a good dispersion in rubber matrix, but it is not the origin of the Payne effect, because these reagents do not reveal the same effect for the emulsion SBR to which the reagents have no effect toward the modification of the polymer terminal.

In case of the plastic rupture, the fracture occurs locally at the tip of crazes, and the strength depends on the molecular structure rather than the cohesion heat or the glass transition temperature. Crystalline polymers may be vulnerable to the impact deformation rather than amorphous polymers having no cleavage plane.

For improvement of impact strength the incorporation of the rubbery particle is useful. According to Kinloch's experiments[7] on the epoxy-resin ingradiated with the carboxyl-terminated nitrile rubber, the strength depends mainly on the volume fraction of rubber, and it attains a maximum at 13% volume fraction of rubber and at 33% volume fraction of glass particles. These facts can be explained with Eq. (21). Also Eq. (21) indicates the improvement of the impact strength and that its index I at

the maximum is proportional to the elasticity ratio E_2/E_1. Since the elasticity of epoxy resin E_2 is constant below its T_g, whereas that of nitrile rubber E_1 decreases with temperature T. The following is assumed:

$$\log I = A - H_1/2.3RT \qquad (28)$$

Equation (28) is found to fit Kinloch's data giving the heat of pseudo-links H_1 of 2.5 kcal. This value is regarded as that of nitrile rubber. And if so, the rubber particle of low elasticity is to be efficient for reinforcement. For the dispersion of glassy particles, the large slippage may occur on the surface of the particle and the surface tension of the plastics may replace the elasticity E_1.

Wu[8] pointed out the existence of the critical distance d_c between neighboring rubber particles, and it is 0.4 μm for the nylon–nitrile rubber dispersion.

The particle distance d can be controlled with changing size of the particle d_0 of sphere particles as well as the fraction ϕ and is expressed as

$$d = d_0[(6/\pi\phi)^{1/3} - 1] \qquad (29)$$

Beyond d_c the effect of rubber particle disappears and within d_c the effect is mainly depending on the fraction ϕ but not on the distance d. The meaning of the critical distance d_c is not yet elucidated. d_c was taken to be equal to the craze/bulk boundary layer which is a characteristic dimension for given matrix, and wherein the entanglement strands are stretched from underformed state to the maximum extension ratio.[9,10] It was claimed that the brittle/tough transition occurs when d_c attains connectively (percolation) threshold. From the pseudo-crosslink concept the critical distance is regarded as a relaxation distance for the craze propagation. Within d_c the rubber particle can retard the craze propagation. The relaxation time τ_b of the smallest pseudo-crosslink of the size b is

$$\tau_b = \tau_0\exp(bE_0^*/RT)n_B^{0.5} = \tau_0 n_b^2 n_B^{0.5}$$

where E_0^* is the activation energy of the dissociation of the segment (see the Appendix) and

$$d_c = n_b^2 n_B^{0.5} l \qquad (30)$$

Taking 2 as b, 4 as n_b, $10^{2.4}$ as n_B and 10^{-9} m as l. d_c becomes $10^{-6.6}$ m. The calculated value is quite compatible with the literature. It is interesting to note that the Payne effect affords the relaxation time

for the link of largest size, whereas the craze effect gives that of the smallest size. It was already pointed out that d_c is a fundamental micromechanical parameter, which is determined by molecular and morphological process, and cannot be predicted from macroscopic stress–strain relationships.[10,11] On the other hand, Eq. (30) predicts the magnitude of d_c from a molecular concept, and it is not inconsistent with the above interpretation of Wu et al.

On the other hand, the brittle fracture is dealt with mostly with the mechanical theory,[12] but it is difficult to explain the optimum amount of rubber particles and the existance of the critical particle distance. Size b at T_g is estimated to be 2 from the equation for the contitutional equation (see Appendix).

CONCLUSION

Pseudo-crosslink model seems to be useful for the elucidation of the mechanism of elastic and viscoelastic phenomena such as the rupture of rubber and plastics. The model is based on the entanglement of polymer chains with cohesion, and it is versatile for solving the rheological problems from a thermodynamical viewpoint.

APPENDIX

A constitutional equation for the size of pseudo-crosslink b was derived from the equilibrium between the dissociation energy bH_0 and the entanglement energy of chain length n_b as 2).

$$bH_0 = RT(\ln n_b^3) \qquad (31)$$

Since the cohesion energy H^0 can be replaced by $2RT_A$ and n_b is equal to b^2 and T_g is equal to $(4/3)T_A$, T_A and T_g being the transition point of the pseudo-crosslink and the glass transition, respectively, it follows that

$$b/\ln b = 3T/T_A = 4(T/T_g) \qquad (32)$$

Equation (31) is approximated when b is large,

$$b = 12T/T_A - 8 \qquad (33)$$

but it attains a minimum at b of 1.2. At T_g, b becomes 1.2 or 10. On the other hand, at T_g the multiple link

among chains is formed and the second-order transition takes place inducing a change of size b from 10 to 1.2.

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