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Chemical Aspects Concerning the Friction and Abrasion of Rubber

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The frictional force (f_F) is proportional to the normal force; for rubber it is corrected by a factor involving the pressure and elasticity due to a change of the contact surface. During friction induced by a slider, f_F fluctuates, which is conventionally explained by a stick-slip mechanics. However, the effect of the temperature and velocity on f_F as well as the frequencies of vibration and pattern abrasion producing worn products of various size, are not studied using mechanical model.

On the contrary, the author discusses here the chemical mechanism of stick-peeling based on a model involving pseudo crosslinks of multi-sizes. The frictional force (f_F) is taken to be equal to the peeling force (f_P), For adhesives, f_P is proportional to the adhesion force (f_A) affected by such rheological factors as the peeling velocity (v), the thickness (h), and the relaxation time (τ); $f_P = f_A(\tau v h)^{0.5}$. Here, f_A is proportional to the fraction of the pseudo link (ν) and the wetting energy (W) divided by the peeling distance, which is almost equal to the bond length (l) and f_A is expressed as $f_A = (\nu/N)^{2/3}(W/l)$. ν is the number of links formed on the surface of the rubber, and is varied with the sizes of the links 4 (link A) and 16 (link B) and their relaxation times of $10^{-3.4}$ s (τ_A) and 10^{-1} s (τ_B).

Also, for the frictional force (f_F) the same equation is obtained when v and h are taken to be the velocity of the slider and the thickness of the rubber layer deformed by the slider, respectively. Friction produces two kinds of vibrations by the dissociation of links A and B; their frequencies are given by the reciprocal of τ_A and τ_B, respectively.

Abrasion is caused by the scission of rubber chains connected with links A and B in the peeling process. The former abrasion yields powdery wear products by crazing, whereas in the latter the scission of chemical bonds of the energy (D) develops to give crest-shape tearing i.e. so-called pattern abrasion. The sizes of wear products are proportional to the relaxation distances corresponding to τ_A and τ_B. The resistance to abrasion of rubber is expressed by a ratio of the force at a break (f_B) to f_F, $f_B/f_F = (\nu/N)^{1/3}(D/Wl^2)(v\tau h)^{-0.5}$. Carbon black improves the abrasion resistance due to its reinforcing ability, and the resistance is enhanced by increasing the content, specific surface area and adhesion ability of carbon black. Their optimum values were also estimated theoretically.

A large number of reports concerning the friction and abrasion have been published especially about rubber. They deal with hydrodynamics in terms of the contact area and roughness of surface, etc. However, the coefficients of friction and abrasion are also affected by the chemical nature of rubber as well as the rheological conditions, such as the temperature and velocity. Many empirical relations are known among friction, abrasion, elasticity, viscoelasticity of rubbers and plastics with or without active fillers. Although the mechanisms of each relation is proposed, comprehensive theories are rather few.

As a related problem, the author has proposed a new theory of adhesives based on the cohesive and adhesive forces of polymeric materials.[1] This theory has been extended to friction and wear. This paper involves a theoretical approach with the special emphasis on the role of the chemical nature of rubber.

Friction and abrasion are characteristics of materials. For polymers, especially rubber, they greatly depend on the temperature and velocity, and show a spectrum similar to that of stress-relaxation. There are transition temperatures which depend on the chemical nature.

Theory

In a preceding paper concerning adhesion[1] proportional relations were proposed among the force of adhesion (f_A), that of peeling (f_P), and the wetting energy (W). The frictional force (f_F) is also proportional to the normal force and f_F is assumed to be equal to f_P in the horizontal components. Though W and f_A are expressed by the values per area of contact, f_P and f_F are expressed per width of the adhesives tape and that of the moving slider, respectively. For the sake of simplicity values per unit area or width are used in this paper.

Mechanical Effect on Friction. The frictional force (f_F) is proportional to the load or normal force, or a product of the pressure (p), and a ratio of the contact area (S_c) to the apparent area (S),

$$f_F = \mu p(S_c/S), \tag{1}$$

where μ is the coefficient of friction. S_c is smaller than S affected by the roughness or asperity. S_c increases with increasing the load and becomes close to S, especially in the case of a rubber having a low elasticity (E). Denny,[2] Lincoln,[3] Schallamach,[4] and Tokita et al.[5] took the factors concerning the contact area into consideration, and expressed μ as

$$\mu = \mu_0(p/E)^m. \tag{2}$$

The exponential index (m) was determined experimentally for natural rubber, and is smaller than 1.

Here, μ_0 is the intrinsic coefficient of friction between the contact materials. It involves the chemical natures, especially the adhesion of the polymer to the slider and is also affected by such rheological factors as the temperature and velocity of the slider. The coefficient (μ) tends to increase with increasing the velocity, but reaches a maximum. For the effect of temperature the WLF-type equation can be applied.

Abrasion is a very complicated phenomenon, which is influenced by the conditions in-door and out-doors. Wear is a kind of rupture of rubbers or polymers, and is classified into various types, such as abrasion wear, fatigue wear, oily wear, and pattern wear. The mechanisms are not so simple as to be affected by various factors according to the test conditions.

Forces of Adhesion and Peeling. As explained in a preceding paper concerning adhesion,[1] the force of adhesion (f_A) per unit area is given by the wetting energy (W) per unit area and the fraction of the adhesive links formed on the surface of a unit area, $(\nu_A/\mathrm{N})^{2/3}$, which is equal to the surface fraction of the links in rubber i.e. $(\nu/N)^{2/3}$, ν and N being the number of linked and total segments existing in a unit volume or 1 cm^3, respectively. Thus, f_A per unit area is expressed as

$$f_A = (\nu/N)^{2/3}(W/l), \tag{3}$$

where l is the segment length and W/l is the bond force acting on a pseudo link. W is given by the difference between the cohesion energy of a segment of the adhesives (1) and that of the adherend (2). W was estimated from the solubility parameter (δ). Since δ_2 is a molar cohesion energy divided by a molar volume of a segment and W is an interfacial energy for a unit surface area, Wl^2 is equal to $\delta^{2/3}$, and therefore, of a unit segment of volume (V/N_A or l^3) as

$$W/l = 2\delta_1\delta_2 - \delta_1^2 = \delta_2^2 - (\delta_1 - \delta_2)^2. \tag{4}$$

W attains a maximum when δ_1 is equal to δ_2. In a system comprising the rubber (1) and a hard adherend (2), δ_1 is smaller than δ_2 and Eq. 4 is simplified as

$$W \approx 2\delta_1\delta_2 l. \tag{5}$$

Although the adhesion force (f_A) is essentially proportional to the surface tension, the direction is different, and perpendicular to the interface. The peeling force (f_P) is proportional to f_A. Since f_P is enhanced by the viscous resistance in the adhesives layer according to Eq. A12 in Appendix, f_P is expressed as

$$f_P = f_A/(1/h + 1/\tau\nu) \sim f_A(\tau\nu h)^{0.5}. \tag{6}$$

Rubber is deformed in depth or thickness (h) by the load. Here, τ is its stress relaxation time and ν is the peeling velocity.

Chemical Nature of Friction. For polymers, friction is affected by the temperature. Its temperature-spectrum resembles the spectrum of elasticity and that of adhesion, as explained in the "Discussion" section. Thus, the friction is greatly affected by the factors of adhesion; it is possible to assume that friction is induced by the peeling force during the process of sticking (adhesion) and peeling, as shown in Fig. 1. Since the friction force (f_F) is taken to be equal to the peeling force, Eq. 6 can be applied. Thus, f_F is expressed as the product of the adhesion force (f_A) and the peeling factors with respect to the peeling velocity (ν), the relaxation time (τ), and the thickness (h) of the adsorbed layer; f_F becomes

$$f_F = f_P = (\nu/N)^{2/3}(2\delta_1\delta_2/l)(h\tau\nu)^{0.5}. \tag{7}$$

The coefficient of friction (μ) increases with increasing the velocity, and shows a spectrum similar to that of adhesion. The spectrum is shifted by changing the temperature according to the WLF-type equation. Also, the coefficient of friction (μ) is proportional to the peeling force (f_P) in the dynamic condition. Equation 7 involves the number of pseudo crosslinks (ν), the elasticity (E) and the solubility parameter (δ). These variables arise due to the cohesive nature of polymers and enhance the friction.

On the other hand, Eq. 2 indicates that although the contact area as well as the friction increase with decreasing the elasticity (E) the effect is limited to the case of very low elasticity.

In rubber, pseudo crosslinks of various sizes exist between 4 and 16, or link A and B, respectively. Similar to these points, corresponding links, A′ and B′ exist on the surface, and their sizes are taken to be equal to A and B, respectively. Upon peeling these links are dissociated, and the smallest link (A′) induces an ultrasonic vibration, and the largest link (B′) produces frictional vibration. The latter is known as Schallamach's wave. A rupture also takes place in the rubber layer near to the surface, giving rise to abrasion.

Transition Points in Friction. As explained in Appendix, there are many transition points, such as T_m (melting), T_s (softening to melting), T_B (onset of softening), T_g (glassfication or rheological point of solidification), and T_A (thermodynamic point of solidification).[16] The conventional temperature of the heat distortion is close to T_g. It is also known regarding adhesives that mechanism of adhesion and peeling changes dramatically at T_s, T_B, and T_g, because

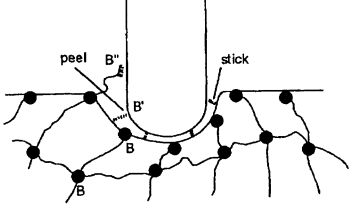

Fig. 1. Friction model of stick-peeling mechanism. B, B′, and B″ are the pseudo links of the largest size in rubber layer, on the surface and in the terminal chain, respectively giving the pattern abrasion.

the elasticity and the relaxation time change at these points.

For rubber, although the friction increases with increasing the velocity (v) according to Eq. 7, a transition takes place at T_B from tacky to viscoelastic and at T_g from viscoelastic to glassy. There are two peaks of friction at these points. At room temperature, the corresponding velocity (v) becomes 10^1 cm s^{-1} at T_B and $10^{3,4}$ cm s^{-1} at T_g, as derived in Appendix.

Vibration Caused by Friction. When a hard slider is moved on the surface of a polymeric material, a frictional force is induced with vibrations on the surface, and a dissociation of the cohesion bond or the pseudo link on the surface.

In mechanics, the rubber deforms due to the load, and some depth of the rubber layer is extended by squeezing by the slider. At the maximum elongation the slider suddenly slips. This process repeats periodically based on the stick-slip mechanism. Although the length of elongation is calculated from the period of the vibrations and the elasticity of rubber (E), the period of the pattern is not derived theoretically.

On the other hand, in molecular dynamics friction is caused by repeated adhesion and peeling. Figure 1 indicates the mode of adhesion and peeling in one period. In this case, the deformation (α) and elastic force (f) of the rubber layer of the interface change by repeated adhesion-peeling. Vibrations are induced by the dissociation of the links B′ and A′, and the wavelength for B′ is large, whereas that of A′ is small. Figure 2 indicates vibrations along with their amplitudes and periods.

In more detail, the period can be calculated as follows: Friction by the moving slider induces a large extension of chains; also, some part of pseudo crosslinks migrates along the extensional direction. E is decreased and the change in the force (f) is expressed as[17)]

$$f = E\alpha \exp(-t/\tau), \tag{8}$$

where t is the time for deformation and τ is the relaxation time. At a constant rate of deformation f attains a maximum under the condition $t = \tau$.

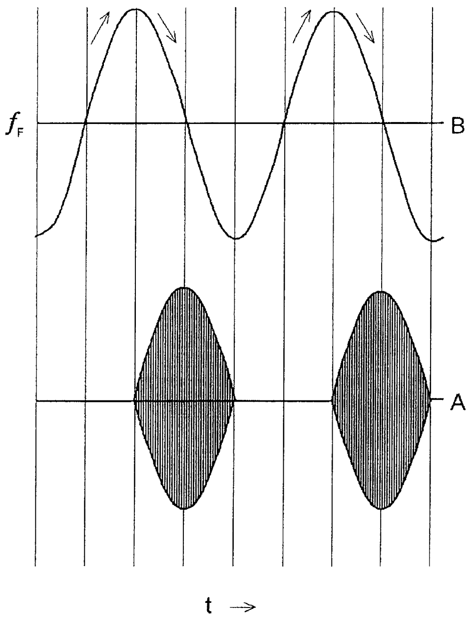

Fig. 2. Schematic profile of vibration in friction. The frictional force as a function of the wave length indicates that the ultrasonic wave A is accompanied in the peeling zone of the frictional wave B.

In the process of friction a change in the force, expressed by Eq. 8, occurs during time (t) of the movement of the slider passing the distance between two neighboring links. This process repeats to give a periodic vibration. The period is determined by the distribution of pseudo links on the surface; their sizes ($b_{A'}$ and $b_{B'}$) are assumed to be equal to those of the links (b_A and b_B) in rubber. Accordingly, link sizes and chain lengths of A and A′ or B and B′ are not distinguished hereafter.

The well-known Schallamach's wave evolves from the largest B-link, whereas the ultrasonic vibration evolves from the smallest A-link. Based on this assumption and the model of multi-sized pseudo crosslinks, the frequency (ω) or the relaxation time (τ) is predicted to be

$$\omega = 1/\tau, \tag{9}$$

because the loss modulus (E'') is given as a function of τ and the frequency (ω) as

$$E'' \approx \omega\tau/(1 + \omega^2\tau^2),$$

where ω is $1/\tau$ at the maximum E''. According to Eq. A9 in Appendix, the relaxation time (τ_b) for the b-sized link is

$$\tau_b = \tau_0 n_b^2 n_B^{0.5}, \tag{10}$$

where τ_0 is the relaxation time of the unit segment, and is given by Eq. A8 in Appendix as

$$\tau_0 = (h/kT)\exp|E^*/(2/3)R(T - T_A)|.$$

Here, h is Planck's constant, k is Boltzmann's constant and h/kT is about 10^{-13} s. E^* is the activation energy for viscous flow, and is equal to one third of the heat of vaporization (H). For a polymer segment, H is expressed as a function of the heat of cohesion (H_0) and the coordination number ($z-2$), z being that for a free segment. The factor (2/3) arises from the condition that the translation of a segment is limited to two directions, except along the chain, unlike a free molecule. H_0 is equal to $2RT_A$. As a result,

$$\begin{aligned}\tau_0 &= 10^{-13}\exp|(z-2)(H_0/3)/(2/3)R(T - T_A)| \\ &= 10^{-13}\exp|(z-2)/(T/T_A - 1)|. \end{aligned} \tag{11}$$

Taking that z as 10—8, T is 300 K and T_A is 200—230 K for rubber, and τ_0 becomes about 10^{-7} s. Since τ_0 runs parallel to the cohesion energy (H_0), τ_0 of rubber having a small H_0 is small. The factor $n_b^2 n_B^{0.5}$ for links A and B is $10^{3.6}$ and 10^6, respectively, and τ_b is $10^{-3.4}$ s and 10^{-1} s, respectively.

In the same way, it follows that $\omega_A = 10^{3.4}$ Hz, $\omega_B = 10$ Hz, and thus, $\omega_A/\omega_B = 10^{2.4}$. The distance ($l_b$) for relaxation is that for the migration of the link, and it is given as

$$l_\mathrm{b} = l_0 n_\mathrm{b}^2 n_\mathrm{B}^{0.5}, \tag{12}$$

where l_0 is the segment length (about 1 nm). The lengths of chains connected with links A and B become $10^{0.6}$ μm and 1 mm, respectively.

Effect of a Filler on Fibration. The addition of fillers decreases the rubber portion, and thus l_b and τ_b decrease, whereas ω increases with increasing the content of the filler (ϕ) as

$$\tau = 1/\omega = 1 - 2.5\phi, \tag{13}$$

where the factor of 2.5 is taken to be equal to that in Einstein's equation of the viscosity of the colloid solution. Thus, ω increases with increasing ϕ.

Rolling Resistance of a Tyre. For a tyre, although the rolling resistance is important as well as friction, it occurs not on the surface, but in the tyre, itself. The resistance is caused by a viscoelastic deformation, and runs parallel to the dynamic loss or tan δ of the rubber and the tyre cord, and is proportional to their relaxation times. Therefore, the rolling resistance is correlated in part with the friction through the relaxation time of the rubber of the tyre tread.

Abrasion and Resistance to Abrasion. In mechanics, abrasion is mostly dealt with as a stick-slip process involving the formation of a craze and its growth. On the other hand, in molecular dynamics, peeling and friction are caused by the scission of pseudo links forming on the surface. At the same time, a scission of the molecular chains partly occurs to produce abrasion.

For plastics the size (b) of pseudo links and the length (n_b) of the connected chains are very small; b is 4 for link A and n_b is 4^2 for chain A. Upon rupture the link A is broken below T_g, and a brittle fracture occurs to give powdery wear products.

On the contrary, for vulcanized rubber, b and n_b are of the largest link and chain due to the effect of chemical crosslinks and b of 16 for the B-link and n_b of 16^2 are involved in friction and abrasion. An elastic rupture of the B-chain takes place to give crest-shape tearing products, leaving a pattern abrasion on the rubber surface. In this case, abrasion is promoted by the peeling force (f_P) but retarded by the strength i.e. the force at a break (f_B) and the ratio ($f_\mathrm{B}/f_\mathrm{P}$) is taken as the degree of resistance to abrasion (denoted with R_A).

The strength at break (f_B) is given as[15)]

$$f_\mathrm{B} = (\nu/N)(D/V), \tag{14}$$

where D is the bond strength i.e. about 100 kcal for the main chain of rubber. ν is a sum of ν_B and the chemical crosslink and almost equal to 2 ν_B. Equation 14 involves a decreasing factor due to the non-uniformity of chain elongation, which is enhanced by vulcanization. The frictional force (f_F) is given by Eq. 6 and the resistance to abrasion (R_A) is expressed as

$$\begin{aligned} R_\mathrm{A} \sim f_\mathrm{B}/f_\mathrm{P} &= \left[(\nu/N)(D/l^3)\right] / \left[(p/E)^m(\nu/N)^{2/3}(W/l)(h\tau v)^{0.5}\right] \\ &= (\nu/N)^{1/3}(D/Wl^2)(E/p)^m(h\tau v)^{-0.5}. \end{aligned} \tag{15}$$

Accordingly, R_A is proportional to $(\nu/N)^{0.33}E^{m-2/3}f_\mathrm{B}$, or roughly Ef_B. R_A also decreases with increasing τ and v.

On the other hand, in a plastic rupture, D is replaced by the cohesion heat (H_0) of the pseudo crosslink in Eqs. 14 and 15.

Role of Carbon Black and the Ingredients. Carbon black (CB) is an essential material for an abrasion-resistant tyre. CB has a strong cohesion, which produces the self-aggregates of the chain structure as well as a strong adhesion with rubber matrix. Therefore, the behavior of CB is very complicated and various theories have been proposed for the reinforcement by CB, especially of the chain-like aggregate.

On the contrary, the author[15)] assumed the formation of pseudo links in the interface between the CB and rubber. The elasticity (E_0) of vulcanized rubber is enhanced to E with filler, because an actual deformation of the rubber matrix is enhanced by the excluded volume effect of a filler. E is expressed as

$$E = E_0/(1 - a\phi) = E_0(1 + a\phi), \tag{16}$$

where a is the factor due to the immobilized rubber layer adsorbed on the filler. Equation is similar to Einstein's equation for viscosity η of colloidal solution i.e.,

$$\eta = \eta_0(1 + 2.5\phi), \tag{17}$$

where a is 2.5, which was derived from an excluded volume effect in which the solvent molecules are attached to a colloid particle. The rotational energy of a particle and solvent molecules attached and in the neighborhood was calculated by a tensor analysis to obtain the increases in viscosity.

It is likely to employ the same effect to the elasticity of rubber for a small deformation. Since the calculation of the immobilized layer may be similar to that of a matrix molecule in a colloid solution, the same factor is employed.

However, at a large deformation slippage occurs in the interface, and the coefficient (a) may change. The deformation of chains at a break is very large to induce slippage in the interface; also, the resistance to the viscous flow of the layer plays a role in enhancing the strength of rubber.

On the other hand, the effect of CB on friction may be slight, because the contact area between the CB and the slider is smaller than that between the CB and the matrix rubber. Incorporation of CB results in a decrease in the fraction of rubber, as well as the relaxation distance or time; therefore, CB may decrease the friction.

It can be assumed that the reinforcememt by CB is proportional to its fraction (ϕ), its specific surface area (s_0/v_0), and the fraction of rubber ($1 - 2.5\phi$). Thus, the abrasion resistance (R_A) becomes

$$R_\mathrm{A} \approx (s_0/v_0)\phi(1 - a\phi)(H_\mathrm{A}/Wl^2)(E/p)^m(h\tau v)^{-0.5}, \tag{18}$$

where H_A is the heat of adhesion and V is the average molar volume of a unit segment of rubber i.e., l^3. Here, s_0 and v_0 are the surface area and volume of a CB-particle, respectively and s_0/v_0 is the specific surface area, which is equal to $6/d_0$ for a spherical particle of diameter d_0. These variables must be modified in the case of non-spherical particle, and are affected by the micro structure of the surface. The coefficient (a) is associated with s_0/v_0, and also, the diameter of a coil of the B-chain equal to $n_B^{0.5}l$, where $n_B^{0.5}$ is 16 and l is about 1nm. Accordingly, the coefficient (a) may be expressed as

$$a = 16(s_0/v_0) = 16(6/d_0)\ \text{nm}. \tag{19}$$

Thus, a becomes unity for a d_0 of 100 nm.

Equation 16 gives a maximum a under the conditions

$$2 \times 2.5\phi = 1 \text{ or } \phi = 0.2 \tag{20}$$

and

$$(s/v) = 6/d_0. \tag{21}$$

Taking 100 nm as d_0, the specific area (s_0/v_0) becomes 0.06 nm^{-1} or 60 $\text{m}^2\,\text{cm}^{-3}$.

The distance (d) between the neighboring particles is given by

$$d = d_0\left[(\pi/6\phi)^{1/3} - 1\right]. \tag{22}$$

At a ϕ of 0.2, d for the maximum of R_A is 0.38 d_0. However, if the factor due to occlude rubber for ϕ is taken into consideration[5] d becomes 0.2 d_0.

Discussion

Friction. Equation 7 implies that the frictional force (f_F) or coefficient of friction (μ) is proportional to the cohesive energy and relaxation time (τ) of the polymers and they run parallel to the transition temperatures (T_g, T_s, or T_m). The values of μ and T_m of polymers were obtained from various hand books[19] and plotted as shown in Fig. 3. μ roughly runs parallel to T_g.

In the case of rubber, μ increases as the velocity increases and μ attains a maximum;[6,7] this fact is expected from Eq. 7, and the maximum occurs at the transition points. The effect of temperature is given by the WLF-equation of the shift factor for the stress-relaxation spectrum. The spectrum given by Eq. 7 has two peaks; this fact was also reported in the literature.[7] The first and second peaks, occurring at low and high velocities, may be caused by the friction of links B and A, respectively.

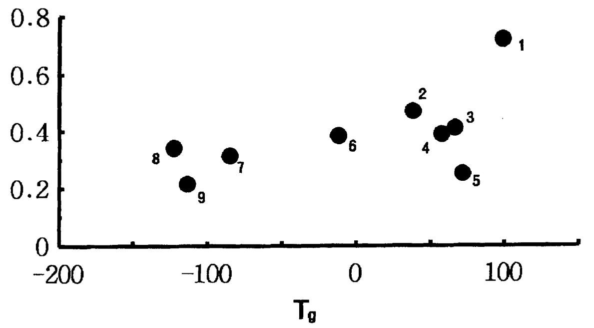

Fig. 3. Coefficient of friction μ and glass transition T_g. 1 Poly(amide), 2 Poly(styrene), 3 Poly(vinyl chloride), 4 Epoxy resin, 5 Urea-formaldehyde resin, 6 Poly(propylene), 7 Poly(acetal) resin, 8 Poly(ethylene), 9 Poly (tetrafluoloethylene). Data from hand books.[18,19]

For rubber, the maximum of μ is attained mostly at 10^1 $\text{cm}\,\text{s}^{-1}$,[8] which corresponds to the value of the link B. For plastics, although μ becomes small below T_g, it seems to run parallel to the cohesion heat or T_g as shown in Fig. 3.

Abrasion. There are many articles[6] concerning pattern abrasions. A saw-teeth profile was seen in a cross-section of the rubber layer forming the pattern in the case of rubber.

Fukahori recently reported on a correlation between friction and abrasion.[9] In friction, the force oscillates with frequencies of about 10 Hz. In addition, the friction is accompanied by an ultrasonic wave having a frequence of about 1000—2000 Hz, which is intrinsic for the kinds of rubber. The latter occurs mostly on the down-hill side of the pattern wave. Abrasion yields grains or chips as the wear product, giving a periodic wear pattern on the rubber surface. The wavelength of the pattern wave grows, and the final value becomes several millimeter after one thousand repeated slidings. For rotating tyre 1000 cycles correspond to only 0.6 min in time at a velocity of car of 100 $\text{km}\,\text{h}^{-1}$, taking 1 m as the periphery of a tyre and therefore, the above stationary value is to be used for friction and abrasion.

Fukahori also accounted for the experimental results based on the concept of the stick-slip mechanism. Rubbery materials exhibit intrinsic ultrasonic vibrations, which produce a notch or craze on the surface. The period of the ultrasonic wave was found to be intrinsic to the rubber species. The craze grows by the tearing mechanism proposed by Thomas.[10] Tearing proceeds by repeated elastic deformation followed by a mechanical slip at the ultimate elongation occurring on the rubber surface. In this way, crest-shape notches are formed, and finally the rubber is torn to give grain-size wear product. Although these explanations may be reasonable in mechanics, they are insufficient to predict the frequencies of the pattern wave. The ultrasonic vibration becomes strong at the top of the hill of the pattern wave of the friction at which the slip takes place; from this point the friction decreases exponentially. However, his experiment showed that the maximum attains at the middle point rather than at the top.

On the contrary, in the stick-peeling mechanism vibrations occur during the peeling process of friction, and ultrasonic waves are induced by the dissociation of the pseudo links of the smallest size A′ and the pattern wave by that of the largest size B′ formed on the interface between the slider and the rubber. If so, the ultrasonic wave becomes strong at the inflexion point of the down-hill slope of the pattern wave, where peeling is very rapid (Fig. 2). Figure 2 is close to the experiment of Fukahori.

Abrasion is caused by the scission of chains in the polymer layer. In the case of plastics a craze is formed due to a brittle rupture of the A-chain to give powdery wear products. In the case of rubber, however, a scission takes place mostly in the largest B-chain and grows by tearing to give a crest-shaped wound, which gives rise to pattern abrasion forming grain wear products. The size of the wear product increases depending on the strength of rubber. Thus, the sizes of wear products are 0.8 μm for chain A in plastics and 2 mm for chain B in rubber. These values run parallel to the relaxation distance of $n_b^2 n_B^{0.5}\ l$, l being the length of a segment, about 1 nm.

In other words, ultrasonic and pattern vibrations are induced by the dissociation of pseudo links in the peeling process of friction. Also, abrasions are caused by the scissions of the chemical bonds in the polymer layer, giving rise to a brittle fracture of the A-chain for plastics and to the elastic rupture of the B-chain for rubbers. Therefore, strictly speaking, the ultrasonic and pattern vibrations are the result of the dissociations of pseudo links in friction, and they are not the origins of abrasions, even though there are close correlationships between vibration and abrasion.

Checking the data of Fukahori, a linear realationship was found to hold between vibrations A′ and B′ for natural rubber, SBR (Styrene/butadiene rubber), silicone rubber, and those loaded with carbon black (Fig. 4). The frequency (ω_A) of the ultrasonic wave is intrinsic to the kind of rubber. It is inversely proportional to the relaxation time of the chain (τ) and that of the unit segment (τ_0) which runs parallel to the the cohesion heat or T_g of the rubber. This trend has been found to hold for various kind of rubber ; T_g of SBR, natural rubber, and silicone rubber are 220, 210, and 140 K, respectively, which run parallel to frequencies A and B.

The addition of carbon black decreases the appearent relaxation time of rubber and increases both ω_A and ω_B. Thus, Eqs. 10, 11, 12, and 13 fit roughly the experimental data in the literature.

Uchiyama[11] has reported that the abrasion of rubber is inversely proportional to the elasticity and strength of rubber. This tendency is expected from Eq. 15.

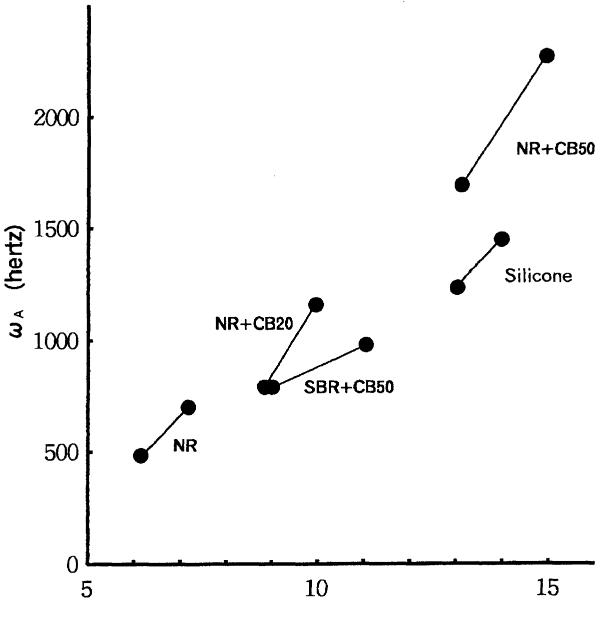

Fig. 4. Relationship in vibrations A and B. Relation in the frequencies ω_A and ω_B in hertz for NR (natural rubber), SBR (styrene-butadiene rubber) and Silicone (Silicone rubber) with or without CB (carbon black) of the contents of 20 and 50%. Data from Fukahori's work.[9]

Carbon Black and Active Filler. Carbon black is the most essential filler for the tyre industry. It has a remarkable effect on the strength of rubber, as well as on the resistance to abrasion without decreasing the friction. There are many papers dealing with the structure and chemical nature of fillers, and many theories exist concerning the mechanism of activity, mostly from a physical or mechanical point of view.

For example, Donnet[12] reviewed the surface structure of single and complexed aggregates of carbon black in detail. Recently, Sone[13] presented an interesting review and pointed out several factors, which affect the resistance to abrasion (R_A). The chain strutcure of the carbon black-aggregates is effective for enhancing the elasticity, but the effect is limited to a small deformation. On the other hand, R_A increases with increasing the CB-content (ϕ), the specific surface area (s_0/v_0) or (area/g) and particle distance (d). However, there are maxima at ϕ of 0.2, a specific area of 140 $m^2\ g^{-1}$ and d of 20—23 nm. He claimed that the particle distance (d) is most important for the formation of an active scrum of rubber chains, whose diameter is about 23 nm, which may be the effective cohesion distance for the formation of a CB aggregate. R_A decreases with increasing the relaxation time of rubber, as expected from Eq. 15.

However, Eqs. 20, 21, and 22 also fit the above experimental data. The maximum of R_A attains at a ϕ of 20% and a specific surface area of 100 $m^2\ g^{-1}$. Equation 20 is derived from Einstein's equation, and also fits the data of other active fillers, such as talc, clay, and calcium carbonate; ϕ for the maximum R_A is 20% in all cases.[14] According to Eq. 22, d becomes almost 20 nm. Therefore, a special meaning for d at the maximum is not always necessary. The van der Waals distance for cohesion may be as small as 1 nm, corresponding to the length of a segment.

It is noticed that friction and abrasion are greatly influenced by the chemical composition of the surface layer of rubber, whose adhesive nature is not always the same as that of the material, itself, and changes by the migration of the mobile terminal chains to the surface and also by the chemical change due to oxidation. The terminal chain may often possess a different end group acive for adhesion. In the same sense, oligomers and branched polymers are effective to exhibit large tackiness. It is also noted that for a large deformation. Equation 7 is not valid due to slippage of the filler to give a plastic deformation of the matrix polymer chains and elasticity, strength, and elongation at a break are to be modified.[15]

Conclusion

Close correlationships were found among adhesion, friction, and abrasion of rubber. The model of the pseudo links formed on a surface gives a comprehensive account for friction and abrasion. The theory may provide a step for studying such complicated phenomena.[15]

Appendix

An outline of theory of pseudo crosslink and adhesion is given in order to explain the equations of this paper.

Pseudo Cross-Link Model.[16,17] A pseudo cross-link is a kind of association of segments in a molecular chain caused by an entanglement of the chains as well as the cohesion of segments. Unlike the association of ordinary molecules, a pseudo crosslink possesses various cluster sizes (b), due to the zipper-like nature of the chain. The links are connected with chains of various lengths, whose number of segments is n_b with various relaxation times (τ_b). They are calculated as follows.

A long-chain molecule forms a spherical coil and entangles with chains by overlapping coils. The diameter of the coil is proportional to the square root of the chain length, and is given by $n_b^{1/2}\ l$, l being the length of a segment. The degree of entanglement is proportional to the square of the volume of a coil. Under the equilibrium condition the following equation holds:

$$bH_0 = RT\ln n_b^3. \tag{A1}$$

After the dissociation of a b-sized link, the b segments translate to the next equilibrium position, which is separated by a distance equal to the diameter of the coil i.e. $n_b^{1/2}\ l$. A migration of the segments is induced by an elastic force of the chain, whose energy is $(\alpha^2/2)RT$, α being the elongation ratio. If dissociation takes place at the maximum elongation, α becomes $n_b^{1/2}$. Accordingly, it follows that

$$bn_b^{1/2}(RT/2) = (\alpha^2/2)RT = (n_b/2)RT$$

and hence

$$n_b = b^2. \tag{A2}$$

From Eqs. 1 and 2, b or n_b is given as a function of the temperature (T) as

$$b/\ln b = 6RT/H_0. \tag{A3}$$

Here, H_0 is expressed with the transition temperature (T_0) as $H_0=2RT_0$. Equation A3 gives the relations that T becomes T_0 at b of 1—4 and $2T_0$ at b of 16. There is a hierarchy between points, T_0 and $2T_0$, which imply the beginning and end of the hierarchy, and are denoted by A and B, respectively. Equation A3 is approximated graphically as

$$b = 12T/T_0 - 8. \tag{A4}$$

Equations A3 or A4 implies that the pseudo crosslinks possess their own transition temperatures.

H_0 is about 0.8 kcal per mole for hydrocarbon polymers, and $2RT$ implies the kinetic energy of two segments participating in the link formation. Below T_A, $H_0/2RT$ is less than unity and a link smaller than A is not recognized except for an extremely rapid or impact deformation. As a result, actual links of size b of 4—16 lie between A and B and T_A and T_B are the transition or melting temperatures of links A, and B, respectively. According to Eq. A4 the transition temperatures for sizes (b) of 2, 3, 4, 10, and 16 are 0.962, 0.910, 0.962, 1.45, and 1.962 times T_A, respectively. Between sizes 1 and 4 there is no significant difference in the transition temperatures, and

$$T_{1—4} = T_A = H_0/2R, \tag{A5}$$

whereas

$$T_{16} = T_B = 2T_A = H_0/R. \tag{A6}$$

T_B is the melting temperature of the pseudo crosslink of the largest size (16). Links B are located on the polymer chain and are successively dissociated along the chain upon melting or squeezing a molecular chain by extension to its terminal, which is denoted by point C. Between B and C the melting temperature is kept constant.

According to Eq. A2, the length (n_b) of the chain connected with the b-sized link is equal to b^2, and n_A and n_B are 4^2 or 16 and 16^2 or 256 or $10^{2.4}$, respectively.

It is noted that although the equilibrium for the b-sized link can be expressed by Eq. A1, it requires the time (τ), which is different depending on the size of the links. τ_b of the b-sized link is given by a product of the time for the unit (τ_0), the probability of dissociation of the link, and the distance for relaxation i.e. equal to the diameter of the largest coil B (or $n_B^{0.5}$). The second factor is expressed by an exponential function of the activation energy (E_b^*) and E_b^* is taken to be equal to two thirds the heat of cohesion (bH_0). As a result, τ_b for the b-sized link is

$$\tau_b = \tau_0 \exp(E_b^*/RT)n_B^{0.5}. \tag{A7}$$

Equation A7 holds for a hierarchy existing between points A and B.

τ_0 is the relaxation time for the unit segment of b of 1, and is given by

$$\tau_0 = (h/kT)\exp\{E_{\rm vis}^*/(2/3)R(T-T_A)\}, \tag{A8}$$

where h and k are Planck's and Boltzmann's constants, respectively and h/kT is the time for the translation of a segment for the distance equal to the segment length, which is 10^{-13} s. $E_{\rm vis}^*$ is the activation energy for viscous flow, and was estimated to be one third of the heat of vaporization, which is equal to the product of H_0 times the coordination number $(z-2)$; z is the coordination number of a single molecule (or 8—10), and H_0 is equal to $2RT_A$. Here, the kinetic energy is assumed to decrease due to the retarding effect of the neighboring segment, and is taken to be $RT-H_0/2$ or $R(T-T_A)$, instead of RT.

From Eq. A1 the factor $\exp(E_b^*/RT)$ becomes n_b^2 and Eq. A7 is rewritten as

$$\tau_b = \tau_0 \exp(E_b^*/RT)n_B^{0.5} = \tau_0 n_b^2 n_B^{0.5}. \tag{A9}$$

Beyond B, or in the zone BC, τ_b is multiplied by the factor $(n/n_B)^{3.5}$ for the disentanglement of a polymer chain of length n.

Theory of Tack Adhesion.[1] The adhesive force (f_A) acts on an adherend surface through pseudo links, and is given by the product of the wetting force (W/l) and the fraction of links in the unit area $(\nu/N)^{2/3}$,

$$f_A = (\nu/N)^{2/3}(W/l), \tag{A10}$$

where W is the wetting energy per unit area and l is the bond length of the pseudo link, almost equal to half the segment length. Upon peeling a tape of pressure-sensitive adhesives, the adhesives layer is expanded to form an elastic stress (σ_e) as well as a viscous one (σ_v). Taking x and y as the directions horizontal and perpendicular to the adherend surface, respectively, the stresses are given by

$$\sigma_e = G(dy/dx) \text{ and, } \sigma_v = \eta\dot{\gamma} = G\tau(dx/dt)(d^2y/dx^2).$$

Assuming $\sigma_e=\sigma_v$, and taking dx/dt as the peeling velocity (v), and the viscosity (η) as a product of the elasticity (G) and relaxation time (τ), it follows that

$$G(dy/dx)dx = Gy \text{ or } (dy/dx) = (y/h) - 1,$$

h being the thickness of the adhesives layer. The above relations lead to an equation for a catenary curve, such that

$$y = h\exp(x/h). \tag{A11}$$

The peeling force f_P is obtained by taking $\sigma_e=f_A$ and $f_P=\sigma_v$. Then, f_P becomes

$$f_P = (v/N)(W/l)(1/h + 1/\tau v) = (v/N)(W/l)(h\tau v)^{0.5}. \quad \text{(A12)}$$

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