Bull. Chem. Soc. Jpn., ***69***, *1797—1803 (1996)*

A Molecular Theory of Tacky Adhesion

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(Received December 18, 1995)

Adhesive force f_a acts on the adherend surface through pseudo links and is given by a product of wetting force W/l and the fraction of links of about 10^{-2}. W is a wetting energy of about $10^{1—2}$ cgs-unit and l is a length of a segment of 1 nm in the adhesives polymer and f_a is about $10^{6—7}$ cgs-unit or 1—10 kg cm^{-2}. On peeling a tape of pressure-sensitive adhesives, the adhesives layer is expanded and voids and fibrils are often formed. The shear forces in fibrils are integrated to give the peeing force P. The layer is deformed to give a concaved shape expressed with a catenary curve. In this model, P increases with increasing the relaxation time τ, thickness h, velocity v, and decreasing the peeling angle θ. P is expressed as $P=(0.7\ f_a/\sin/\ \theta)/(1/h+1/\tau v)$. For the tensile test in parallel plates, the thickness is expanded uniformly and $P=f_a(1+\tau v/h)$. For the shear test, the cohesive rupture occurs and $P=\eta v/h$, η being viscosity.

Various types of adhesives are widely used for bonding of solid–solid, film–solid, and film–film. The bonding force at the interface is determined by the adhesion or chemical force but the peeling force is affected by the mechanical and rheological conditions of the adhesives layer. Pressure-sensitive adhesives tape is a typical case of the film–solid or film–film adhesive and a mixture of rubber and its oligomer is often used for the adhesives layer.

The peeling force varies depending on the type of deformation such as peeling, tensile or shear deformation. Various theories were proposed by many scientists from viewpoints of mechanics, but they did not give comprehensive accounts of mechanisms, due to so many rheological factors being involved.

On the other hand, the rheology of the bulk polymers was mostly explained by means of mechanical models composed of springs and dashpots, whereas the author proposed a concept of pseudo crosslinks of multi-cluster sizes. The links are formed by the entanglement of molecular chains and they are dealt with thermodynamically. The links connect chains of various length bearing various times of stress relaxation. In terms of links and relaxation times, various rheological phenomena are explained: e.g., stress relaxation, strength at break, or effects of fillers on rubber and plastics.[1a,1b,1c,1d)]

The model is extended to the polymer adhesives. The adhesion force f_a is proportional to the wetting energy and the number of crosslinks forming on the surface of the adherend plate. The force f_a propagates to the backing film through the adhesives layer with aid of the links connecting chains and is enhanced by viscous force. In the previous paper,[2)] P of a pressure-sensitive adhesive tape of a width of 1 cm and a thickness of h is expressed as a function of a fraction of links v/N in the layer, a relaxation time τ, a peeling angle θ and a wetting energy W as

$$P=(v/N)^{2/3}(W/l)(hv\tau)^{0.5}/\sin\theta, \tag{1}$$

where v and N are the number of linked and total segments existing in a unit volume of the layer or 1 cm^3, respectively, the number of pseudo crosslinks being $v/2$.

This paper deals with the mechanism of adhesion and peeling in more detail.

Theory

Mode of Peeling. In the case of the pressure-sensitive adhesives, one face of the adhesives layer is bonded with the solid adherend surface and the other face is bonded with the thin backing or supporting film. On peeling, the backing film is pulled up with an angle θ, and the volume of the layer is expanded in some range of the surface area of the adhesives layer before the onset of peeling (Fig. 1a). Voids and fibrils are often formed in the layer (Fig. 1b).

In theories which appear in the literature, the deformation and also the energy of peeling are calculated mostly in terms of the bending moment of the layer and the backing film. On the other hand, the author assumed the formation of pseudo links caused by adhesion in the interface between the adherend and adhesives. The links connect chains in the layer which transfer the force by the elastic and viscous deformation.

Adhesion and Bonding Force. Adhesion force f_a is regarded as the bonding force between adhesives and adherend through pseudo links of a number of v_a, which is composed of the functional group of the adherend and segments of chains in the layer or possibly the functional segments in the polymer terminal. f_a is proportional to the wetting force and

$$f_a=(v_a/N)(W/l). \tag{2}$$

The force f_a is balanced with the elastic force f_e in the layer. f_e is given by a product of the elasticity E and the elongation $\alpha-1$, α being a ratio of the end-to-end distance of an elongated chain to that of a coiled one. E is proportional to

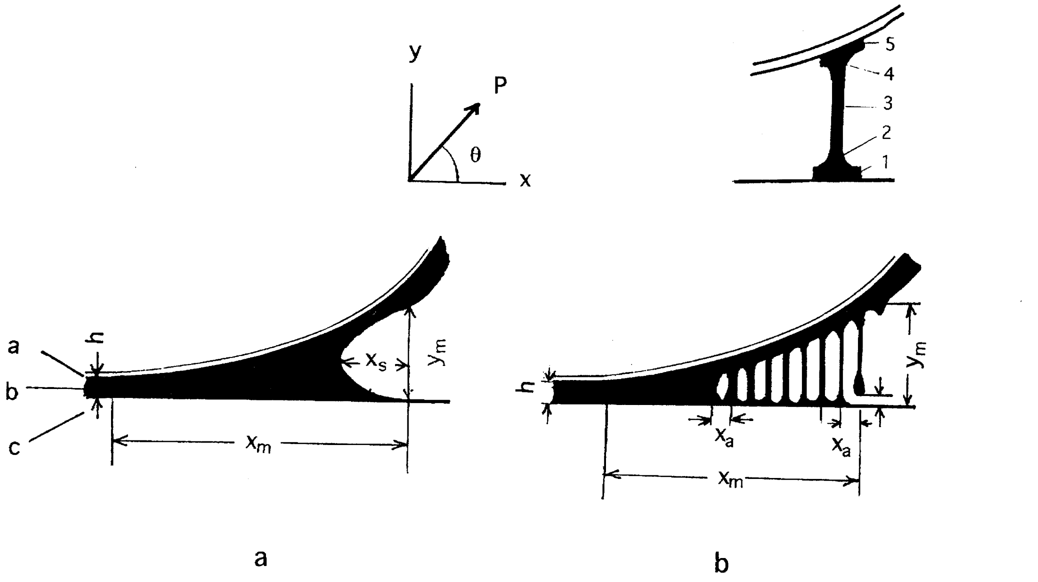

Fig. 1. Deformation of the adhesives layer. 1-a: Backing film, b: Adhesives layer, c: Adherent. 1-b: Formation of voids and fibrils.

a fraction of chains, i.e., v/N and a kinetic energy RT, where v is the number of chains and N is that of segments existing in 1 cm^3, R, T, and V being the gas constant, temperature, and a molar volume of a segment, respectively and

$$f_a = (v/N)(RT/V)(\alpha - 1) = E(\alpha - 1). \tag{3}$$

In the melt or plastic state, E, $(\alpha - 1)$, and (v/N) are about 10^6 cgs-unit, 10, and $10^{-2.4}$, respectively and W and l are $10^{1\text{—}2}$ cgs-unit and 10^{-7} cm, respectively. Adhesion force f_a of a tape of a width of 1 cm becomes of the order of $10^{6\text{—}7}$ cgs-units or 1—10 kg.

On peeling, the adhesives layer is expanded in some area of the tape, and voids and fibrils are often formed. Therefore, the peeling force P is affected by many factors arising from the elastic force and viscous resistance of the layer and fibrils. The surface energy of voids, fibrils, and the meniscus in the edge of the layer are also to be taken into consideration.

Peeling without Void Formation. The elastic force f_e or the shear force σ_e is balanced with the adhesion force f_a. But the actual peeling force P is larger than f_a or σ_e, because the flow resistance of chains in the layer enhances it. At the position of the backing or supporting film inclined with an angle θ, the force becomes $P\sin\theta$, since the shear force acts in the direction perpendicular to the adherend surface. In Fig. 1a, x and y are taken as the components of deformation in the direction along and perpendicular to the adherend plate, respectively. Then, the shear γ and shear rate $\dot{\gamma}$ are equal to $(\mathrm{d}y/\mathrm{d}x)$ and $\mathrm{d}(\mathrm{d}y/\mathrm{d}x)/\mathrm{d}t$, respectively. And

$$\sigma_e = G\gamma = G(\mathrm{d}y/\mathrm{d}x), \tag{4}$$

$$\sigma_v = \eta\dot{\gamma} = G\tau(\mathrm{d}x/\mathrm{d}t)(\mathrm{d}^2y/\mathrm{d}x^2), \tag{5}$$

where G, η, and τ are the shear elasticity, viscosity and relaxation time, respectively, and $(\mathrm{d}x/\mathrm{d}t)$ is the peeling velocity v.

Deformation takes place in an area range between the position of zero shear and the meniscus point and the forces are integrated to give

$$\int G(\mathrm{d}y/\mathrm{d}x)\mathrm{d}x = Gy \text{ or } (\mathrm{d}y/\mathrm{d}x) = (y/h) - 1. \tag{6}$$

This gives an equation for a catenary curve such that

$$y = h\exp(x/h). \tag{7}$$

Accordingly, Eqs. 4 and 5 become, respectively,

$$\sigma_e = G\gamma = G\exp(x/h) = G(y/h) = G\alpha, \tag{8}$$

and

$$\sigma_v = \eta\dot{\gamma} = G\tau(v/h)(y/h) = G\tau(v/h)\alpha, \tag{9}$$

where y/h is equal to an elongation ratio α. Peeling force P is obtained by taking $\sigma_e = f_a$ and $P = \sigma_v$. P becomes

$$P = (v_a/N)(W/l)(1 + \tau v)/\sin\theta. \tag{10}$$

Peeling with Formation of Voids and Fibrils. At the meniscus point, the height y becomes large and the surface energy of the meniscus is increased, and voids are formed in order to minimize the energy. The void is of the open cell type having smaller energy than that of a cavity. The surface energy of the void is proportional to $2y$ whereas that of the meniscus denoted with a suffix m is y_m. Therefore, the position of the formation of a void is given by

$$y_m/y = 2 = \exp\{(x_m - x)/h\},$$

or

$$x_a = x_m - x = (\ln 2)h = 0.7h, \tag{11}$$

where x_a is the interval of the position for the formation of voids or fibrils and is equal to the diameter of a fibril at its foot. At the meniscus point, the forces σ_e and σ_v are proportional to x_a or 0.7 h.

However, the contribution of the surface tension γ_s to the peeling force P is very small and negligible for the evaluation of P, because the surface energy is $2\gamma_s y$ whereas the elastic force is $G\,(y/h)\,(0.7\,h)$ and $2\gamma_s y$ is equal to $2\,G\,(y/h)l$, l being a segment length. In Fig. 1b, it is assumed that the shear force at the meniscus point is balanced with the force of adhesion f_a and

$$\sigma_e = f_a = (0.7h)(\nu_a/N)(W/l). \tag{12}$$

During the extension of fibrils, the shear force varies at positions 1, 2, 3, 4, and 5 of a fibril as σ_e, $\sigma_e \exp(-kt_2)$, σ, $\sigma_c\{1-\exp(-k't_3)\}$ and σ_c, respectively. Here, $\exp(-kt_2)$ implies the decrease in the cross-sectional area and $\alpha\{1-\exp(-k't_3)\}$ implies the increase in the length of a fibril, k and k' being the rate constants of dissociation of the link and its regeneration after slippage, respectively.

Since $k't_3$ is assumed to be almost equal to kt_2, σ becomes twice a harmonic mean of σ_c and σ_v as follows:

$$\exp(-kt_2) + \{1-\exp(-k't_3)\} = 1 = \sigma/\sigma_c = \sigma/\sigma_v. \tag{13}$$

A similar relation holds also at the positions 4 and 5 and the effect of the viscous force disappears at the position 5. The process resembles the deformation of a dumbbel-shaped specimen of rubber in the elongation test. However, at the meniscus point, the adhesion bonds are broken before the viscous effect propagates to the position 4 and the force becomes σ.

Finally, the peeling force P becomes

$$P = \{0.7f_a/\sin\theta\}/\{(1/h)+(1/\tau v)\}. \tag{14}$$

Equation 14 indicates that P increases with increasing τ, v, and f_a or W and decreases with increasing θ. The equation gives linear relations between $(1/P)$ and $(1/h)$ or between $(1/P)$ and $(1/\tau v)$.

Effect of Backing Film. In case of the hard backing or supporting film(s), the film possesses its own bending angle θ_s the actual contact angle is smaller than the peeling angle θ and is equal to $\theta-\theta_s$, which is to be employed instead of θ. Then Eq. 14 is modified to

$$P \backsim 1/\sin(\theta-\theta_s). \tag{15}$$

Tensile Adhesion Force between Parallel Plates. In this case, the thickness of the adhesives layer increases uniformly and the area of x_a in Eq. 14 is replaced by the area of the plate or disk. i.e. πR^2 for a circular disk of a radius R as

$$P = (\pi R^2)f_a/(1+h/\tau v). \tag{16}$$

P is almost proportional to $f_a \tau v/h$.

Shear Force in Parallel Plates. In this case the component of shear in the direction perpendicular to the plate is zero and the rupture occurs not at the interface but in the adhesives layer and P is proportional to the surface area S, velocity v, and viscosity η but inversely to h as

$$P = S\eta v/h. \tag{17}$$

P becomes very large.

Stress Relaxation Spectra of Polymer. The rupture of adhesives by peeling, shear or tensile elongation involves rheological variables such as the relaxation time τ and the elasticity G. They increase with decreasing temperature T and/or increasing velocity v and the effect is demonstrated as a spectrum for the adhesives. For the bulk polymer, the stress relaxation spectrum is composed of the following four zones divided by three transition points, A, B, and C which are the transition point of the smallest link A of a size of 4, that of the largest one of 16 and that of the terminal of the molecular chain, respectively; the glassy zone A, the viscoelastic or transition zone AB, the plastic or plateau zone BC, and the viscous flow zone CD. The ranges of the AB and BC zones in a logarithmic scale are 4.8 and 3.5 log (n/n_B), respectively, n and n_B being the length of the molecule and the B-chain, respectively [See Appendix].

The dynamic stress relaxation spectrum is given as functions of τ or the frequency ω as follows:

$$E_{AB} = E_A(\tau/\tau_A)^{-0.5} = E_A(\omega/\omega_A)^{0.5}, \tag{18}$$

$$E_{BC} = E_B. \tag{19}$$

In the static spectrum, the shear elasticity G is decreasing in the time of deformation t in the AB zone due to the change of link size, whereas the viscosity η increases. G and η are obtained by taking t equal to τ.

In the BC zone G also decreases with increasing time t, whereas the viscosity η becomes constant: In the BC zone, the size of link is kept constant at B, but the link-B migrates along a molecule by squeezing the molecular chain and the diameter of the unperturbed coil is prolonged. G decreases due to the decrease of actual ratio of elongation, whereas τ increases and η or $G\tau$ becomes constant.

At high shear rate, η decreases by a factor of $\dot{\gamma}^{-m'}$ caused by loosening links, m' being 3/4. G and η for each zone are as follows:

$$G_{AB} = G_A(t/\tau_A)^{-0.5}, \tag{20}$$

$$\eta_{AB} = \eta_A(t/\tau_A)^{0.5}, \tag{21}$$

$$G_{BC} = G_B(\alpha/\alpha_B)^{-0.5} = G_B(t/\tau_B)^{-0.5}, \tag{22}$$

$$\eta_{BC} = G_B\tau_B = \eta_B(\gamma\tau_B)m', \tag{23}$$

$$\eta_{CD} = \eta_B. \tag{24}$$

The relaxation spectrum is associated with that of rupture of polymeric materials such as rubber and adhesives. In the case of rupture of vulcanized rubber, the spectrum expressed with a log–log plot of σ and $\dot{\alpha}$ resembles the dynamic spectrum of the stored elasticity E' and that of α against $\dot{\alpha}$ resembles the dynamic spectrum of the loss elasticity E''. The spectrum between σ and α is well known as the failure envelope of T. L. Smith. These spectra can be derived from the pseudo crosslink model.

Adhesion Spectra. In the case of peeling, the spectrum is somewhat complicated because of non-uniform distribution of stress in the adhesives layer or the fibril. In the plastic and flow state or the BC and CD zones, the mechanism is proposed in the preceding paragraphs.

However, in the viscoelastic states or the AB zone or at rapid peeling. t is equal to τ and the reinforcing effect of viscosity disappears. Moreover, the elastic rupture takes place at the interface and the force at break is affected by the non-uniformity in stress. The peeling force is expressed as

$$P_{\mathrm{AB}} = f_{\mathrm{a}} \exp\{(-f_{\mathrm{a}}V/RT\}. \qquad (25)$$

This means that P_{AB} decreases with lowering temperature and/or increasing velocity according to the WLF-equation.

Figure 2 shows schematically the adhesion spectrum with respect to the peeling velocity, together with the stress relaxation spectra.

Discussion

Adhesion Force. The adhesion force f_{a} is given by the wetting energy W divided by a segment length l as the distance for separation. W is expressed as a function of solubility parameters of the adhesives δ_1 and the adherend δ_2. Bond energies before and after wetting are proportional to $-\delta_1^2$ and $-2\delta_1\delta_2$, respectively. Accordingly,

$$W = -\delta_1^2 - (-2\delta_1\delta_2) = \delta_2^2 - (\delta_2 - \delta_1)^2. \qquad (26)$$

W becomes large for a large δ_2 of the adherend and attains a maximum at $\delta_1 = \delta_2$.

Effect of Peeling Velocity. Figure 2 is quite compatible with the experimental spectrum reported by Sheikh and Wong[3] for pressure-sensitive adhesive composed of poly(butyl acrylate). The effect of velocity on W proposed by Shega[4] may correspond to that on P and the data agree also with Eq. 14.

The experiment of Gent[5] for natural rubber adhesives shows two peaks occurring at the high velocity point of transition and the low velocity point corresponding to the point B or the beginning of softening and the point C for flow, respectively in the stress-relaxation spectrum. However, unmasticated rubber has no peak at the low velocity point C, i.e. the flow or tacky point perhaps due to the remaining net work structure or the lack of the reactive polymer terminal on the surface.

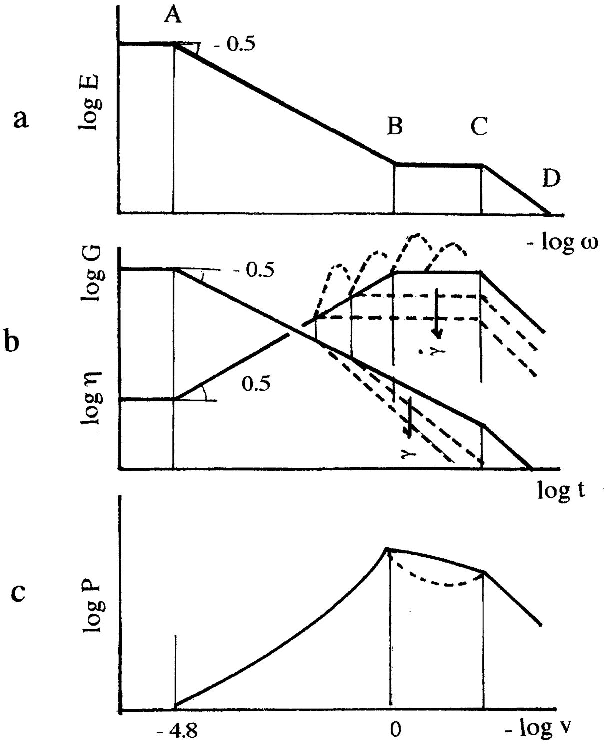

Fig. 2. Spectra of dynamic relaxation (a), static relaxation (b), and peeling force (c).

The stick-slip mechanism was often proposed in the literature; the peeling force fluctuates at the border point between B and C, the period of the fluctuation in the distance in the x-direction is about 0.4 mm. The author[1c] pointed out that this is alternatingly occurring adhesion-peeling phenomenon rather than the stick-slip one and it is associated with phenomena such as the Schallamach's wave in friction, the periodic pattern in abrasion and the Payne effect i.e. the dynamic loss occurring at the small amplitude in rubber loaded with carbon black. In all cases, the amplitude for periodic fluctuations is about 0.4 mm which corresponds to the relaxation distance d of the terminal chain or the largest chain whose chain length is n_{B}. d is

$$d = n_{\mathrm{B}}^{2.5}\, l = 10^{2.4\times2.5}10^{-9}\ \mathrm{m} = 0.4\ \mathrm{mm}. \qquad (27)$$

Effect of Peeling Angle. It is expressed conventionally by the following equation proposed by Hata:[7]

$$P = W/(1 - \cos\theta). \qquad (28)$$

This is derived from the relation in which the wetting energy W is given by a product of P times the distance between adhesives and adherend at the meniscus point, and it is extended by a distance of $L\,(1-\cos\theta)$ during peeling, L being the peeling length. Accordingly, Eq. 28 is based on an assumption that the adhesion force acts in three dimensions and governs in long range.

On the contrary, the pseudo link model is based on another assumption that the adhesion force is a component of van der Waals force acting to the direction perpendicular to the adherend surface in a short range equal to the bond length l. In the former, P is an order of W per 1 cm of peeling length and P is very small as compared with f_{a} or (v_{a}/N) (W/l) of the latter case. P is given by Eq. 14 or

$$P \backsim 1/\sin\theta.$$

P attains a maximum and a minimum at θ of 0° and 90°, respectively. Beyond 90°, P is increased with increasing θ with a hard backing film whereas P is kept constant with a soft one. The linear relationship in a plot of P against $1/\sin\theta$ is shown in Fig. 3 and it is more satisfactory than Eq. 28 in the experiment of Hata:[7] The effect of the peeling velocity does not change the inclination but raises the value of P.

Equation 14 is also valid in the experiment of Uekita[9] with different kinds of adherend. As shown in Fig. 4, P is proportional to $1/\sin\theta$ in a range between 0° and 90°. The inclination of the straight line is different depending on the sort of adherends. Beyond 90°, P becomes constant as expected in the case of a soft backing film.

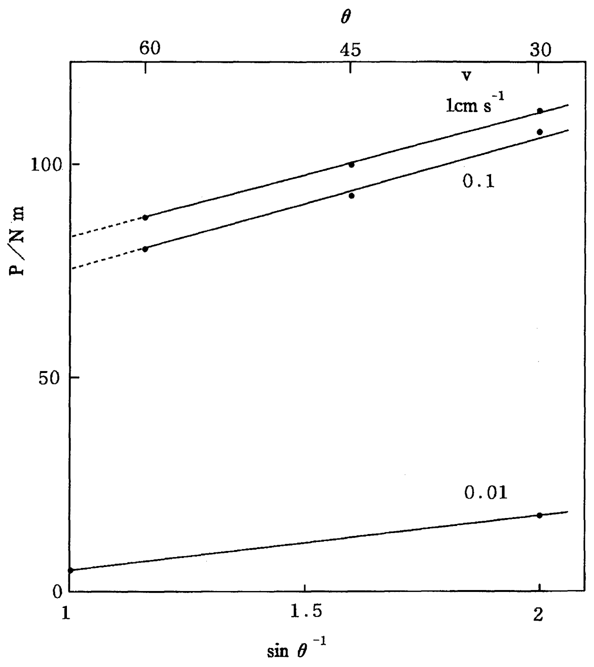

Fig. 3. Effect of peeling angle θ with changing velocity v on peeling force P for polyisobutylen adhesives against glass plate checked by Eq. 14. Data of Hata.[7)] Peeling force: P (dyne cm^{-1})$\times 10^4$.

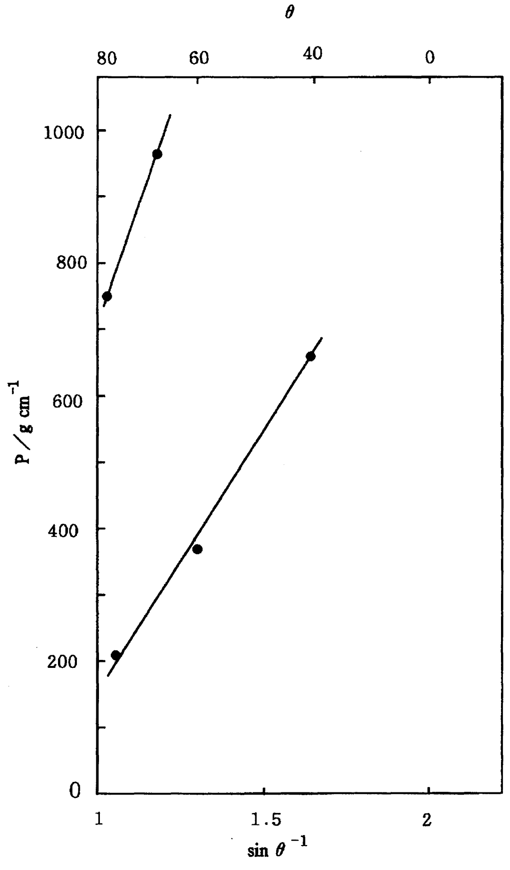

Fig. 4. Effect of peeling angle with various adherent checked by Eq. 14. Data of Uekita.[9)] Adherend: poly(methyl methacrylate) (PMMA) and polyethylene (PE). Peeling force: P (g cm^{-1}).

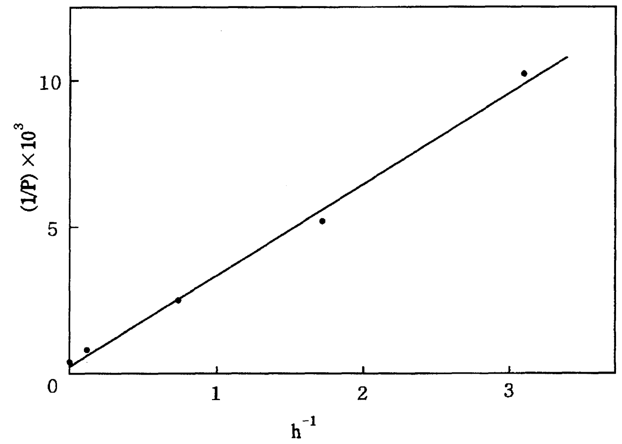

Fig. 5. Effect of thickness checked by Eq. 14. Data of Gardon.[11)]

According to Fukuzawa[6)] P is proportional to $1/(1-\cos\theta)^{1/4}$. However, this is not valid for small angles less than 40° in his experiment.

For the hard supporting film, the actual contact angle is smaller than the peeling angle by the bending angle of the film θ_s and is $\theta-\theta_s$. In his data the angles at the maximum and minimum are shifted by about 40° as θ_s. Beyond an angle $(\theta-\theta_s)$ of 90°, Eq. 15 still holds and P increases again.

Effect of Thickness of Adhesives. Gardon[11)] derived an equation for bending moment of the film and as a result P becomes proportional to h^m, where m decreases from 1 to 0 as the thickness h increases from 0.3 μm to 10 μm for butyl acrylate adhesives. Similar relations were presented by Fukuzawa[6)] and Bikerman.[10)]

However, a simple linear relation of Eq. 14 is also compatible with the data of Gardon, as shown in Fig. 5. The relation between the bending moment and shear viscosity is interesting to study but is not done as yet.

Conclusion

Adhesion force is given by a product of the wetting force and the fraction of pseudo links in the interface between the adhesives and the adherend. Necessary peeling force P is affected by the rheological condition, especially the viscoelastisity of the adhesives layer. P increases with increasing the peeling velocity and thickness of adhesives. On the contrary, in the tensile and shear test, P decreases with increasing the thickness. Pseudo crosslink model of multi-sizes is useful for estimation of factors arising from the viscoelastic and chemical nature of adhesives. The theoretical equation is found to be compatible with literature data quantitatively.

Appendix[1b,1c)]

In the multi-sized pseudo crosslink model, a thermodynamic equilibrium is assumed between the link energy of the b-sized link i.e. bH_0, H_0 being the cohesion heat of a unit link and the kinetic energy of the entanglement of the connected chains of a segmental length n_b and at the temperature T

$$bH_0 = RT\ln n_b^3. \qquad (29)$$

After dissociation of the *b*-sized link, the *b* segments translate to the next equilibrium position separated by a distance $n_B^{0.5}$ caused by the elastic energy at the ultimate elongation. Then n_b becomes equal to b^2 and b is expressed as

$$b/\ln b = 6RT/H_0, \tag{30}$$

$$\text{or } b \cong 12T/T_A - 8, \tag{30a}$$

where T_A is the transition temperature of the link of a size *b* of 1—4. Either Eq. 30 or Eq. 30a yields two transition points A and B at *b* of 1—4 and 16 whose transition temperatures are T_A and $2T_A$ or T_B, respectively. The melting point of the crystalline polymer is somewhat higher than T_B due to the negative entropy for orientation on crystallization, i.e. $-R$ per a repeating unit.

The regeneration of the dissociated link requires the time τ_b for dissociation and translation and τ_b is expressed as

$$\tau_b = \tau_0 \exp(E_b^*/RT) n_B^{1/2} = \tau_0 n_b^2 n_B^{1/2}, \tag{31}$$

where τ_0 is the time for a unit segment. E_b^* is the activation energy for the dissociation of the *b*-sized link and is taken to be equal to (2/3) H_0. $n_B^{1/2}$ is a diameter of the largest B-coil and it is equal to the distance of translation for relaxation.

In the BC zone, the relaxation time is prolonged and at the terminal point C a factor $(n/n_B)^{3.5}$ is multiplied, *n* and n_B being the segmental chain length of a molecule and the B-chain, respectively and

$$\tau_C = \tau_B (n/n_B)^{3.5}.$$

τ_0 is very large as compared with a free segment due to a "three-legged race" effect or the effect of retardation by a connected chain, which is assumed to be $H_0/2$ as energy of retardation. The coordination number of a segment is smaller by 2 than that of a free segment i.e. *z* or 8—10. Since H_0 is equal to $2RT_A$, it follows that

$$\tau_0 = (h/kT)\exp\{(z-2)(4/3)T_A/(T-T_A)\}, \tag{32}$$

where *h* is the Planck's constant.

T_A is a thermodynamic transition temperature but it requires a time τ_A to attain the equilibrium. A rheological transition point for T_A is T_g and it is given by taking the cooling time *t* equal to τ_A. T_g is almost equal to (2/3) T_B as

$$\begin{aligned} T_g &= T_A + T_A\{(z-2)\ln(h/tkT) + \ln(n_b^2 n_B^{1/2})\} \\ &= (4/3)T_A = (2/3)T_B. \end{aligned} \tag{33}$$

The stress relaxation spectrum given in the preceding paragraph is obtained from a log–log plot of the elasticity *E* against the relaxation time τ or the inverse of the frequency ω for the dynamic spectrum. For the static spectrum, the shear elasticity *G* is plotted against the time of deformation *t*. In the former case, deformation is limited by the amplitude and the effect of deformation is not revealed, unlike in the latter case.

Since $E_b = (\nu_b/N)RT = RT/n_b$ and τ_b is proportional to n_b^2, the relation between *E* and τ or the frequency ω is shown as the AB zone in the dynamic spectrum as

$$E_{AB} \sim \tau_{AB}^{-1/2} \sim \omega^{1/2}.$$

For the BC zone, the B-link slides along the molecular chain from the point B to the polymer terminal C in a mode of squeezing the molecular chain. In the dynamic relaxation spectrum, ν is kept constant at ν_B giving the plateau zone and

$$E_{BC} = E_B.$$

Beyond C, it is followed by the viscous flow zone CD, where the viscosity is given as

$$\eta_C = \eta_B (n/n_B)^{3.5}. \tag{34}$$

There is a temperature effect, because τ_0 is varied by the temperature. From Eq. 32 the temperature shift factor a_T of the spectrum is obtained as

$$\log a_T = \log(\eta/\eta_g) = -16(T - T_g)/\{50 + (T - T_g)\}.$$

It is quite identical with the WLF-equation.

On the other hand, the static spectrum is given by replacing the relaxation time τ by the deformation time *t* and the following equations are obtained:

$$\begin{aligned} &G_{AB} = G_A(t/\tau_A)^{-1/2}, \\ &\eta_{AB} = \eta_A(t/\tau_A)^{1/2}, \\ &G_{BC} = G_B(\alpha/\alpha_B)^{-1/2} = G_B(t/\tau_B)^{-1/2}, \\ &\eta_{AB} = G_B(t/\tau_B)^{-1/2}\tau_B(t/\tau_B)^{1/2} = G_B\tau_B = \eta_B. \end{aligned}$$

For the extension experiment, a bulk specimen is deformed in shape. The cross-sectional area is decreased by a factor of $\exp(-kt)$ and the length is increased by a factor of $\alpha\{1-\exp(-k't)\}$, *k* and k' being the rate constants for dissociation and regeneration of the B-links, respectively. When a product $\exp(-kt)\alpha\{1-\exp(-k't)\}$ becomes larger than unity or α becomes larger than 1+e, the extensional viscosity increases steeply with the time *t* of deformation. This is due to the loosening of the B-sized link by the external force or energy *W* as follows: *W* is given by a product of the force *f* acting on the unit area, the size *b*, the cross-sectional area of a chain l^2, *l* being a segment length, the loosened distance of the link δl and divided by the concentration of the links (ν/N), because the force is concentrated on a link. *f* is equal to $(\nu/N)\alpha RT/l^3$. Accordingly,

$$W = bfl^2\delta l/(\nu/N) = b\delta\alpha RT. \tag{35}$$

And τ or η becomes

$$\tau = \tau_B \exp(-W/RT) = \tau_B \exp(-b\delta\alpha) = \tau_B\alpha^{-m} = \tau_B\alpha^{-m'}, \tag{36}$$

where *b* is 16 and δ is equal to a fraction of the free volume, i.e. 0.1 diviuded by 3 or 0.1/3 and *m* becomes 4. m' is equal to $m/(m+1)$ or 3/4, when the elastic force $E\alpha$ is taken to be equal to the viscous one as $E\alpha = E(\tau\alpha^{-\mathrm{m}})\dot{\alpha}$.

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