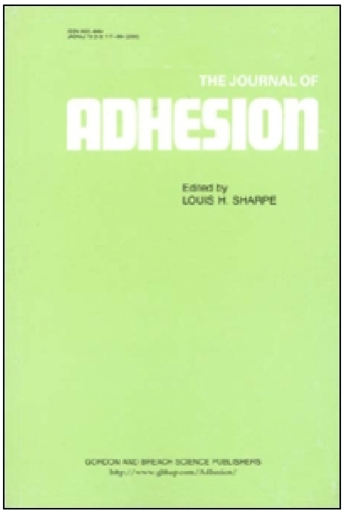

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Rheological, Interfacial and Thermal Control of Polymer Adhesion. I. Isothermal Theory†

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We have developed an isothermal theory of separation in polymer–solid adhering systems. The model used is based on the (observed) drawing of filaments between a bulk polymer and a solid. In the isothermal theory, a criterion is set up, demarcating filament elongation *vs.* detachment of the filament base from the solid. It employs a dimensionless parameter, Ω, that relates free energy of adhesion, elongational viscosity or yield strength of the polymer, and filament size, to adhesive performance. The isothermal theory can be applied directly to the separation processes that occur with pressure-sensitive adhesives. Certain observations by Aubrey and Sherriff, by Gardon and by Kaelble are explained. The validity of the demarcation is believed to extend beyond pressure-sensitive systems, to all thermoplastic adhesives and/or coatings.

KEY WORDS Free energy of adhesion; rheological control of separation; viscosity; elongational viscosity; demarcation between interfacial and cohesive separation; filamentation; polymer adhesion.

INTRODUCTION

The adhesion of a polymer to a solid is profoundly influenced both by the rheological properties of the polymer and by the free energy of adhesion of the polymer/solid interface. But just how these properties are coupled has not been clear. In this communication, we will examine the mechanism of coupling, for linear polymers.

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The thermodynamics of adhesion, spreading and wetting has been very extensively reviewed by many authors.[1,2,3] Reference 3 contains a very recent discussion that is directly relevant to the theory that is presented below.

An elementary interpretation[4,5] of the free energies of cohesion, ΔG^c, and of adhesion, ΔG^a, in terms of cohesive strength, F^c, and adhesive strength, F^a, respectively, is given by Eq. (1):

$$F^c = \Delta G^c / d, \tag{1a}$$

$$F^a = \Delta G^a / d \tag{1b}$$

where d is the distance over which the force F (which is assumed to be constant) acts and beyond which F drops to zero. Good[5] has carried out a theoretical treatment in which the force F was not assumed to be constant, but to be related to experimental intermolecular potential functions.

It has been known for over half a century that the theoretical strength, as calculated by Eq. (1), was several orders of magnitude too high.[5] This discrepancy between theory and experiment is broadly attributed to the defects of the geometry in the model of the separation zone, for a practical system in which a polymer is being separated from a solid.[5–7] The neglect of thermal effects[8–12] also contributes to the failure of Eqs. (1a) and (1b).

It is well established that, in the peeling of pressure-sensitive tapes or labels off solids, filaments of polymer exist, extending from the adhesive layer on the backing, down to the solid.[6,7] See Figure 1. The filaments are often observable with the naked eye. In many cases, they terminate in discrete "bases" at the solid surface.

The polymeric adhesives for modern pressure-sensitive tapes, labels and note pads are often tailored such that, on peeling off a solid, no residue remains. On the other hand, the polymer may be chosen such that the adhesive "splits"; the filaments may rupture, and a residue of polymer may remain on the solid. In the latter type of system, the adhesive may have been designed for permanent attachment, with the cohesive strength of the adhesive being greater than that of one or the other adherend. The mode of separation, *i.e.* interfacial, *vs.* "cohesive failure within the adhesive polymer", is commonly observed to be a function of the rate of separation. Figure 2 illustrates this rate dependence.[13] In the study reported in

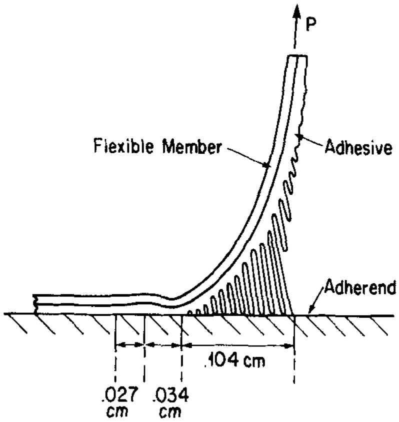

FIGURE 1 Disbondment zone of a pressure-sensitive tape. Re-drawn from D. H. Kaelble, *Trans. Soc. Rheol.* **9**, 135 (1965).

Figure 2, tape peeling was carried out at a range of speeds, and at temperatures from −33° to +39°C, and the data were superposed at 23° by a time–temperature shift. Aubrey[13] attributed the transitions in the data to a transition from viscous to rubbery behavior. He did not explain the major discontinuity in region BC. We will propose a

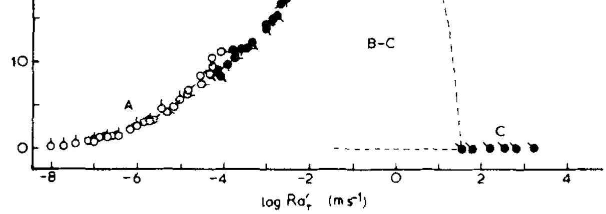

FIGURE 2 Aubrey and Sherriff's report on the relation between viscoelasticity and peel adhesion. "Master curve of peel force against pulling rate at 296 K for the system 6:4 NR:Piccolyte S115, showing superposition of experimental data; (○) cohesive separation, (●) adhesive separation." Substrate: Glass. Reprinted with permission of the copyright owner.

more satisfactory explanation, which will include a theory that predicts the existence of the major discontinuity.

When the filaments are present, the peeling force is expended (dissipated) in the elongation of the filaments.[9] The formation of filaments probably occurs by at least two different mechanisms, depending on whether or not interfacial (or bulk) voids or flaws are present. The "meniscus-instability" mechanism, proposed by Argon,[14-16] probably applies in the absence of flaws. Filaments may also be formed by coalescence of voids in the bulk, which grow (under tension) from minuscule cavities or from interfacial unwetted areas.[17,18] The commonly observed increase in peeling strength, with time after contact has been made, is probably due to the spontaneous elimination of interfacial flaws and, hence, to transition from the interfacial void mechanism to the meniscus-instability mechanism. We will not analyze the meniscus-instability or interfacial void mechanisms; and we will start our analysis at the point in the over-all separation process where the filaments have already formed. We will examine the questions of whether separation will occur at the interface between the base of the filament and the solid, or if rupture will occur somewhere along the body of the filament. Parenthetically, it is very possible that with an *elastomer* pressed onto a solid, crosslinking or chain entanglements will suppress the formation of filaments during separation. Maugis and Barquins[19,20] have proposed a theory which explicitly excludes filament formation; and, consequently, they exclude the deposition of polymer on the solid due to filament rupture. We will point out, below, that the Maugis and Barquins mechanism probably has some relevance to the separation of filament bases from the solid.

We will not treat, here, the "weak boundary layer" mechanism advocated by Bikerman.[21] It has been shown[22-24] that while the presence of weak boundary layer material is a sufficient condition for weakness of an adhering system, it is not a *necessary* condition. Therefore, it is no serious limitation on our analysis, to specify the absence of boundary layer material that is grossly lacking in cohesive strength.

Connelly *et al.*,[25] have analysed the force requirement for peeling an adhesive, by calculating the force required to elongate filaments to the breaking point, with the break occurring somewhere along the filament, and summing over all the filaments in the disbondment zone. See also the earlier paper by Gent and Petrich.[26] Gupta[27] has recently criticized some aspects of this model; we will develop this criticism, by pointing out important transitions that can be expected between deformation modes.

We will assume that, in the processes described below, there is not an appreciable temperature rise. We will, in a later paper, relax this assumption. In terms of material and system properties, the main factors that make the isothermal approximation valid are: slow separation and slow propagation of the separation front, and low glass temperature of the polymer.

MODEL FOR SEPARATION OF LINEAR POLYMERS FROM SOLIDS

We will assume that filaments extend from the bulk polymer down to the region of contact with the solid. Figure 3(a) shows an undisturbed element of the polymer–solid interfacial region. In

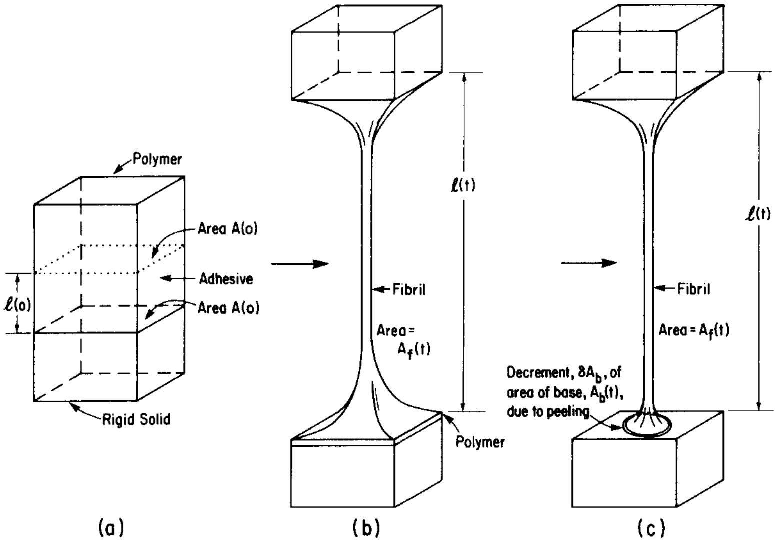

FIGURE 3 Model that describes filament drawing between a polymer and a solid. (a) Undisturbed system. (b) Filament, at its lower end, merges into a continuous, thin layer that completely covers the solid. (c) The filament, at its lower end, has a base with a limited polymer/solid interfacial area.

3(b), a filament extends from the bulk polymer to a thin, continuous layer that adjoins the substrate. The condition shown in 3(b), if it *cannot* pass into condition 3(c), is the same as the condition that precedes failure in "autohesion," or "cohesive separation in the bulk". In every case, the filaments will rupture. After separation, polymer will be found on the solid surface. We will not discuss processes that are modelled by Figure 3(b) *without* the possibility of passage to configuration 3(c). For the process in which interfacial detachment at the base, and filament rupture, are physically real alternatives, Figure 3(c) is relevant.

In 3(c), a filament terminates at a discrete base, with polymer/solid interfacial area A_b. Such an interfacial configuration may arise on account of incomplete polymer–solid contact (incomplete wetting) before the application of a normal force. This is likely to occur on low-energy solids, but it may also occur on high-energy solids. It is less likely when the free energy of spreading,[1,3] ΔG^s, is negative and large, and when the adhering material has gone through a stage where its viscosity was low while contact with the solid was being made.

Under stress, the base configuration shown in (3c) may develop out of the configuration 3(b) by the break-up of the continuous layer, with nucleation of bare areas. This nucleation may be an important component of the detachment mechanism.

Two alternative processes may occur under load. In one, energy is expended in surface work, and none in filament rupture. In the other, there is no surface work, and the only energy expenditure is in filament elongation. The system will deform (at any instant) *via* the process which will take place with the lower incremental expenditure of energy: dW_1, a differential of elongational work, *vs.* dW_2, a differential of work associated with the change in polymer/solid area.

(a) Elongational work

In a previous paper,[7] the yield strength, σ_y, of the polymer was employed as characterizing whether or not a filament would elongate further. But, in the present treatment, we are interested in the continuous, *dynamic* process of filament elongation; therefore, yield strength is not a wholly appropriate parameter. The elongational viscosity, η_E,[28–31] is better suited to the needs of the problem. Elongational viscosity is commly employed in the rheological analysis of the drawing of textile fibres. It is the analog, in extension, of η, the familiar viscosity coefficient, which is defined for shear deformation. The following, somewhat intuitive explanation (inspired in part by Pipkin[30]) will help to elucidate this quantity, which is unfamiliar to most investigators of adhesion.

The geometry of a system in which elongational viscosity controls deformation is that of a column of fluid without lateral constraint, under tension. A fibre of a polymer which is being stretched is a practical case. For linear polymers at very low elongation rates, the deformation in an extensional process involves the motion of molecules or molecular segments past each other. This motion is different from (and in some ways less complex than) that in simple shear. In the absence of lateral constraint, the cross section decreases, whereas, in simple shear, the cross section is constant. The result of this difference in geometry is that

$$(\eta_E/\eta) \rightarrow 3 \quad \text{as rate} \rightarrow 0 \tag{2}$$

For Newtonian fluids, $\eta_E = 3\eta$ at all rates of deformation.

When the fluid consists of flexible, linear polymer molecules, the mean chain end-to-end distance increases by several orders of magnitude during elongation, as the chains become extended and oriented parallel to each other. As this process advances, the resistance to further extension and orientation increases. The resulting change in mechanical behavior is called "elongational strengthening." On the other hand, in simple shear, the increase in chain end-to-end distance is much more modest. When fully relaxed, the chains of flexible polymers are in a roughly spherical conformation. Under shear, the spheroids are deformed into ellipsoids. The extent of this deformation is limited, because shear imparts a rotational motion to the ellipsoids. (There may also be a decrease in chain entanglement.) So the ratio of major to minor axes does not approach the value that corresponds to the fully-extended length of the molecule. Shear viscosity commonly decreases with increase in shear rate; this decrease is called "shear thinning."

The result of the molecular difference between elongation and shear is that when the deformation rate is appreciable, η_E will be considerably larger than η. Indeed, η_E may well be as much as one or two orders of magnitude larger than the low-rate shear viscosity, η_0. This rate effect has been observed[32] and it is well documented for polymer solutions.[33]

The force against which the work of stretching is done is $\eta_E\dot{\varepsilon}A_f$, where $\dot{\varepsilon}$ is stretch rate, $\frac{1}{l}\frac{dl}{dt}$, and A_f is cross section area.† This product will be a constant over the length of the filament. In steady state deformation, at any instant, $\eta_E\dot{\varepsilon}A_f$ exactly balances the applied force:

$$F = \eta_E\dot{\varepsilon}A_f \tag{3}$$

$$dW_1 = F\,dl_f \tag{4}$$

A complete analysis of filament elongation must include another term which corresponds to addition of polymer to the top of the filament by flow from the bulk. Kramer[34] calls this "surface drawing." He has suggested that surface drawing comes to an end, well before the filaments reach their full elongation, because of chain entanglements in the region from which the filaments are drawn. The flow field that describes surface drawing has not yet been analyzed. For tractability of the problem, we will assume that the shape and volume of the transition region at the top of the filament are constant, and that surface drawing has ceased. Then, $l_f - h_b$ is the length of the fibre between the top of the base region and the bottom of the region of transition to bulk polymer. The volume of filament, V_f, plus base volume, V_b, is assumed to be constant:

$$V_f + V_b = \text{constant} = V. \tag{5}$$

If the applied force exceeds a critical value for a filament, then a steady state will no longer exist; and the filament will deform until it ruptures. This rupture may occur by a necking-down mechanism.

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† We will, for convenience, assume that at any instant all filaments have the same cross section, A_f. In reality, there will be a distribution of radii about some mean value. We will also assume that there is a single base area, A_b, though recognizing that it is to be expected that a broad distribution of areas will be present. We will reserve, for subsequent studies, the examination of the effect of distributions of radii of filaments, and of bases, on strength properties.

We may write, for the critical force,

$$F_c = (\eta_E \dot{\varepsilon} A_f)_c \tag{6}$$

There may also be a recoverable, elastic component in dW_1. To be most general, the filament may be considered to be viscoelastic.

The force given by Eq. (3), summed over all the filaments that are present, equals the macroscopic force of peeling. This will be true *only* if the force, Eq. (3), is less than that required for interfacial separation.

(b) Surface work and deformation of filament bases

It is unlikely that an entire filament base will lift off as a rigid unit. A cylindrical plug of viscoelastic polymer, adhering to a rigid, flat solid, would suffer Poisson contraction under tension. This would lead to a concentration of shear stress at the rim. The local shear strength of the interface, at the rim, is likely to be surpassed before the tensile strength of the interface in the center of the base is exceeded. So the rim of the cylinder would separate first from the solid.

In principle, separation at the interface between base and solid might start by a lift-off mechanism, as indicated in Figure 4(a), with

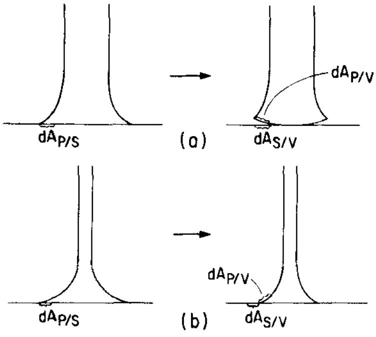

FIGURE 4 Two possible modes of local peeling of a filament base. (a) For a differential decrease in polymer/solid area, $dA_{P/S}$, the newly-formed solid/vapor area, $dA_{S/V}$, and polymer/vapor area, $dA_{P/V}$, are geometrically the same as $dA_{P/S}$. (b) For a differential decrease in solid/polymer area, the new solid/vapor area, $dA_{S/V}$, is geometrically the same as $dA_{P/S}$. But the new polymer/vapor area is geometrically deformed, and will be less than $dA_{P/S}$. Note, also, that in (b), the height and volume of the base region decrease, as separation proceeds.

minimal plastic deformation. The function that describes this process is approximately the free energy of adhesion, ΔG^a_{ij}:

$$\Delta G^a_{ij} = \gamma_{ij} - \gamma_i - \gamma_j \tag{7}$$

where γ is surface free energy, and i and j refer to the free surfaces of substances i and j, respectively, and ij to the interface. Alternatively, separation might start with a large degree of plastic deformation of the base, near the rim, so that the base region retained its shape but shrank over-all. See Figure 4(b). Comparing the increments of area, it may be seen that, when plastic deformation occurs, the area $dA_{P/V}$ will be larger than $dA_{P/S}$ by a factor that depends on the cosine of the contact angle and on the base radius.

Neither of these extremes will be exact, so the free energy for the process indicated in Figure 3(c), for the decrease of base area by δA_b, will be something between the free energy of adhesion, Eq. (7), and the free energy of spreading, Eq. (8)

$$\Delta G^s_{i/j} = \gamma_{ij} + \gamma_i - \gamma_j \tag{8}$$

We introduce the term, ΔG^*, for the free energy requirement. It will be of the same order of magnitude as ΔG^a, particularly if ΔG^a is large.

$$\Delta G^a > \Delta G^* > \Delta G^s \tag{9}$$

This relation, and the approximation of using ΔG^a for ΔG^*, will have to do until more detailed information about the bases becomes available.

The radial resistance to separation of a filament base from the solid may be approximated in terms of ΔG^a. For a change in base area, dA_b, the surface work is

$$dW_2' \cong -\Delta G^*_{P/S}\, dA_b \cong -\Delta G^a_{P/S}\, dA_b \tag{10}$$

If the polymer were a low-viscosity Newtonian fluid, Eq. (10) would account for all the work done in changing the polymer/solid area. For a practical polymer, deformational work must be added in. To analyze this work, we need to employ the shape of the base region—a property that is not, in general, known at present. It is reasonable, and it simplifies the analysis, to approximate the base shape as a cone; see Figure 5. (In Figure 5, a conical configuration at the top of the filament is drawn for convenience only. As already

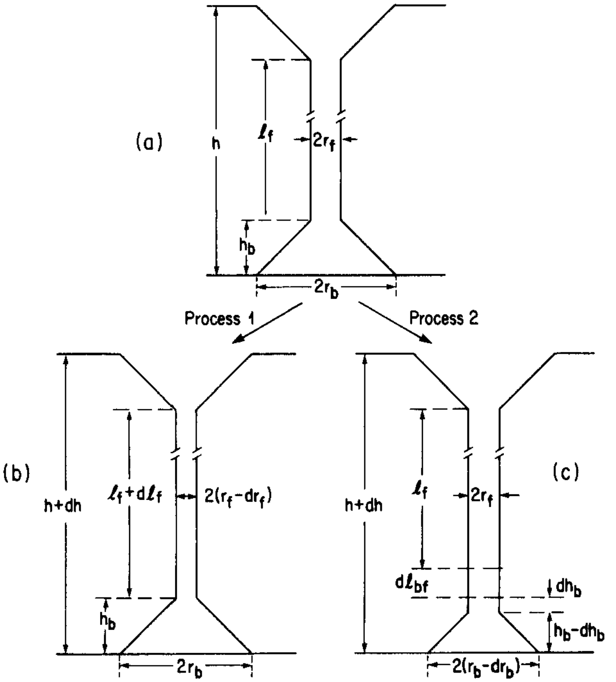

FIGURE 5 The alternate processes in response to a tensile stress. (a) "Initial" condition. (b) Filament has elongated; base area and volume are constant. (c) Filament radius is constant; base area and volume have decreased, and fibre elongation is due solely to flow of polymer from base.

noted, the shape and volume of that region are assumed to be constant.)

The flow field, corresponding to the passage from Fig. 5(a) to 5(c), must be complex; it has not yet been analyzed. We may write, for the force that does work W_2'' deforming the base,

$$F' = \sigma_{yb}\bar{A}_b \tag{11}$$

$$dW_2'' = F'\,dl_{bf} \tag{12}$$

where σ_{yb} is an effective yield strength and $\bar{A}_b$ the mean area of the base cone. We could, perhaps, replace σ_{yb} with a term, $\eta_{Eb}\dot{\varepsilon}_b$, i.e. an effective elongational viscosity times an effective extension rate. Then,

$$dW_2 = dW_2' + dW_2'' \tag{13}$$

(c) The processes as alternatives

The "least energy" principle, mentioned above, will control the mode of change for the system. Thus,

Process 1: $dW_1 < dW_2$: Filament elongates continuously (14a)

Process 2: $dW_1 > dW_2$: Filament begins to detach from solid (14b)

Figure 6 shows a block diagram of the possible sequential processes, and indicates the branchings dictated by the least-energy principle. Consider, for example, the time regime where filaments have just begun to form, *i.e.*, before appreciable surface drawing or constant-mass stretching has occurred. If the interfacial force between polymer and solid is small enough that the bases detach

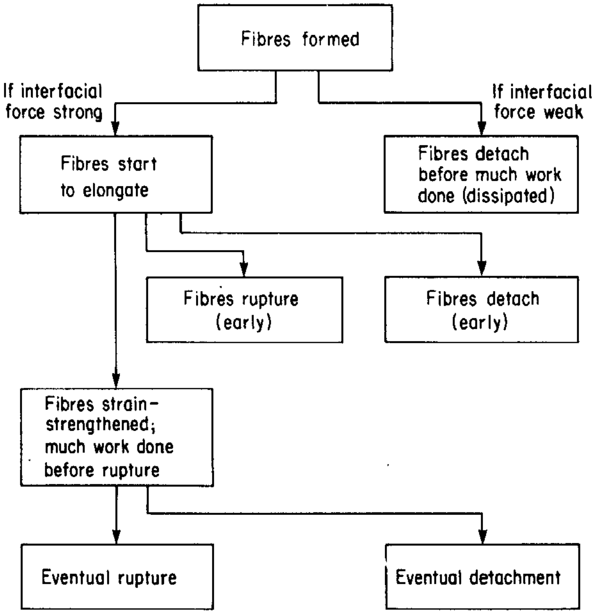

FIGURE 6 Block diagram of possible events that occur for a filament between a bulk polymer and a solid. The initial condition, "Filaments formed", exists after the end of the "surface drawing" stage of filament formation.

cleanly *during this time regime,* very little surface work is done during detachment; and little work is done in motion in the normal direction before detachment. Very few filaments will exist at any instant, to contribute to the resistance to separation. Hence, little macroscopic force will be required; and the effective, macroscopic adhesion will be weak.

There is an important difference between processes (1) and (2). After process 2 (base detachment) starts, there will be no further changes in the properties of the polymer that contribute to resistance to separation. But during process 1, filament elongation, η_E, and also $\dot{\varepsilon}_f$ and A_f, all change continuously. Hence the criterion, $dW_1 < dW_2$, may hold at the early stages of elongation but, at a later stage, the criterion $dW_1 > dW_2$ may hold. An examination of Figure 6 shows how this change-over from process 1 to process 2, at various stages of process 1, leads to various outcomes as to macroscopic separation.

The condition,

$$dW_1 = dW_2 \tag{14c}$$

demarcates between filament elongation and base detachment, at any instant. Evaluating dW_1 using Eqs. (3) and (4), and dW_2 using Eqs. (10) to (12), we obtain

$$\eta_{Ef}\dot{\varepsilon}_b A_f \, dl_f = -\Delta G^*_{P/S} \, dA_f + \eta_{Eb}\dot{\varepsilon}_b \bar{A}_b \, dl_{bf} \tag{15}$$

Since $\bar{A}_b$ will be larger than A_f, the relations will hold: $\dot{\varepsilon}_{bf} < \dot{\varepsilon}_f$, and $dl_{bf} < dl_f$. η_{Ef} will be considerably larger than η_{Eb}; this will be increasingly true as the deformation proceeds. Hence we can, as an approximation, drop the last term in (15). Then we can write the relations that will describe the alternative processes:

$-\Delta G^*_{P/S} \, dA_b < \eta_E \dot{\varepsilon} A_f \, dl$: Interfacial detachment of filament bases (16a)

$-\Delta G^* \, dA_b > \eta_E \dot{\varepsilon} A_f \, dl$: Continuous deformation of polymer; filaments elongated (16b)

$-\Delta G^* \, dA_b = \eta_E \dot{\varepsilon} A_f \, dl$: Criterion demarcating between interfacial detachment and filament elongation. (16c)

Interfacial detachment by shrinkage of a base (local peeling) should not be confused with *macroscopic* interfacial separation. First, macroscopic separation involves the drawing-out of microscopic filaments in the interfacial region. So we must define the "microscopic" scale as being the dimensional magnitude in which there are *not* any yet-smaller filaments formed. The model of Maugis and Barquins[19,20] may be appropriate for the peeling separation of the fibre base areas.

Second, macroscopic peeling separation occurs along a linear front. But the microscopic separation of a filament base proceeds radially inward, with the force requirement proportional to the base perimeter and, hence, with a decreasing force per unit change in radius. This implies a mechanical instability: after inward peeling has started, the work will be smaller, per unit change of base radius, in completing the separation, than that done in the corresponding motion elongating the filament *without* shrinkage of the polymer/solid area. We next set the quotient of the left and right sides of (16) equal to a dimensionless parameter, Ω, and rewrite (16c) in the form,

$$\Omega \equiv \frac{\Delta G^*}{\eta_E \dot{\varepsilon} A_f} \frac{dA_b}{dl} \tag{17}$$

If Ω drops below unity, the base will detach from the solid. If Ω is above unity, the filament will elongate further.

To eliminate the differentials, dA_b and dl, from Eqs. (16c) and (17), we examine the change in volume which accompanies the change in base area. We assume the model, shown in Figure 5, of a truncated cone whose height is h_b and whose base radius is r_b. Under an external force, F, the base starts to detach, with a differential decrease in polymer/solid interfacial area. The base volume, V_b, decreases by dV_b and the filament volume, V_f, increases by dV_f when polymer passes from the base into the filament: $dV_f = \pi r_f^2(dl_{bf} + dh_b)$. Also, $dh_b \ll dl_{bf}$. The volume, V, of base plus filament, can be expected to be constant; see Eq. (5). If ϕ is the cone apex angle, $h_b = r_b \cot \phi$; and, since $A_b = \pi r_b^2$, Eq. 16 may be written,

$$V = \frac{\pi r_b^3 \cot \phi}{3} + \pi r_f^2 l \tag{18}$$

Differentiating Eq. (18) while keeping r_f, V and ϕ constant, we obtain

$$\frac{dr_b}{dl} = -\left(\frac{r_f}{r_b}\right)^2 \tan\phi \tag{19}$$

It is a reasonable approximation to assume that $\phi = 45°$, so that $\tan\phi = \cot\phi = 1$ and $r_b = h_b$. Since $dA_b = 2\pi r_b\, dr$, Eq. (19) may be written,

$$\frac{dA_b}{dl} = -2\pi r_b\left(\frac{r_f}{r_b}\right)^2 \tag{20}$$

We may combine Eq. (20) with (19), together with the relation, $A_f = \pi r_f^2$. The demarcation criterion then becomes,

$$\Omega \equiv \frac{2\Delta G^*}{\eta_E \dot{\varepsilon} r_b} \tag{21a}$$

$$\Omega > 1: \text{ Filaments are elongated further} \tag{21b}$$

$$\Omega < 1: \text{ Bases detach from the solid} \tag{21c}$$

If, instead of being geometrically flat, the solid is rough, the method that has been used to treat the contact angle of a liquid on a rough surface[35] may be employed. We define a as actual area of interface and A as area projected on a plane parallel to the envelope of the surface. The roughness ratio, ρ, is

$$\rho \equiv \frac{a}{A} = \frac{da}{dA} \geqq 1 \tag{22}$$

We assume the scale of the roughness to be much smaller than the base diameter. (If it is comparable to the base diameter, then the detachment process will be strongly dependent on the local slope of the solid surface.) For separation that faithfully follows the true interface of a rough surface, the general criterion becomes:

$$\Omega \equiv \frac{2\rho\Delta G^*}{\eta_E \dot{\varepsilon} A_f}\frac{dA_b}{dl} \tag{23}$$

$$= \frac{2\rho\Delta G^*}{\eta_E \dot{\varepsilon} r_b} \tag{24}$$

The ratio, r_b/r_f, may be a constant for the filaments that form in a particular adhering system. (The ratio will probably be of the order of 2.) If this is true, then we may write,

$$\beta \equiv r_b/r_f \tag{25}$$

Hence, a form that is equivalent to Eq. (24) is,

$$\Omega = \frac{2\rho}{\eta_E \dot{\varepsilon} r_f} \cdot \frac{\Delta G^*}{\beta} \tag{26}$$

This form has the convenient characteristic that the properties of the filaments are grouped in a product in the denominator: $(\eta_E \dot{\varepsilon} r_f)$. But Eq. (24) contains one less assumption than (26), and so is more fundamental.

We can now examine the predictions that are made by the theory, in regard to the force needed for separation. The variables, ΔG^*, ρ, η_E, $\dot{\varepsilon}$, and r_b control the practical force, in two disparate ways. These are, (a) in determining whether the manner of separation is by interfacial detachment or by filament elongation and rupture and, (b) in determining the force requirement for filament elongation, when elongation and rupture occur.

As already indicated, if $\Omega < 1$ initially, the force needed for separation will be smaller (and often, smaller by several orders of magnitude) than the force required if $\Omega > 1$.

If $\Omega > 1$ initially, then (21b) will hold. The macroscopic force will depend on the force, F, required to elongate (or to continue elongating) each filament, summed over all the filaments in the separation zone. See Figure 1 and Eqs. (3) and (6). How many filaments are in the separation zone at any instant will depend on, (1) how many have not yet elongated to the point of rupture and (2) how many have not suffered base interfacial detachment. Of the conditions (1) and (2), the former is controlled by the dependence of the elongational viscosity, η_E, and the filament cross section area, A_f, on $\dot{\varepsilon}$ and on time. For a particular macroscopic rate of deformation, dl/dt, $\dot{\varepsilon}$ itself is also a (decreasing) function of time. It is probable that the strain-strengthening effect dominates the rate-dependence of the force. This is why the trend in regions A and B, Figure 2, is what is commonly observed. We will discuss Figure 2 at greater length, below.

The same strain-strengthening may (or may not) lead to a sufficient increase in the product $(\eta_E \dot{\varepsilon} r_f)$, to lead to a change-over to the condition,

$$2\rho \Delta G^* < \eta_E \dot{\varepsilon} r_b$$

and hence to condition (21c), $\Omega < 1$. If this condition is achieved for each of the filaments only just before rupture, then the peeling force requirement will be almost as great as if the elongation had continued all the way to rupture. This combination of large force and interfacial separation is, precisely, one of the effects that we laid out as central matters that needed to be explained.

If Ω is initially large, and if $(\eta_E \dot{\varepsilon} r_b)$ stays constant, then Ω will, of course, remain appreciably less than unity, and clean interfacial separation will not occur. The macroscopic force will be large if $(\eta_E \dot{\varepsilon} r_b)$ is not too small and if the number of filaments per unit area in the disbondment zone is large.

If separation is slow, *e.g.*, in a "creep" range for the polymer, then the increase in η_E with time may be small because of molecular relaxation of the polymer. This means that, if the value of Ω is initially greater than unity, it is likely to remain so until the filament ruptures. Hence, separation with polymer deposition on the solid is predicted.

If Ω is initially less than unity, then even if $(\eta_E \dot{\varepsilon}_b A_f)$ would decrease with time so that Ω would increase to a value above unity, the *initial* value (rather than a value achieved later on) will govern the practical adhesion. This is true because interfacial detachment will occur early in the process, before Ω could rise above unity.

The predictions that we have just made, in regard to macroscopic force of adhesion, are in agreement with common observations, e.g., those reported by Aubrey[13] (see Figure 2), by Kaelble[37] and by Gardon.[38,39] See also, below, the discussion of Table I.

APPLICATION OF THE ISOTHERMAL THEORY

Equations (17), (21), (24) and (26) contain terms which can be evaluated experimentally, so that we can, in principle, use a form such as Eq. (21) or (24) as a predictor.

If covalent or ionic bonds exist across an interface, the value of

ΔG^a will be of the magnitude of $-5\,\mathrm{J/m^2}$. (This estimate is based on the C—C bond energy, 3.74×10^4 J/gm mole.) We may take this as an estimate of ΔG^*. For low-energy solids, interacting with polymers, ΔG^a is in the range, -50 to $-200\,\mathrm{mJ/m^2}$. This estimate is based on contact angle measurements of various organic liquids on Teflon® and on polar polymers, and the use of the Young-Dupré equation,[1]

$$\Delta G^a = -\gamma_l(1 + \cos\theta) \tag{27}$$

For order-of-magnitude calculations, we may use the lower range of known values of ΔG^a for an interface of a polymer *vs.* an organic compound, *i.e.*, about $-50\,\mathrm{mJ/m^2}$, as an estimate for ΔG^*.

For computation by Eq. (24), we need values of η_E at rates of extension that are relevant to peeling of pressure-sensitive tapes. Kaelble[6] has reported that, for a typical tape-peeling process, the zone in which the filament elongation takes place is about 1 mm wide. See Figure 1. At a peel rate of 1 mm/sec., this zone will travel past a point in space in 1 second. This means that an order of magnitude estimate of the time to break, t_b, is 1 second for this peeling rate, and $\dot{\varepsilon} \cong 3\,\mathrm{sec}^{-1}$.

The rate of true strain, $\dot{\varepsilon}$, for a filament in the separation zone of a pressure-sensitive tape, will decrease as elongation progresses. So if η_E is constant, the value of $(\eta_E\dot{\varepsilon})$ will be greatest immediately after a filament achieves its constant-mass condition, *i.e.*, at the end of surface drawing. This argument gives a basis for estimating a value for the "initial" length, l_0, *e.g.* $l_0 \cong l(\mathrm{break})/30$. See below.

Connelly *et al.*,[25] have measured the elongational viscosity of rods of a hot-melt polyester adhesive. They found that the strain at break, defined for finite strain, $\varepsilon_b = \ln(l_b/l_0)$, was 3.35; *i.e.*, $l_b/l_0 = 30$, where l_b is length at break. This value agrees with the estimate just given, based on the probable geometry. From Connelly's data, we have estimated the initial value of η_E. Although, in general, η_E depends on the stretch rate, the initial value of η_E for the polymer studied by Connelly *et al.*, appeared to be independent of $\dot{\varepsilon}$, and was approximately 1×10^6 Pa-sec. As stretching continued, they found that η_E increased by a factor of 10. (The force per filament, $(\eta_E\dot{\varepsilon}A_f)$, generally goes through a maximum because of the decrease in A_f and $\dot{\varepsilon}$). We have allowed for the increase in η_E by making the calculations for Table I using the initial η_E and also a value of η_E ten times as large, to correspond to η_E when the filament is close to rupture. For a filament drawn from the adhesive of a pressure-sensitive tape, we may assume the diameter to be of the order of 0.01 mm, and $r_f \cong 0.005$ mm. So the base radius, r_b, should be about 10^{-2} mm. We will also assume a roughness factor $\rho \cong 4$. For ΔG^*, we may assume values of about 50 mJ/m^2, as representing strong forces.

Table I shows the results of using these data in Eq. (24).

TABLE I
Estimation of Ω, and qualitative prediction of separation mode and adhesion strength, for weak and strong interfacial forces

ΔG^*, J/m^2	η_E Pa-sec	$10 \times \eta_E$ Pa-sec	Ω for a filament	"Cohesive" *vs* interfacial separation	Magnitude of adhesive strength
0.05	1×10^6		0.015	Interfacial	Small
0.05		1×10^7	0.0015	Interfacial	Small
5.0	1×10^6		1.5	Cohesive	Large
5.0		1×10^7	0.15	Interfacial	(May be large)

The transition shown in the last two columns, from the behavior in the first row to that in the third row, with increase in ΔG^*, is not surprising; an increase in the free energy of adhesion can be expected to lead to a tendency to change from interfacial to cohesive separation. But the prediction of a transition, as between the third and fourth rows, is novel. The elongational strengthening is manifested as an increase in η_E and in the dynamic resistance to elongation, such that Ω is reduced from a value (1.5) that predicts elongation to rupture, to a value (0.15) that predicts interfacial detachment of the filament base. The general prediction of strength, in the last entry in the fourth row, may be "large" if the increase in η_E occurs during or after a considerable amount of work has been done. Or it may be "small", if η_E increases rapidly enough that Ω drops below 1 before much work has been done.

We may now discuss in detail the investigation by Aubrey and Sherriff[13] which has been mentioned above; see Figure 2. These authors constructed a master plot of force *vs*. temperature-shifted rate. Three distinct regions were identified. In region A, peel force increased strongly with pulling rate. "Much filamentation . . . occurred", and the separation mode was filament rupture rather than detachment. In a small overlap region between A and B, the separation mode was variable. In region B, the increase in force with peel rate continued but the separation locus was at the adhesive/substrate interface. Filamentation was "still present through much reduced". Between regions B and C, there was a "stick-slip . . . oscillation of force" and, with the start of region C, a discontinuous drop to near zero (5 to 10 gm/cm). In region C, the force was nearly independent of rate. There was "no apparent filamentation, and the surface of the adhesive after peeling [was] smooth and glossy". The measurements in region C were carried out of the lowest temperature. When the temperature-rate shift was carried out, the rate in region C corresponded to speeds in the range of about 30 to 2000 m/sec. at room temperature. For comparison, the range of speed of propagation of a crack in brittle fracture of a glassy polymer has a maximum value about 1/3 of the speed of sound.[37]

Equation (24) and the discussion above, following Eq. (26), provide a qualitative explanation for the transitions observed by Aubrey and Sherriff. In region A, where Ra'_T, and hence $\dot{\varepsilon}$, are small, separation occurs by rupture of filaments. Small values of $\dot{\varepsilon}$ correspond to large values of Ω and, hence, to "cohesive" separation. With increasing rate, the value of Ω decreases and interfacial separation sets in. The existence of an overlap region of B with A is to be expected, on account of random variation in properties such as filament and base radii. The existence of high over-all strength within region B, despite interfacial separation, has been anticipated ("post-dicted") above; see, *e.g.*, the discussion of Eqs. (24) and (26), and of Table I. For region C, the very high effective rate would lead to the condition, $\Omega < 1$, before appreciable work could be done in elongating the filaments.

The oscillatory region, B–C, between large values of force (as within region B) and negligible force (as in C), correspond to alternation between the occurrence of interfacial separation before appreciable work has been done in elongating filaments, and separation after such work has been done. A patch or band of local separation at a high force could lead to a decreased radius of curvature for the tape backing, and hence a decreased rate of extension, $\dot{\varepsilon}$, and possibly a decrease in η_E for the filaments. The decrease in $\dot{\varepsilon}$ and η_E would lead to base detachment, and a lower force for the adjoining patch or band, and an increase in radius of curvature for the backing. An oscillation between $\Omega > 1$ and $\Omega < 1$ could occur.

The conclusions regarding the temperature-rate-shifted data are probably valid, because the free energy of adhesion probably changes little with decreasing temperature. The filament radii may well change only moderately with decreasing temperature. The dominant change is in the elongational viscosity, η_E, which must increase very rapidly with decreasing temperature, so that at the lower temperatures, the chain relaxation that would permit filament drawing may not occur rapidly enough to keep up with interfacial separation of the filament bases.

An alternative or supplemental explanation of region C may involve a locally adiabatic process, and local heating close to the interface. If this is so, then the time-temperature scaling employed by Aubrey and Sherriff may have led to an unduly enlarged abscissa scale ($\log Ra'_T$) at the lowest actual temperatures, i.e. within region C. But the qualitative conclusions in the previous three paragraphs are unchanged.

Kaelble[6,37] and Gardon[38,39] have observed transitions with increasing rate, from cohesive to adhesive separation, similar to that seen by Aubrey and Sherriff. The terminal region C, however, was not clearly present in Gardon's work; and a smooth decline in peel force at high rates was observed by Kaelble.

FINAL COMMENTS

It is clear from Table I and Figure 2 that the qualitative prediction of the transition between (a) cohesive separation or interfacial separation with a large force requirement and (b) interfacial separation, is in agreement with experiment. The observation that large practical adhesive strength can be compatible with true interfacial separation also supports the theory that we have proposed. We may, additionally, point out that prior theories of adhesion[21] had made the incorrect prediction that macroscopic adhesive strength would always be high even when the free energy of adhesion was small, provided weak boundary layer matter was absent.

Our theory introduces surface roughness explicitly and quantitatively, by way of the roughness ratio, ρ. It is, of course, well known that an increase in the roughness of a solid usually increases effective adhesive strength. The theory shows that this increase comes about by the raising of Ω, and hence, an increase in the degree of anchoring the fibres to the solid. Therefore, strength should not be a linear function of roughness; and this prediction agrees with experiment.

It is not yet possible to predict, for a particular polymer/solid system, the exact values of experimental variables (such as rate of peeling) at which the transitions from one separation mode to another will occur. Nor is it yet possible to predict the absolute value of the peeling force. Only for a very few polymers are data as to elongational viscosity available. Realistic estimates of filament and base diameters are not yet at hand.

Perhaps equally important, as limitations on predictions, are the geometric approximations that were made. Obviously, there is need to remove the approximations as to the constancy of filament diameters and of shape of the filament bases, together with the neglect of the term that corresponds to deformational work in the base, in Eq. (15). To do this may, in part, be an experimental problem; but, to be general, it will be necessary to solve the problem of the flow field during deformation of the bases. This is part of the more general problem of surface drawing at the tops of the filaments.

We will examine, in a separate paper, the consequences of removing the limitation to isothermal systems that we have used so far. We will discuss in some detail the conditions (such as rate of deformation and of propagation of the separation front) under which it is necessary to treat the system as adiabatic. It remains, however, that our isothermal theory provides the first broadly useful treatment of the different modes of separation for linear polymers whose Tg's are not too far above the ambient temperature.

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