Theories of adhesion and uses of adhesives: a review

W. C. Wake
The City University, St John Street, London, EC1V 4PB, UK
(Received 3 November 1977)

Theories of adhesion are based on adsorption and wetting, on diffusion, on donor/acceptor or electrostatic interactions and on simple mechanical interlocking of the adhesive into irregularities of its substrate. The principal contributions of recent work to these theories are outlined. Joint strength is also a matter of stress distribution and knowledge of this has been advanced both by formal mathematical methods and by the use of finite element analysis. The tack of adhesives is now better understood as involving the interaction of both bulk and surface properties with the rate of separation. Fracture mechanics has been applied to the investigation of the failure of structural adhesives in humid environments. The properties determining adhesive behaviour comprise T_g, solubility parameter, surface free energy, viscosity and the microstructure of the polymer. The latter, more recently explored, is examined in detail. The structure of the adhesives for use at high temperature and the changes in technology demanded by impending legislation conclude the review.

INTRODUCTION

The dichotomy between theory and practice deplored by so many writers on adhesion and adhesives arises because the former embraces a far wider range of phenomena than the latter, concerned as it is mainly with the strength of joints between different materials. Both depend in the last resort on molecular attraction or, more frequently than was at one time believed, on the formation of chemical bonds across the interface. These bonds may be those arising from the sharing of electrons or from charge transfer and are then electrostatic in nature. Hydrogen bonding, which may be regarded as intermediate in nature between these two extremes, is probably an important form of interaction across some interfaces. Diffusion of long chain molecules is counted in this introductory summary as a form of molecular attraction dependent on secondary or van der Waals's forces.

Another reason for the gap between theory and practice is the large dependence of joint strength on the mechanical properties of the adhesive rather than on its behaviour at the interface. Good interfacial interaction is a necessary but not a sufficient condition for joint strength, hence the undoubted contribution which fracture mechanics and finite element analysis have made in the applications of adhesives. But the behaviour of flexible adhesives in peeling and the tacky nature of pressure-sensitive adhesion are also reflections of bulk property. A measure of the extent to which a theoretical approach by way of surface energetics has married with practice is the recent explanation of joint failure in moist environments in which interfacial failures accompanied by corrosion predominate over mechanical fracture occurring within the adhesive.

These generalities are intended only as an introduction to a more detailed examination in subsequent sections of this review which will emphasize matters of interest to polymer science ignoring other aspects of adhesion such as the structure of glass[1] or carbon reinforced plastics, the pelletization of powders[2], cell adhesion[3], so important to the understanding of the functioning of multicellular organisms and their malfunctioning to develop cancers, biological adhesives[4] and dental prostheses[5]. It will also ignore the preparative routes used in adhesives formulations as the intermediates, monomers and polymerization procedures are identical with those generally used in polymer science.

THEORIES OF ADHESION

To be successful, theories of adhesion and of adhesive action need to explain in terms of molecular structure, thermodynamic or kinetic properties of large molecules and mechanical stress distributions the behaviour of adhesive layers and the properties of joints. There is a wide range of phenomena to subsume and an explanation which covered all would be of useless generality. It is therefore convenient to divide the subject matter into phenomena essentially associated with physical adsorption, with diffusion, electrical charge distribution or with chemisorption by which is understood the formation of a primary valency linkage between adhesive and substrate as the result of some chemical reaction. Stress distributions are discussed under the heading Theories of Joint Strength.

Adsorption theories

The physical adsorption of gas molecules to solid surfaces may be regarded as well understood and dependent on the secondary or van der Waals's forces. These forces have themselves been ascribed to attractions arising from a quantum mechanical effect due to the valency electrons of organic materials or those existing in a metallic body as a free gas. Two main types of explanation have been proposed for the attraction between electrically neutral bodies whether of molecules for each other or of one array of molecules (a plane surface) for another. One explanatory

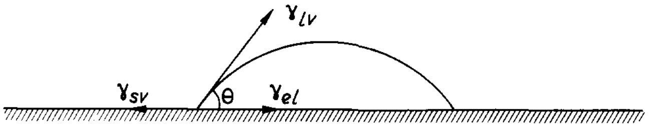


Figure 1 Contact angle and tensions for liquid drop on solid surface.

process starts from elementary bodies such as two hydrogen molecules and builds from there to arrays of atoms or molecules. This is a *microscopic* process and is described in simplified mathematical detail by Grimley[6]. The other details the Maxwell field in the space between two dielectric bodies and is called a *macroscopic* approach. This originated with Lifshitz[7] and has been developed by workers in the Low Countries. It also is outlined by Grimley[6]. These quantitative theories have led to a number of attempts at the direct measurement of the attraction between electrically neutral surfaces, originally between a sphere and a flat plate but more recently between two hemicylinders with their axes at right angles, a conformation geometrically equivalent to the sphere and plate. This work has shown the expected dependence on the cube of the distance for separations above about 80 nm gliding smoothly down to a square law dependence at 8 nm and below[8]. The transition corresponds to that from retarded to non-retarded forces, an expression used to indicate the need for a relativistic correction for the finite speed of the interactive electromagnetic radiation.

The most recent work on the direct attraction (adhesion) between bodies with perfectly mating surfaces has involved one deformable surface in contact with a hard surface. Using optically flat rubber surfaces, Roberts and Thomas[9] have shown that the area of contact expected from the Hertz law is exceeded, due to attraction between the surfaces. Under conditions of dynamic loading, as the contact area increases, the force required to separate varies in a way predictable by the surface energies but if an overload has been applied, separation forces needed are enhanced and time effects associated with hysteresis in the bulk rubber appear. Direct measurement of minute distances and small forces pose experimental problems which are avoided by using a thermodynamic approach concerned solely with surface energetics rather than forces of separation. Unfortunately, turning to thermodynamics involves turning away from kinetic happenings to equilibrium situations in which models are formulated in terms of liquids adhering to solids rather than solids being placed into contact with and then separated from, other solids.

Wetting: a form of adsorption?

The Dupré equation states:

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12} \tag{1}$$

i.e. the thermodynamic work of adhesion of a liquid to a solid, W_A, is equal to the sum of the surface free energies of liquid and solid less the interfacial free energy. The latter is not directly measureable except in the case of two liquids. Recourse is had therefore to the Young equation in which a vector diagram is obtained from a model of a drop of liquid on a solid (*Figure 1*). The subscripts refer *sv*, to the solid–vapour interface, *lv* to the liquid–vapour interface and *sl* to the solid–liquid interface. Horizontal resolution of forces, obtained by equating free energies and tensions, yields the Young equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta \tag{2}$$

Equation (2) can only be substituted in equation (1) by further equating γ_{sv} with γ_l which is often done, although it is more instructive to introduce a spreading pressure, $\pi = \gamma_s - \gamma_{sv}$, and hence to obtain the Young–Dupré equation:

$$W_A = \gamma_{lv}(1 + \cos\theta) + \pi \tag{3}$$

So much is the common exposition of the thermodynamic basis of the adsorption theory of adhesion for several decades even though its assumptions are many and opportunities for its application few. However, direct proof of the substantial correctness of the Young–Dupré equation is not lacking. Bailey[10] has experimented over many years with measurements of the attractive force between freshly cleaved mica sheets. If sheets are either partly cleaved or cleaved and held together at one end and separated at the other, the shape of the sheets should be given by cantilever beam theory but deviations from it, which are deduced from interferometric measurements, can be used to determine the nature of the attraction law operating near to the closed end. If sheets are cleaved beneath the surface or recombined after coating with a monolayer of, for example, a fatty acid by the Langmuir–Blodgett technique, the total work done in moving from one equilibrium position to another can be obtained. This is equivalent to the strain energy of the sheets, easily obtained from beam theory, plus the energy to generate the new surface. The contact angle of the liquid (or fatty acid) against mica can be measured in a separate experiment and hence the situation if equation (2) is rewritten (equation 4):

$$\gamma_{sl} = \gamma_{sv} - \gamma_{lv} \cos\theta \tag{4}$$

where γ_{sl} is measured by cleaving mica under liquid or with monolayer; γ_{sv} is measured from mica freshly cleaved in dry air, and γ_{lv} and $\cos\theta$ are both known by direct measurement.

It has been assumed that for solids of low surface free energy such as the polyolefins and fluorinated polymers, the spreading pressure π is negligible. Good[11] has now established this reasonably firmly with both theoretical and experimental demonstration.

On surfaces of high surface free energy most liquids will spread spontaneously and hence $\cos\theta = 1$ and equation (3) becomes equation (5):

$$W_A = 2\gamma_{lv} + \pi \tag{5}$$

This expression has been used to justify the usual situation in an adhesive joint in which failure is cohesive either in adhesive or adherend and that truly adhesive failure at the interface is rare in a properly made joint since $W_A = W_C + \pi$ and π is invariably large when spreading is spontaneous.

The use of the Young–Dupré equation is really limited to systems where the contact angle is finite and the spreading pressure negligible and such systems are those in which normal adhesives are ineffective. For example, it is possible to calculate W_A for an epoxy resin applied as a liquid to a polyolefin, subject to the fairly reasonable assumption that the surface energy of the epoxy does not change on

Table 1 Dispersion component of surface energy of SBR rubber

Liquid	γ_l (mN/m)	γ_l^d	Contact angle, θ	$\gamma_s{}^d$ (mJ/m^2)
Tricresyl phosphate	40.9	39.2	34°	34
Glycerol	63.2	37.0	84°	35
Formamide	58.2	39.1	75°	34

hardening. The result is not useful because the adhesion is too small to support the shrinkage stresses which occur during the hardening process. Attempts have therefore been made to estimate the interfacial free energy which must, of course, be related to the energies of two separated surfaces. The earliest of these, the Antonov equation, $\gamma_{12} = \gamma_1 - \gamma_2$ has long since been superseded by expressions which derive from the concept of energy additivity of components of the surface energy derived from a separate consideration of non-polar forces arising from the London dispersion and polar forces, including hydrogen bonding. Girifalco and Good[12] proposed a geometric mean term to allow for the interaction at the interface of dissimilar liquids such as mercury and hydrocarbons where interaction could depend only on the London dispersion forces:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d\gamma_2^d)^{1/2} \tag{6}$$

The superscripts in equation (6) show that only that part of the surface energy due to dispersion forces is involved in the geometric mean interaction term because there can be no interaction between mercury and hydrocarbon due to the behaviour of electrons specific to intermetallic bonds. Similarly, a liquid such as water which can form internally and externally directed hydrogen bonds cannot do so with aliphatic hydrocarbons. Hence, although hydrogen bonding plays a major role in determining its own surface energy, the interaction at an interface with hydrocarbon can only occur through a field to which both components of the system can respond, namely, the London dispersion field. However, interaction between pairs of molecules are often quite specific and cannot necessarily be computed from knowledge of the contribution made by given components of the surface energies of the substances in question. Fowkes[13] points out that chloroform is acidic with respect to polycarbonate and that the interaction between these two is enhanced by the formation of an acid–base complex but this cannot be inferred from the individual surface energies since no acid–base component exists for either chloroform or polycarbonate considered separately. The work of adhesion of a polar/non-polar liquid–surface combination can be obtained by combining equations (1) and (6):

$$\begin{aligned} W_A &= \gamma_1 + \gamma_2 - \{\gamma_1 + \gamma_2 - 2(\gamma_1^d\gamma_2^d)^{1/2}\} \\ &= 2(\gamma_1^d\gamma_2^d)^{1/2} \end{aligned} \tag{7}$$

but it is not correct when both components are polar to write:

$$W_A = 2(\gamma_1^d\gamma_2^d)^{1/2} + 2(\gamma_1^P\gamma_2^P)^{1/2} \tag{8}$$

even if their individual energies may be represented by $\gamma_i = \gamma_i^d + \gamma_i^P$. This is not to say that use cannot be made of the many measurements of contact angles and surface tensions in practical adhesion studies nor that the difference $(W_A - W_A{}^d)$ cannot be used to assess the contribution made by polar interactions to the work of adhesion. Fowkes[14] has provided data on the dispersion components of the surface energy of a number of liquids and *Table 1* shows how three very different liquids can be used to estimate the component of the surface of a vulcanized styrene–butadiene rubber. If γ_{sl} is eliminated by taking equations (2) and (6), equation (9) is obtained and it is this that has been used to calculate the last column of *Table 1*[15].

$$\gamma_s^d = \left\{\frac{\gamma_l(\cos\theta + 1)}{2(\gamma_l^d)^{1/2}}\right\}^2 \tag{9}$$

Such a surface is difficult to stick with a polyurethane, a desirable adhesive for plasticized poly(vinyl chloride). If the rubber surface is chlorinated then the force needed to separate two 25 mm strips of the rubber joined by a polyurethane adhesive increases from 4.5 to 13 kgf. The contact angle of tricresyl phosphate is but slightly affected whereas those for glycerol and formamide are drastically reduced to 61° and 42°, respectively. The difference can be expressed as the increase in the work of adhesion W_A or, using equation (3), as the spreading pressure. This is negligible for tricresyl phosphate but amounts to 21.8 and 28.4 mJ/m^2 for glycerol and formamide both of which are capable of participation in hydrogen bond formation and the latter a not unreasonable model for the urethane grouping of the adhesive. Hence the conclusion that polyurethane adhesives operate by forming hydrogen–halogen bonds on these surfaces. If, erroneously, an attempt is made to calculate a polar or hydrogen bonding term for the surface, $\gamma_s = \gamma_s^d + (\gamma_s^P + \gamma_s^H)$ from the contact angles found, a different figure is obtained for each liquid (actually 18.1 and 42.2) when, clearly, the surface has only one surface free energy.

Another most useful equilibrium-based concept in connection with surface energies is that advanced by Zisman and his colleagues[16]. The surface energy of solids being in general inaccessible to experiment, Zisman defined γ_c, the critical surface tension of the surface. This he carefully distinguished from the true surface energy of the surface but it is clearly closely associated with it and is easily determined. It is the surface tension of the liquid which will just, and only just, wet the surface of the solid and is obtained as an extrapolated value of a series of contact angle experiments with a range of liquids of differing surface tension. This concept is most useful for characterizing surfaces of moderate or low surface energy; in particular it is extensively used for characterizing polymers both highly polar and those of very low surface energy. A surface treatment of a polymer which did not appreciably change the value of γ_c of that polymer, is unlikely to have much influence on bond strengths obtained with adhesives. The well-known corona discharge treatment of polyethylene raises the critical surface tension of polyethylene[17] from 31 to about 40 mN/m.

The most recently published list of values is that of Shafrin[18] covering some 150 natural and synthetic polymers. The same volume contains an article by Zisman[19] himself in which, *inter alia* the more refined use of the critical surface tension to explore the nature of polymer surfaces are reviewed.

The relation between γ_c and the surface energy of the

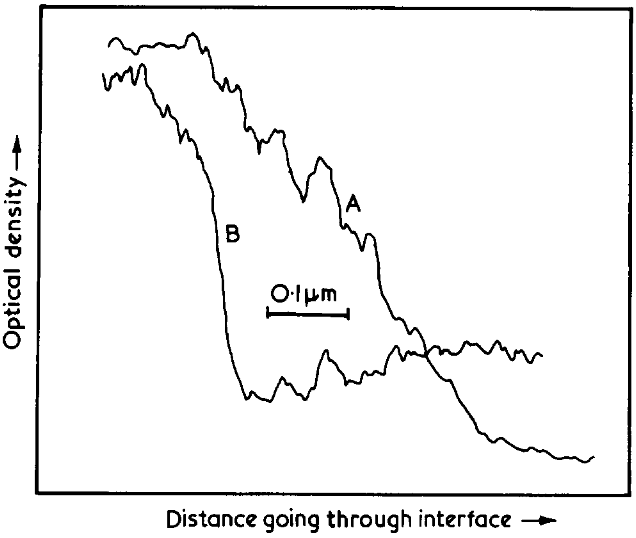


Figure 2 Photometry traces of electron photomicrographs of interface between poly(vinyl chloride) and A, poly(methyl methacrylate) and B, poly(butyl methacrylate). [Reproduced from Voyutskii, S. S. *J. Adhes.* 1971, **3**, 74 by permission of Gordon and Breach Publishers Ltd, London ©]

solid has been explored by Good[20] in the course of work with others on calculation of the interfacial free energy from the free energies of the air surfaces of two components. He arrived at an expression:

$$\gamma_c = \Phi^2 \gamma_s \tag{10}$$

where:

$$\Phi = \frac{4(V_1 V_2)^{1/3}}{(V_1^{1/3} + V_2^{1/3})} \times \frac{2(I_1 I_2)^{1/2}}{I_1 + I_2}$$

in which the subscripts refer to the wetting liquid and the solid surface, V is the molar volume and I the ionization potential of the molecule. Lee[21] has shown that γ_c can be calculated from either the parachor, the solubility parameter or the glass transition temperature.

The importance of the adsorption theory of adhesion is that it describes the essential process of wetting the adherend by the adhesive and shows that this does have a very definite correlation with the possibility of making a good joint, though not with the load required to break a strong joint between rigid adherends.

Diffusion theories

The interdiffusion of high polymers across an interface is possible when the polymers are at temperatures above, preferably greatly above, their glass transition temperatures. It is an important adhesive process being the basis of the self-tack of rubbers for which the term *autohesion* was coined by the Russians[22] many years ago and they have been largely responsible for the development of the theory. It is important also because in many applications of solvent or aqueous adhesives, two adherends are separately coated and, on removal or substantial removal of the vehicle, the dried polymers are combined. Failure along the plane of combination is not normally expected because diffusion across it should make the two layers one without the possibility of regenerating the interface. The proponent of the theory was Voyutskii[23] who pointed out its extensive applications in the heat sealing of plastics and the gaining of coherence of emulsions of film-forming polymers on drying out. Its mathematical formulation by Vasenin has been more accessibly outlined (to Western readers) by the present writer[24] and stands as the sole example of where completely fundamental principles and figures have been used to explain actual bond strengths though of flexible rubbery systems. Adsorption theory cannot be said to have had the same success in explaining the strengths of rigid joints with structural adhesives.

A fundamental feature of the theoretical treatment of diffusion is that thermodynamic compatibility must exist between the materials. With autohesion there is no problem but the theory could not automatically be applied to the adhesion of, for example, poly(methyl methacrylate) and poly(vinyl chloride) (unplasticized) for which solubility parameters are 18.6 and 19.4 $\mathrm{MJ^{1/2}/m^{3/2}}$, respectively. However, adsorption of one polymer on the other, with perhaps some adlineation of dipoles might be thought a more probable explanation for their adherence. Voyutskii[25] has published the results of studies based on luminescence analysis in u.v. light showing that an interfacial zone exists between these two polymers, about 0.4 μm wide in which interdiffusion has occurred, whereas poly(butyl methacrylate) shows, as can be seen in *Figure 2* a far sharper boundary with a suggestion of some diffusion of poly (vinyl chloride) into the poly(n-butyl methacrylate) but none of poly(butyl methacrylate) into PVC. The solubility parameter of poly(n-butyl methacrylate) is about 16.6 $\mathrm{MJ^{1/2}/m^{3/2}}$. The question of when sufficient compatibility exists for diffusion to be an important contribution to adhesion is therefore open to argument, though data exist relating peel strength with thermodynamic compatibility. At the time when Voyutskii's ideas first made an impact attempts were made actually to measure diffusion rates. As far as self-diffusion is concerned, Skewis[26] showed that figures of the right order of magnitude could be obtained with tritium-labelled hydrocarbon polymers and that, using styrene–butadiene rubber variation with molecular weight was obtained. However, SBR, butyl, ethylene–propylene and natural rubbers gave diffusion coefficients lying on the same straight line when log (diffusion coefficient) was plotted against log (molecular weight) implying the same diffusion rate for all the rubbers. This is not in accord with Vasenin's treatment nor yet with the autohesive behaviour of these rubbers. No inter-diffusion of butyl and SBR could be found, but, as the author notes, this did not in his experiments preclude limited diffusion over a short range such as is evident in *Figure 2.* Such limited diffusion is all that is needed to bring about adequate adhesion. Skewis attempted to relate his diffusion measurements to the observed 'tackiness' of the rubber as measured in a tackmeter but more recent work (*vide infra*), using the Williams–Landel–Ferry transform, indicates that tack is a complex property involving bulk as well as surface properties although diffusion must be the main determining feature of self-tack. Less fundamental in the physicist's sense but definitely relating autohesion to diffusion is Campion's[27] semi-empirical use of the Kauzmann–Eyring theory of diffusion in liquids. This is a kinetic theory in which segments of the polymer move into spaces or 'holes' when random fluctuations allow holes of requisite size to form at or diffuse to sites contiguous to the segment. The hole, formed by thermal fluctuation of the surrounding

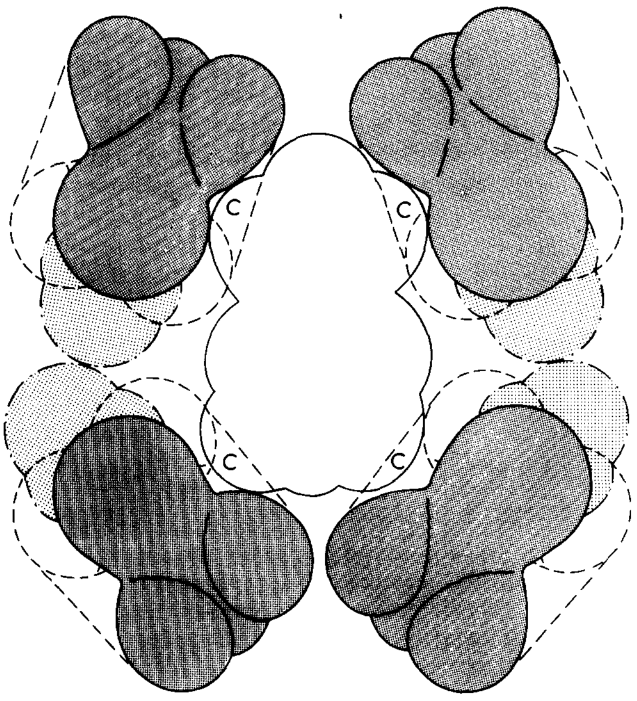


Figure 3 Hole formation involving the participation of large accessible cavities; natural rubber type. Measurements indicated that the r.m.s. distance between chains has increased by only about 15 per cent from the close-packed situation compared with an increase of 27 per cent required for ethylene–propylene rubber. [Reproduced from Wake, W. C. 'Adhesion and the formulation of adhesives', Applied Science, 1976, p 82 (after R. P. Campion) by permission of Applied Science Publishers Ltd, Barking ©]

polymer molecules, precedes a jump by the segment and the sum of the process over many molecules constitutes the diffusion process. Vasenin, in his development of the process, used the cross-section of the polymer repeat unit at its bulkiest point to quantify the space necessary for its movement. Campion considers the existing free volume in the bulk polymer and the way part of this is associated with the shape of the repeating unit and its packing behaviour with its fellows. *Figure 3*, from Campion's paper, shows how hole formation to allow the acceptance of a segment of natural rubber is cooperatively easier because of its particular shape. Calculations based on the interchain free volume, packing numbers and hence of cross-sectional areas available for diffusion enabled Campion to produce figures which, for the first time, rated all known hydrocarbon rubbers in order of their known autohesive behaviour.

The above remarks treat the union of two polymeric surfaces both above their glass transition temperatures as if a single process only were involved. Vasenin's treatment specifically refers to the processes which occur after true molecular contact has been established and, if interpreted rigorously, can refer to only a short period of time after contact has been established. Anand[28] and others have concluded that the kinetics of bond strength are adequately accounted for by rheological processes involved in making intimate contact without diffusion being involved whilst Bister, Borchard and Rehage[29] have detected stages in the autohesive (i.e. diffusive) combination of rubbers during which different rate processes apply. Vasenin's expression gives adhesive strength as proportional to $(\text{time})^{1/4}$ which certainly gives a good fit to data but root functions are insufficiently sensitive over the required range easily to distinguish and Rehage and his colleagues fit square root functions to each of the stages they claim for the process. Certainly they are correct in drawing attention to a change in failure pattern which occurs as the time allowed before separation is attempted increases.

Electrostatic theories

When originally proposed by Russian scientists led by Deryaguin[30], the electrostatic theory of adhesion postulated that all adhesion phenomena could be largely explained in terms of charge transfer across the interface giving rise to electrical double layers. This universal explanation was hotly contested by Voyutskii[23] with respect to the adhesion of rubbery polymers to one another. If contact potentials gave rise to double layers of the strengths required to explain adhesion why, he asked, were dissimilar polymers less adherend than similar polymers? Potential voltage differences would be greater between dissimilar polymers and zero when autohesion was involved. This type of argument together with the difficulties of experimentation led to the neglect of explanation based on charge transfer except in specific areas detailed below. The evidence originally presented depended on the rapid peeling of flexible polymers from rigid substrates. It is a well-known dark room demonstration that electrical discharges are present when adhesive tapes are stripped very quickly from glass. The original experiments involved measurement of discharge voltage and distance as a function of gas pressure. The key factor in this experiment was the calculation of the condenser discharge energy and its correlation with the measured work of adhesion[31]. Unfortunately, no one else has attempted to confirm the change in peel strength with gas pressure and the rather unsatisfactory situation remains that the results then reported could equally well have occurred if electrical phenomena accounted for *x*% of the observed work of peeling. Since a large part of the work of peeling involves dissipative processes in the peeled member *x* must be small and it need be only a proportion of the non-dissipative part of the process. This is indeed likely for the adhesion of fine particles to surfaces has been shown to be due to a combination of dispersion and electrostatic forces and the ubiquitous xerography is a constant reminder of this fact[32–34].

Electrostatic adhesion, described in terms of the DVLO* theory may also be regarded as an accepted theory for cell adhesion.

Adhesion in a simple form arising from direct contact electrification has been demonstrated for thin films of metal sputtered on to pleastic plastics surfaces[35,36]. Before discussing this case it is necessary clearly to distinguish it from the so-called electroless processes for coating plastics with metals (*vide infra*). The latter involve several types of adhesive mechanism arising from the chemical etching which precedes a complex deposition process. To validate his observations, Weaver[35] showed that adhesion could be measured by a fine chrome–steel point drawn across the coated surface, the normal load applied being related to the shear strength of the adhesive bond. Applied to a range of metals on to cleaved halide surfaces, the shear strength was completely accounted for by van der Waals's forces and was not changed by the application of a glow discharge. Applied to plastics surfaces, adhesion was greater

---

* The current theory of colloid stability based on the existence of an electrical double-layer is referred to by the initials of those associated with its development, viz Deryaguin, Vervey, Landau and Overbeek.

than could be attributed to dispersion forces, increased with time and was instantaneously reduced to a very low value by the application of a glow discharge after which it gradually climbed with time as before. The adhesion obtained with any given metal varied with the substrate being lowest with polytetrafluoroethylene and, of the materials he tried, highest with poly(methyl methacrylate). The original Russian theories would have explained these results by transfer of electrons to the plastics materials from the metals. Weaver[36] does not accept this explanation. To achieve such transfer the metal electron would need about 3 eV of excess energy to overcome the potential energy barrier at the interface and as metals have work functions of 4–5 eV, this excess is unlikely. Weaver postulates positive hole injection with the electron moving from polymer to metal. i.e. the Fermi level of the polymer before contact lies above that of the metal. The nature of the charge-carrying bodies in polymers is obscure but all polymers carry a wide range of additives arising from the polymerization process if not from the later stages of preparation. It would be interesting to have data on radiation polymerized material made from highly purified monomer. A slightly different approach to electrostatic adhesion has been realized by Fowkes[13] in the form of donor→acceptor relationships existing at interfaces but not within the bulk of either phase separately. Acrylic copolymers containing maleic acid or acrylic acid have greatly enhanced adhesion to metal (oxide or hydroxide) surfaces. The polymer interfacial surface can be regarded as having an array of negative charges and the metal as positively charged. More generally, oxygen atoms, amides, double bonds, etc., can be regarded as donors and chlorine, acidic chlorinated polymers such as poly(vinyl chloride) or fluorinated bodies can be regarded as acceptors. Acid–base interactions are not the sole ones which can occur at an interface and add substantially to the van der Waals's dispersion forces which must, of course, always be present. Examples where ionic bonds have been postulated as acting across an interface are, of course, in reality examples of electrostatic adhesion and it is to be presumed that the adhesion of, for example, aluminium oxide for its substrate metal is essentially electrostatic in origin. Cases where oxide to metal failure have occurred with the oxide parting with the adhesive are known, though not with aluminium. They are, however, usually ascribed to cohesive failure within the oxide film. Fowkes[37] takes at their face value Russian experiments with the stripping of pressure-sensitive tapes and ascribes most of adhesive force to an electrostatic component but, as remarked previously, the adhesive component of the stripping force is but a small one and Gent and Schultz[38] believe that they had isolated it in some of their experiments and that its magnitude is only that of the dispersion forces.

Chemical bonds across the interface

In a crude descriptive form the presence of chemical reactions across interfaces has been invoked in specific cases for a great many years. Buchan and Rae[39] were able to explain a number of phenomena connected with the adhesion of rubber to metal by the brass plating process whereby a mixed organo–cupric sulphide linkage was postulated. A more refined modern analysis might find a layer of cupric sulphide[40] of a few micron electrostatically adherent to the brass surface and adsorbed to this layer some evidence for some form of mixed compound possibly involving sulphur donation. Other reactions postulated to occur across interfaces are those of isocyanates with adventitiously introduced hydroxyl groups on rubbers and poly(vinyl chloride) and those involved when siloxane coupling agents are used on glass or metal surfaces (presumably hydrated oxides) and provided with appropriately reactive groups terminal to one of the attachments to the silicon atom. These comprise primary amines for reaction with epoxy resins, mercaptans for sulphur-vulcanizing rubbers and ethylenic unsaturation for unsaturated polyester resins dissolved in styrene. A more general approach has however been advanced whereby the nature of the attachment process is unspecified, indeed it could involve only secondary valencies except that instead of a field force it is necessary to consider attachment at localized sties. Electrostatic forces could equally well be regarded as localized with unspecified charge carriers or donor–acceptor groups at the interface. All that is needed for the development of the theory is specification of the number of bonds and their strength. The failure process is then considered as one direction of an activated kinetic balanced reaction of bond formation and breaking which is biased in the latter direction by the application of stress. The kinetic equations developed involve an energy of activation which can be determined, in principle at least, by a reciprocal temperature plot if the process has been studied over a range of temperatures. Some validation of the theory has been supplied by Lewis and Forrestal[41] who used radiation grafting to establish a known surface concentration of bis(2-chloroethyl) vinyl phosphonate onto polypropylene powder which was used as a hot melt adhesive for a metal sandwich. The mode of bond formation–bond breakage originated with Zhurkov[42] and has been used by a number of authors including Lewis and Saxon[43] and with Forrestal[44] for whom it is a preferred explanation for joint strength and Allen and Shanahan[45] to explain the creep phenonema associated with adhesive joints under continuous load. It is claimed that most adhesive data, if properly presented, can be cast into a form appropriate to a bond attachment theory and it is reasonable that adsorption and donor–acceptor reactions at interfaces should be so cast, but a theory which can cover all the phenomena is automatically suspect, the generalities hiding real differences in mechanisms. And if it can be shown to be successful for structural adhesives it may be doing little more than rewriting the adsorption theory, which fundamentally must refer to equilibrium conditions in a form appropriate to kinetic processes of joint failure. The energies of activation which have been deduced are extraordinarily high and seem to refer to activation volumes which are not understood in terms of the physical volume of flow-units or polymer segments. There are advantages in this type of explanation when dealing with joint properties because failure is more often cohesive than adhesive and bond breaking can occur within the bulk of the adhesive as well as at the interface although different bond energies would be involved. The conceptual disadvantage then focuses on the known dissipative processes than precede fracture, namely the plastic deformation around the tip of the growing crack, and ignorance of whether this is the primary volume in which bond breaking occurs.

Less general matters deal with specific cases in which the strong probability or certainty of chemical reaction occurring across the interface have led to the formation of stronger joints. In the case already cited[41] the strong probability exists because one side, at least, of the interface was known to be chemically coupled.

Acting on the assumption that chemisorption may be important in the establishment of a high degree of interaction between substrate and adhesive, Brenman and Lerchenthal[46] have sought to provide this by generating free radicals by mechanochemical means at the interface. The mechanochemistry of polymers although perhaps originating with Staudinger was explored by Watson and his colleagues[47] from 1952 onwards. Shortly afterwards Russian workers[48] coined the name 'mechanochemistry' and showed that minerals fractured under the surface of liquids or polymers possessed surfaces of enhanced adsorptive activity. Brenman and Lerchenthal proposed combining these factors to increase adhesive interaction with the substrate by abrading the substrate whilst it is covered with liquid adhesive†. The technique is not new as DeLollis[49] mentioned the mechanics of the process, ascribing the improvement in bond strength to the removal of contaminant material under conditions where the adhesive would replace the contaminant. The results quoted by the authors show that abrasion in the presence of adhesive or priming material (e.g. the polyamide crosslinking reagent for an epoxide adhesive) gives superior bond strength to mere abrasion in air before application of the adhesive.

Mechanical adhesion

The earliest instinctive ideas of joint strength pictures the adhesive flowing into interstices of the surface, solidifying there and being inextractible as the result of re-entrant angles and tortuous flow passages. In failing, these extensions of the adhesive mass were broken off from the main mass and it was the work involved in doing this that gave rise to joint strength. This picture assumed the joint to be easily formed with materials for which true wetting, as shown by zero contact angle, was always achieved. It was the realization that in making the joint surface irregularity could only serve as an adverse influence that turned attention to specific adhesion ideally characterized and measured by using smooth surfaces. Specific *versus* mechanical adhesion was a conceptual battleground appropriate to the 1940's and opinion alerted by de Bruyne to the use of synthetic adhesives and the importance of the non-polar/polar dichotomy of adhesives and adherends, veered towards a belief that specific adhesion, adsorption in fact, was the important factor and that mechanical factors were of no importance. Salomon referred in 1965 to the present writer's own work on textiles, to that of Bikerman on gluing paper and cardboard, and to some work of Marian on wood, as showing that interlocking on a microscopic scale is an essential factor but goes on to state[50] 'but except for such specific cases the interlocking hypothesis has been abandoned'. Opinion has since changed and a more balanced view of present opinion requires mechanical factors to be considered. There are cases in which, although specific adhesion due to the London dispersion forces must always exist, it is fair to ascribe the bond strength to mechanical keying. The present writer does not agree however with the many plastics technologists who regard electroless plating of plastics as a simple interlocking process; this too is an oversimplification based on a lack of background knowledge.

As early as 1949 the important mechanical feature of the adhesion between rubber and spun-fibre textiles was seen to be the embedding of fibre ends in the rubber[51]. If these were sufficiently long, the specific adhesion, even if quite small but acting over the area of the fibre, could in shear exceed the tensile strength of the fibre. In this way the bond strength became a function of the number of fibre ends projecting from the textile surface and of their mechanical strength. Variations in specific adhesion, such as providing the normally polar fibre with a chemically reacted waxy coating, made only a minor difference. A series of papers elaborated this. Where strong adhesives are used as for tyre-cords or in Vee belts there is good evidence that chemical bonding exists between adhesive and rubber on the one side and adhesive and textile on the other and although ultimate failure is a mechanical failure of the filaments of the cord, it is no longer reasonable to regard the bond as mechanical; it is a specific adhesion dependent on a chemical bond.

The adhesion of polyethylene to metals is a subject of considerable importance for the packaging and electronic industries and has been studied in detail by a number of people. Initially, poor adhesion was identified with a weak boundary layer (*WBL*) caused by the presence of degraded material of low molecular weight[52]. Support for this view was provided when Schonhorn[53,54] showed that by crosslinking the surface of the polymer in a glow discharge atmosphere stronger bonds could indeed be formed. This work drew attention to *WBL* as a frequent cause of failure of joints in service. Later work[55] showed that instead of purifying polyethylene from components of low molecular weight or crosslinking it, perfectly satisfactory bonds could be formed either by deliberately oxidizing the polyethylene or applying it to the metal in an oxidizing atmosphere. If the metal is copper, the polyethylene must be oxidized before application because during application the presence of copper seems to inhibit oxidation of the polymer[55] whereas the adhesion obtained by sintering powdered polyethylene to steel is good because iron catalyses oxidation[56]. To further the understanding of these phenomena, instead of using an aluminium surface prepared by the standard acid–dichromate treatment, Packham, Bright and Malpass[57] examined adhesion to aluminium anodized in a pore-producing electrolyte and said[58] to give a surface oxide structure similar to that given by acid–dichromate. The idea was to use a similar surface but to eliminate possible oxidation catalysis by chromium. As a further point, adhesion tests were made with the anodized aluminium in both porous and sealed conditions. They found that oxidation of the polymer is necessary to obtain good adhesion to a surface with sealed pores but not for adhesion to a porous surface. In fact, the best recorded peel adhesion was with polymer containing 0.5% antioxidant on an unsealed porous surface. *Figure 4*, taken from a second paper by the same authors[59], shows the effect of the porosity on the configuration of the interface by showing the polyethylene after the adherend has been chemically removed. The high adhesion figure clearly depends on the penetration of the polymer into the pores and this alters the stress distribution at a micro-level. It is therefore a mechanical factor although retention of the polymer within the pores must be associated with specific adhesion between polymer and wall, in this case due to the London dispersion forces. It is exactly analogous to the penetration of the fibre ends of staple yarn into the rubber or poly(vinyl chloride) of a polymeric coating on to cotton.

The electroless plating of plastics provides an example of a situation complementary to that described above with the metal penetrating into the polymeric material instead of the polymer entering pores in the oxide. The procedure

---

† Brenman and Lerchenthal of the Technion Institute, Israel, have coined the acronym SABRA from Surface Activation Beneath Reactive Adhesives, the word having another connotation in an Israeli context.

Figure 4 Polyethylene from aluminium anodized in 4% phosphoric acid at 20 V for 60 min at 24°C. [Reproduced from Wake, W. C. 'Adhesion and the formulation of adhesives', Applied Science, 1976, p 70 by permission of Applied Science Publishers Ltd, Barking ©]

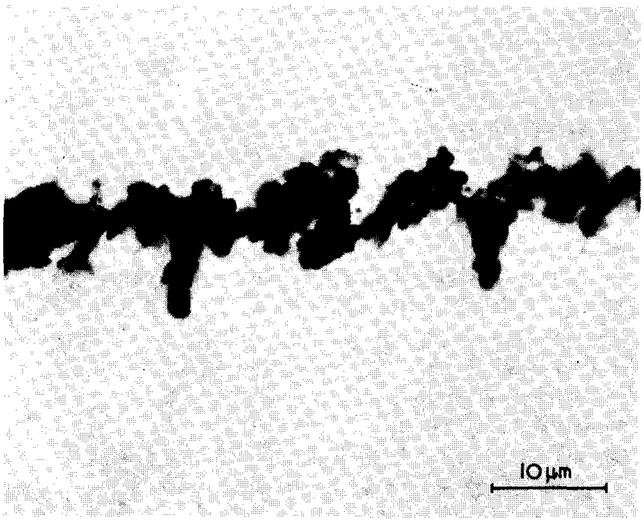


Figure 5 Section showing electroless nickel plated on polypropylene. [Reproduced from Wake, W. C. 'Adhesion and the formulation of adhesives', Applied Science, 1976, p 67 by permission of Applied Science Publishers Ltd, Barking ©]

adopted is complicated. In the case of high-impact polystyrene or ABS plastics, the plastics surface is etched with an oxidizing acid which preferentially attacks the unsaturated butadiene–styrene copolymer. The etched surface is then sensitized with stannous chloride solution followed by a silver or palladium salt and then a copper or nickel salt is reduced and produces a conductive surface which is electroplated. The nature of the highly reticulated surface produced by etching can be gauged from *Figure 5*. There has been much discussion about the nature of the bond but Perrins and Pettett[60] produced, in the course of a very thorough study, the figures from which *Table 2* is derived.

Table 2 shows that an interaction is involved between mechanical effects and surface activity. In fact, the results can be represented by the expression Peel force = Kbc, where b represents the contribution of a mechanical component and c, that of a surface component. The contribution of the latter is twice that of the former. In this case the specific surface component is most probably an acid–base, donor–acceptor bond.

Lastly, in examining a wide range of surface treatments for the structural adhesive bonding of titanium alloys, the writer and his colleagues[61] found highest bond strengths to be given when the β-phase of the alloy is attacked with removal and some undercutting of the α-phase. This leaves a very rough surface which is further roughened by the redeposition of needle crystals of rutile vertically adherent to the etched floor of the β-phase.

It is evident that the banishment of a mechanical factor from the scientific description of adhesion was premature; it must take its place, albeit a secondary one, with adsorptive, diffusional and other theories each of which are to be accepted as operative in certain systems.

JOINT STRENGTH

The use of adhesives is to make joints. Their diversity arises from the varied nature of the materials to be joined; the nature and magnitude of the stress they are designed to withstand. Given correct preparation of the surfaces to be joined and suitable choice of adhesive, the force required to separate the joint components will be that necessary to break them. Only in exceptional circumstances will failure occur at the interfaces between the components when newly made joints are stressed. Two types of joint, illustrated in *Figure 6*, have attracted most theoretical study; the lap-shear joint used for testing structural adhesives for wood and metal and the peel-type joint for testing both flexible and structural adhesives. The aim of these studies is to predict the strength or other properties of the joint from the properties of the bulk adhesive. This very formulation of the aim is indicative of the fact that for properly designed joints failure is cohesive within the adhesive.

Table 2 Partial separation of mechanical and specific effects in electroless adhesion

	Mechanical component	
Surface chemistry	Well etched with good acid	Poorly etched with bad acid
Surface activity removed by HCl	0.66	0.17
Reactive etch applied after removal of surface activity	3.94	1.37

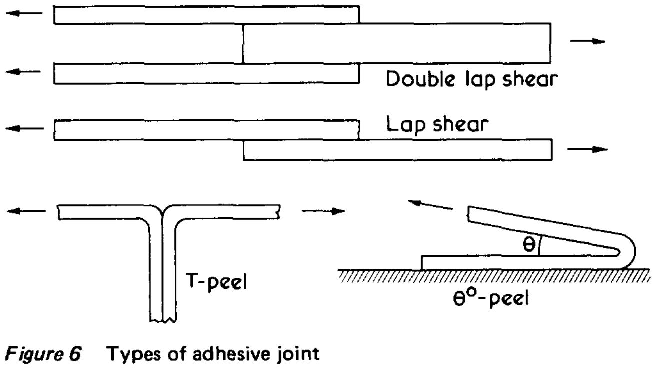


Figure 6 Types of adhesive joint

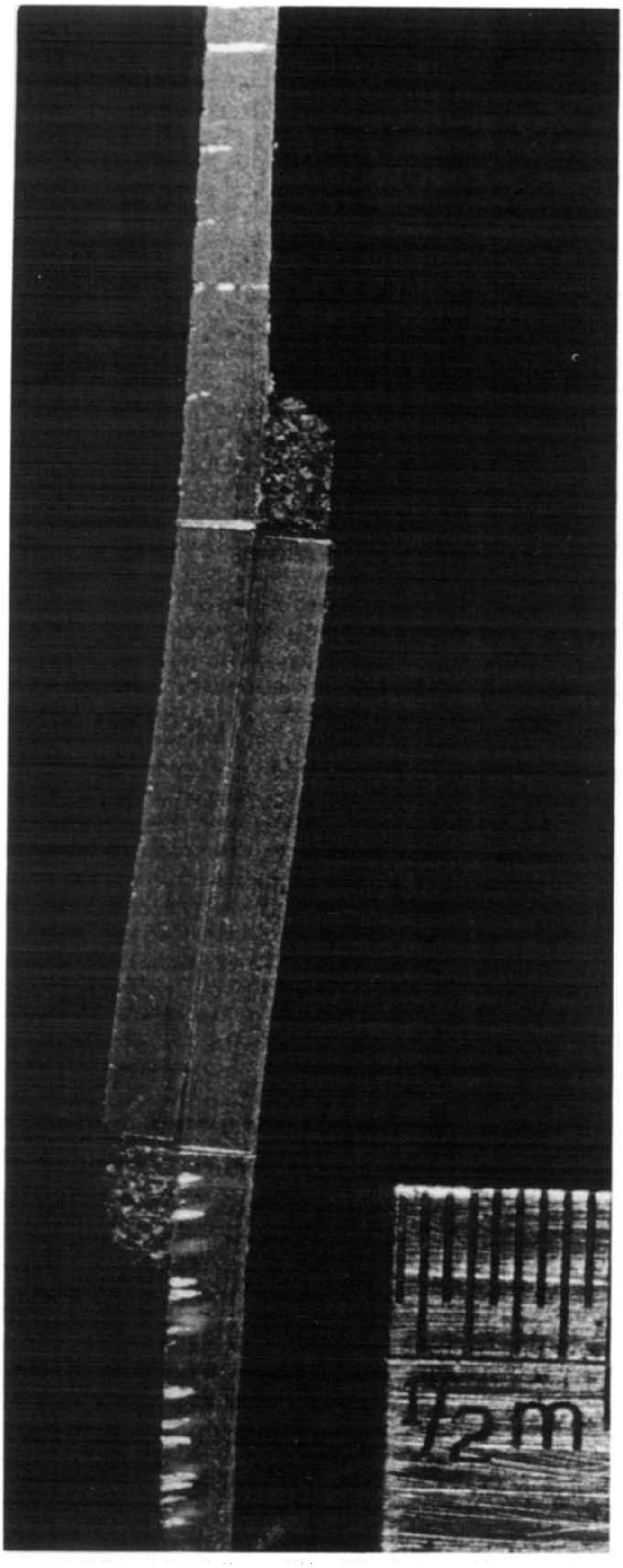


Figure 7 Lap shear joint at moment preceding failure. [© Crown copyright reserved]

The description, lap-shear joint, correctly describes the intention to apply a shearing stress to a joint but, in fact, the highest stress acting when shear is applied to the joint shown in *Figure 7* is a cleavage or opening-mode stress at the ends of the overlap. Perhaps an instructive way of examining the complexity of the stress distribution in the lap-shear joint is to consider the stages in the development of analytical expressions for it. Analysis started with Volkersen^{62} in 1938 who identified the major cause of the non-uniformity of shear along the joint as due to extension of the adherends linearly changing from its maximum value to zero at the end of the overlap as the stress is transferred to the other side of the joint. His original approximation showed an infinity at the extreme end when, of course, the free boundary must be free from shear and this was corrected in a much later paper. The original expression is, however, a very good approximation to what is now considered as the actual distribution. The second major analytical approach was that of Goland and Reissner^{63} and a convenient and mathematically simplified summary of the state of the art at this stage has been given by Sneddon^{64}. Goland and Reissner allowed for the bending moment introduced by angular offsetting of the load from the joint axes which gives rise to the bending of the adherents so clear in *Figure 7* and the resultant cleavage stress. The most recent analytical work on the lap-shear joint has been done by the group at Bristol University$^{65-67}$ led by R. D. Adams. Previous discussion of the lap-joint has referred to stresses in the centre-line of the joint but contraction in the width of the joint when stress is applied to the length is also important and has been studied at Bristol (*Figure 8*). This gives rise to transverse stresses which have their maximum at the corners of the joint.

At one time it was thought that a good case had been made for^{68} the failure of a lap-shear joint under stress to be initiated from a shear failure in a plane of maximum shear stress lying within the joint. The evidence for this might now be regarded as circumstantial rather than compelling. It used the Goland and Reissner analysis to calculate a plane of maximum shear and showed how this varied with changes in the configuration of the joint made by bending the extended pieces of the adherend thus altering the relative positions of the axis of the load and the centre line of the joint as in *Figure 9*. The maximum shear stresses calculated from the load at failure were approximately equal to the shear strength of the adhesive. However, the latest work of the Bristol school^{69} identified the initiating point of failure either at the end of the joint if the adhesive has been squared off to give a boundary exactly in line with the end of the adherend or in the fillet formed as is usual in manu-

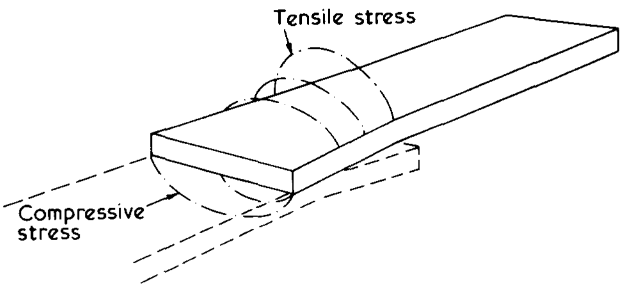


Figure 8 Transverse stress in a loaded lap-shear joint. [Reproduced from Wake, W. C. 'Adhesion and the formulation of adhesives', Applied Science, 1976, p 113 by permission of Applied Science Publishers Ltd, Barking ©]

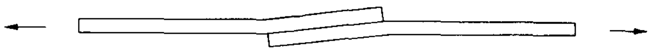


Figure 9 Distortion of lap–shear joint produced by non-congruence of centre line of joint and axis of loading

facture by excess adhesive exuding from the end of the joint. Moreover, failure is here truly a cleavage failure, the adhesive being under high tensile stress. These results were obtained with double lap-shear joints (sometimes referred to as a tuning-fork configuration) but are believed to be valid for the single lap-shear joint. They were obtained with finite element analysis, a powerful tool increasingly used in stress analysis studies involving adhesive joints.

Of very great interest in this connection is the recent demonstration of the relation between the method of analysis used to obtain a prediction for the breaking strength of a lap-shear joint from the properties of the adhesive. Using maximum tensile stress as the criterion for failure, linear (elastic) analysis correctly predicted the breaking loads for a brittle epoxy adhesive[69]. A plasticized epoxy adhesive, however, required non-linear analysis and failure depends on maximum strain. Of the two adhesives studied by Adams and Copplestone, the more brittle adhesive was almost twice as strong as the plasticized, ductile adhesive in pure shear whilst this order of merit was almost exactly reversed in a double lap-shear joint, hence contradicting the earlier criterion of maximum shear strength of the resin being the operative property. In fact, for a ductile adhesive non-linear analysis has demonstrated that a high tensile *strain* to failure can be more important in a structural adhesive than a high tensile or shear *strength*. This conclusion reinforces the attitude of technologists dealing with structural adhesives who have always demanded high metal-to-metal peel strength, measured with thin gauge sheet metal in either T-peel or climbing-drum tests, as well as high figures from a lap-shear test.

Separation by peeling

What may be called the 'statics' of peeling were established about 20 years ago by Kaelble[70] and by Inoue and Kobatake[71]. The simplest case to consider is the flexible adherend being peeled from adhesive on a rigid adherend. The peeled length of the flexible material is then regarded as a lever arm with a fulcrum lying back either within itself or within the adhesive so that, immedately behind the fulcrum there exists a compressive force on the adhesive which moves down the sandwich as the line of peel moves. The cleavage stress is thus represented as a damped oscillatory wave moving backwards into the adhesive from the line of peel. If the angle of peel is shallow there is a substantially shearing force also present and if the cleavage stress within the bond is given by σ and the shear stress by τ with the subscripted zeros representing the stresses at the line of separation, the ratio σ_0/τ_0 is a function of peel angle which rises to a maximum as the angle approaches 90°. Unlike the butt or lap-shear joint, the work of peeling is easily measured as the product of the force and the distance peeled. This work of separation contains a number of terms which are not necessarily additive and of which, the work expended in deforming the flexible adherend can be a major component. The materials used as flexible adhesives are usually highly viscous materials such as bitumen or are viscoelastic polymers. As such, the force of separation is highly dependent on their viscoelastic properties, is therefore rate and temperature dependent and data can be expressed in the form of master curves obtained by the Williams–Landel–Ferry transform[72]. A number of studies in the field of adhesive behaviour have been made with a sufficient range covered by temperature and rate for a spectrum of mechanical behaviour to be constructed via the WLF transform. One of the earliest of these[73] being associated with earlier studies of the mechanics (or statics) of peeling. Later studies[74] have identified peaks in the extended spectrum of mechanical behaviour with the transition from cohesive to adhesive failure and with the glass transition of the adhesive layer. The behaviour of a pressure-sensitive tape on being peeled from a substrate is indeed instructive of the varied response of polymers to mechanical stress and of the more fundamental physical properties called upon by current attempts at explanation. At low rates of peeling deformation of the adhesive by flow processes occur and the force required is strongly rate-dependent, hence the peak in the mechanical spectrum. At high rates, rate-dependence disappears because the adhesive is no longer deformed but at intermediate rates of pulling the mode of failure is unstable[74,75] and becomes jerky and alternates between what is effectively a zero rate with energy being stored by extension of the backing material and a fast rate in which this stored is dissipated. Vibration of the tautly stretched tape then gives rise to the characteristic noise experienced when unwinding rolls of tape. At the very lowest rates of peeling Gent and Schultz[38] have shown that the work of peeling has a low, limiting value and they have deduced that the work of adhesion is given by the *product* of this limiting value and the various energy dissipative factors in which the transformed rate factor is important. This implies that additive functions involving specific adhesion, work done by bending the adherend and that done on the adhesive are too crude as complex interactions are involved. This possibility of choosing test procedures remote from technological practice but from which more fundamental parameters can be extracted has also been exploited by Andrews and Kinloch[76] and among the several independent methods they used was a simple peeling test at low velocity in which the line of separation was treated as a crack propagating at the interface. The analysis employed by them involves a loss factor such that as the hysteretic losses approach zero, the peeling energy approaches a limiting figure to be identified with the thermodynamic energy of adsorption.

Tack

Tack is that property of an adhesive whereby light contact with the surface of another body brings about a condition requiring force to restore the original separated state. To make this definition rigorous would require a number of qualifying clauses which are necessary in research studies but not to a comprehension of what is being discussed. In some cases separation after contact is only achieved by cohesive failure of the tacky material but generally, the property considered is that which retards but does not prevent the removal of a smooth contacting metal probe or the human finger, the most commonly used tack-tester. The measurement of tack involves a two-fold process. In the first place contact is made between the probe and the tacky surface. If subsequent separation is to be resisted then the tacky material must wet the probe surface; i.e. be adsorbed to it. The second stage is that of debonding the probe from the surface. The wetting stage is both thermodynamically and kinetically controlled. The thermodynamic control will become apparent by the use of probes made with materials of different critical surface tension γ_c (*vide supra*), the kinetic control from the dependence of tack on the time of contact and the load applied during contact. Temperature also has an influence but this is exerted as well on

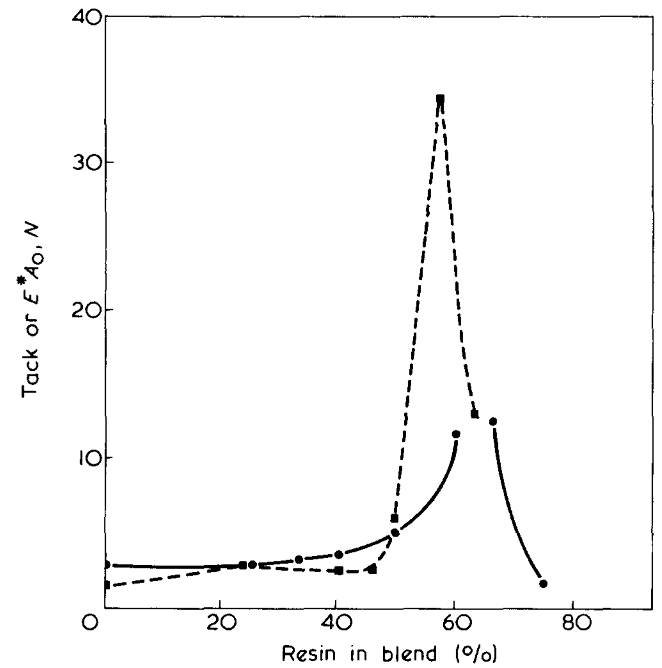


Figure 10 Tack and E^*A_0 of rubber–resin blends. (——), Tack in newtons; (– – – –), product E^*A_0 in newtons where $E^* = G' + iG''$ and A_0 = area of probe. [Reproduced from Dahlquist, C. A. 'Adhesion: fundamentals and practice', MacLaren, 1969, p 150 by permission of MacLaren Publishers Ltd ©]

the removal as on the bond-formation stage. Removal of the probe is rate and temperature sensitive and involves viscoelastic deformation of the bulk of the tacky adhesive before separation occurs and it is the work expended in removal rather than the force used that is the appropriate measuring parameter. It follows from this that the maximum tack will be experienced when the conditions of measurement and the properties of the tacky material combine to give a high energy loss within the material. Dahlquist[77] showed indeed that maxima in the tack/composition relation coincided with maxima in the complex mechanical modulus of the bulk material. *Figure 10* shows the complex tension modulus times the area of probe contact plotted on the same scale as the force measured in the Wetzel tack test[78] and both as a function of the proportion of tackifying resin blended with rubber. This raises the question of the relation of composition of pressure-sensitive adhesives to their tack. Pressure-sensitive adhesives must easily wet the substrates to which they are to be applied as also the probe of the machine testing their tack. They have therefore many of the properties of liquids although, unlike true liquids, they are formulated to withstand some shear. Incidentally, the expression 'pressure-sensitive' arises from the fact that the thickness of a viscous layer between two adherends in the form of discs depends on the pressure exerted when they are brought together. The force then required to separate them is inversely proportional to the cube of their separation and directly proportional to the rate of separation, if the liquid behaves as a simple Newtonian liquid. This derives from Stefan's studies in the last century[79]. The more complex non-Newtonian materials which are, in fact, used will necessarily have more complex dependence on separation distance, but the phenomenon is often referred to as 'Stefan-like' behaviour.

The use of tackifying resins in formulation of pressure-sensitive adhesives undoubtedly leads to two-phase systems for the polymer and resin are not wholly compatible and in the composition range for maximum tack there usually exists resin-rich and polymer-rich phases. The resins used have the special property of a high glass transition temperature, T_g, coupled with a low molecular weight and serve to bring the T_g of the composition to a temperature such that the temperature maximum hysteretic loss is at room temperature[80]. Where compatibility is only partial and two phases exist, the dynamic mechanical spectrum will reflect this complexity and it is herein that the apparent differences between the two-phase and the mechanical loss theories of tack may be resolved. Kamagata and his colleagues[81] correlated the two-phase morphology of pressure-sensitive adhesives of natural rubber and a tackifying resin (the pentaerythritol ester of hydrogenated rosin) showing the way the temperature peak for mechanical loss of natural rubber was only slightly raised by the addition of the resin but that when two phases were present, two peaks developed giving the effect of a very broad dispersion. The peak at the lower temperature corresponding to a rubber-phase gradually decreasing as more resin was added until a single peak, characteristic of the resin, remained. The resin-rich phase, probably containing some rubber of low molecular weight showed a higher mechanical loss than the rubber phase. The two-phase structure, therefore, brings about for rubber–resin mixtures, the conditions necessary for maximum mechanical loss at room temperature and at a frequency corresponding to that of the withdrawal of the contacting probe. If substantial mechanical loss can occur in a single-phase system such as an acrylate copolymer due to its internal architecture, the tackifying resin and the two-phase structure are superfluous.

Tack does vary with the solvent used for depositing the mixed rubber–resin film and this has been convincingly demonstrated[82] to be associated with different surface excesses of resin. In the process of manufacture a nominally homogeneous solution of rubber and resin is deposited, solvent evaporates and a rubber-rich phase precipitates from solution. The relatively mobile solvent/resin mixture moves to the surface and once there loss of solvent is fast enough to prevent rediffusion of resin back into the interior although Whitehouse and his colleagues found that this does occur over a period measured in years rather than in hours. The tack then falls. Thus the two-phase system acts also to assist wetting of the substrate; i.e. making the tack-measured bond, and is more important here than in determining the energy to break the bond, this latter being a bulk-controlled property.

ENVIRONMENTAL DETERIORATION

Undoubtedly, the greatest research effort at the present time is being devoted to an understanding of the mechanisms operative when structural adhesive joints are exposed to variable climatic conditions whilst under sustained or cyclical loading. The major interested party is, of course, the aircraft industry and hence the joints studied have been metal-to-metal joints of aluminium though more recently titanium and stainless steel are coming into the picture. There is no problem with cyclical stressing of an adhesive joint under dry conditions and at normal temperatures. In general, under such conditions, adhesive joints perform in a manner superior to rivetted joints[83] if the correct adhesive has been chosen and the metal surface property prepared. The choice of adhesive must be made on the basis of its dynamic behaviour and not solely on its high strength

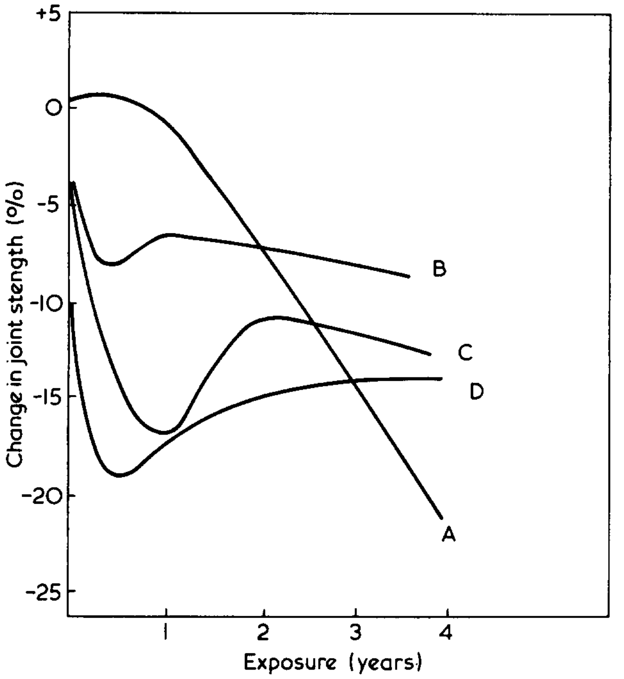


Figure 11 Change in joint strength on outdoors exposure. A, Epoxy–polyamide, unstressed, Southern England; B, Epoxy–phenolic, unstressed, Southern England; C, As B; unstressed in tropical hot–wet climate; D, As C but stressed at 10% of original ultimate strength (after M. G. D. Hockney)

in 'static' lap-shear testing. A very detailed study of the dynamic performance of a poly(vinyl formal)/phenolic adhesive is available[84]. Under cyclical weather changes or continuing high humidity, particularly if combined with continuous loading, joints have been known to fail unexpectedly and controlled studies have shown that fall in joint strength can be catastrophic. *Figure 11* is based on data taken from Hockney's preliminary report[85] on one of the most comprehensive climatic trials of adhesives ever undertaken under fully rigorous control of manufacture, exposure and testing. From a design viewpoint there is the dual problem of deciding safe stress levels for those adhesives which show some loss of bond strength but do not deteriorate catastrophically and that of understanding the mechanism of the loss in order to prevent or minimize it.

Pioneer work by Kerr, Macdonald and Orman[86] established that loss of strength by the adhesive was not a primary cause of decline in joint strength on exposure to water vapour. Ethanol was absorbed in far greater quantity than water by an amine-cured epoxy resin leading to very much greater loss in resin strength but small loss in joint strength. Water showed the opposite behaviour but with both liquids, joint strength was substantially regained on drying. The latter finding was not confirmed for water by Butt and Cotter[87] who found an irreversible loss of joint strength even though the dynamic modulus of the adhesive, reduced to less than 20% of its dry value, was fully regained by drying in high vacuum. Both experiments involved exposure to vapour rather than immersion in water, both employed sulphuric–chromic treatment of the aluminium clad alloy but there were differences in formulation, in particular different amine curing agents were used and this may have been important. The mode of failure of joints reported by the latter authors changed from purely cohesive to apparent adhesive failure at the interface as exposure to water continued emphasizing that interfacial changes are responsible for the effect. There have been two principal lines of attack on this problem. They comprise the fracture mechanical approach pioneered by Patrick, Ripling, Mostovoy[88–90] and their colleagues and, secondly, an extension of the thermodynamics of interaction across interfaces to explain the displacement by water of resin from metal oxide surfaces. It is convenient firstly to deal with the findings obtained by fracture mechanics.

Familiarity is assumed with the concepts of fracture mechanics as it has been developed from Griffith's crack theory by Irwin[91]. The test piece used by Patrick, Ripling and Mostovoy is shown in *Figure 12.* This type of test allows a crack to be opened by a force which is independent of the position of the crack along the beam. Under dry conditions the crack once started in the centre of the glueline continues to run until the energy stored elastically in the cantilever is used by the propagating crack. The crack extension energy G can thus be obtained. With only a fraction of the load necessary to continue propagation of the crack when dry, Patrick and his colleagues found that, in the presence of water, cracks developed spontaneously at the interface with the metal and they refer to this phenomenon as stress–solvolytic failure of the adhesive bond reverting to stress–corrosion in later papers. It has become customary to use the force required to propagate the crack at a limiting low velocity as a measure of the fracture toughness of the adhesive; this is the critical crack extension force G_{IC}, the subscripted I referring to the mode of crack opening in cleavage. In studying stress corrosion of adhesive joints an opening force was applied to the joint and maintained during exposure to water and the rate of slow crack-growth noted. By adjustment of the load a second critical crack extension force was determined, below which no crack growth occurs under water. This has been designated G_{ISCC} where the additional symbols stand for stress corrosion. The catastrophic drop in fracture toughness in the presence of water can be appreciated by considering the figures for an epoxy resin based on the glycidyl ether of bisphenol A and cured with 10 pphr of tetraethylene pentamine at 82°C for 5 h between glass adherends through which crack growth could be easily followed. G_{IC} in the dry condition was about 54 N/m, was halved by exposure to an atmosphere of 55% r.h. and reduced to 14 N/m by immersion in water. Post curing does, however, improve water resistance at least with some hardeners as *Table 3* indicates. The figures in *Table 3* have been deduced from one of the diagrams given by Ripling and his colleagues[89], and refer to an anhydride-cured epoxy.

As already mentioned, accompanying this drastic reduction in fracture toughness is a change in the locus of failure from the centreline of the adhesive to the interface. The interesting point to be emphasized is that the crack which

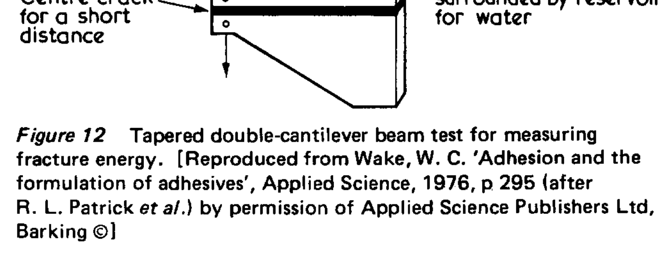


Figure 12 Tapered double-cantilever beam test for measuring fracture energy. [Reproduced from Wake, W. C. 'Adhesion and the formulation of adhesives', Applied Science, 1976, p 295 (after R. L. Patrick *et al.*) by permission of Applied Science Publishers Ltd, Barking ©]

Table 3 Effect of post-curing on stress corrision fracture toughness

Post curing temperature (°C)	G_{IC} (N/m) (Dry)	G_{ISCC} (N/m) (Immersed in water)
100	103	5.3
155	121	12.3
185	102	36.8

starts propagating at the interface under humid conditions is not a continuation of the centreline crack but a new discontinuity initiated at the interface. The morphology of these cracks has been studied by Patrick with the aid of a scanning electron microscope[92]. When fracture toughness is measured in terms of energy rather than force, as is clearly desirable, the figures are such that even G_{ISCC} is far higher than the surface or interfacial energies of adhesive with adherends. When fracture is occurring in the centreline of the joint this is easily and conventionally explained as caused by the dissipation of energy in a plastically deformed or even cavitated zone around and ahead of the tip of the propagating crack. At the interface too, extensive damage occurs on failure both to the resin and the oxide layer on the metal.

The second line of work aimed at clarifying the interfacial aspects of the deteriorating effect of the environment concerns the thermodynamic conditions necessary to displace a resin adsorbed to a substrate by van der Waals's forces. A recent paper[93] is of interest even though it refers to mild steel adherends less likely to be used with structural adhesives than aluminium. The adhesive was an epoxy based on bis-phenol A cured with a tertiary amine and the joints tested were formed by combining two cubes with edges of 2.54 cm. Based on the ideas discussed in an early part of this review, Gledhill and Kinloch satisfied themselves that they could deduce from contact angle measurements and published data for the partition of surface energies into dispersion and polar components that the work of adhesion of an epoxy adhesive to ferric oxide was 291 mJ/m^2 and in the presence of water was -255 mJ/m^2, i.e. the water would be preferentially adsorbed to the ferric oxide surface and would displace the resin. Insofar as their calculations violate the principle expounded in equation (8), the magnitude of their figures is likely to be wrong but it is very unlikely that the sign change involved is wrong. Experimentally, they studied both joint strength and the nature of the surfaces seen after breaking the joint. The interfacial nature of the break after exposure to water was confirmed by electron probe microanalysis seeking iron from the adhesive surface and titanium, used as a marker in the adhesive, from the oxide surface. Behaviour at the interface was not simple as is seen from *Figure 13* and corrosion of the substrate as shown by the change from ferric oxide to magnetite was convincingly shown to occur after displacement of the resin from the surface and not to be a cause of this displacement. Other studies have also suggested that the corrosion of aluminium substrates from joints immersed in water which have either failed or shown reduced strength is, in fact, *post hoc* corrosion.

This somewhat gloomy picture of environmental attack on adhesive joints concentrates on the mechanisms rather than on the steps taken by technologists to minimize its effects. The surface preparation of aluminium alloys, after being fixed by specification for many years, is now being modified to produce surfaces with greater inherent resistance to adverse environments; primers are being increasingly used that, most probably, chemisorb to the oxide surface and siloxanes reactive towards epoxy resins and other adhesives have provided greater stability though at increased cost both in material and processing time.

MATERIALS

The very wide range of materials used commercially as adhesives may be judged from the latest edition of Skeist's Handbook of Adhesives[94] which contains 35 chapters each devoted to a different class or type of adhesive. Inorganic materials are the least important in the present context although large tonnages of soluble silicates are used, mainly in packaging. The adhesion of Portland cement to steel is essential to the performance of reinforced concrete but it would be a misuse of words to regard concrete as an adhesive. The epitome of the adhesive is that it is a high polymer. The earliest adhesives were the naturally occurring polymers of carbohydrate or proteinaceous nature followed in the 19th century by natural rubber. The proliferation of adhesives and their sphere of application has followed the man-made polymer industry. The earlier, naturally-occurring adhesives depended on their ability to dissolve in water and, on drying, to form hydrogen bonds across the interface to the substrates with which they were used. Carpenters' glue forms a strong bond with leather under dry conditions and static loads. It is no use to the shoe industry because shoes are flexed in use and are worn in wet conditions. Traditionally, therefore, shoes were constructed by sewing, not sticking. The advent of synthetic polymers has rendered this method of construction obsolescent and illustrates the changes in traditional technology that adhesives can cause, quite apart from new technologies which they have made possible, such as the used of bonded honeycomb metal in highly stressed but light-weight structures. Carpenters' glue is itself obsolescent as an adhesive although it has other uses in sizing in paper and textile industries. Starch-based adhesives have a continuing market in the form of dextrin and borated dextrin for use in paper-based products such as bags and multiwall paper sacks, tube winding, packaging and labelling, in which fields these materials have maintained their hold by reason of price, non-toxicity and continuous if minor innovation by the producers. Attempts at more radical modification, for example to remove water sensitivity, have been made by grafting various monomers to the starch molecule but such modification has not yet achieved commercial exploitation partly because of cost but mainly because the properties

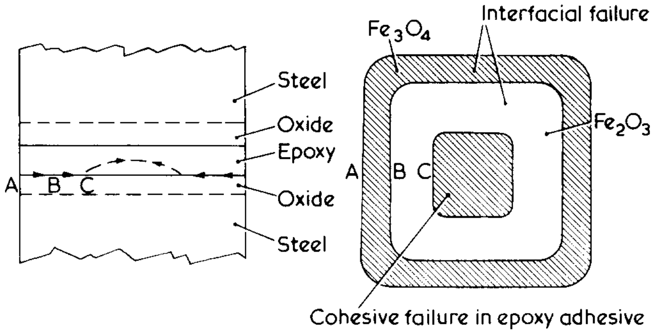


Figure 13 Sketch of locus of failure after immersion of butt joint in water. [© Crown copyright reserved (after R. A. Gledhill and A. J. Kinloch)]

conferred can be matched or surpassed by the existing range of synthetic polymers with much less trouble. However, this is not to be taken as an opinion that natural products may not again become important, not in their simple state nor even upgraded by ordinary chemical processing but as a result of regarding them as building blocks from which more complex, microstructural copolymers may be formed. Starch, casein, cellulose and lignin are, unlike petroleum, renewable materials.

It is perhaps natural to ask why such a wide range of substances as the man-made polymers and of such differing chemical nature is capable of being used in adhesives formulation. There are two answers to this question. The first is that the properties are very fundamental ones possessed by all high polymers; the second answer is that additives can be used to modify these properties to bring certain parametric ones into any desired range. Adhesion depends, as has been detailed above, mainly on the dispersion forces possessed by all molecules, then on means of bringing these into effect by close proximity and lastly on the cohesive behaviour of the adhesive, that is its strength, flexibility and response to temperature. Some polymers will be better adhesives than others due to the enhancement of van der Waals's forces by hydrogen bonding or other donor–acceptor interactions at the interface but these will become special adhesives for stated substrates. The fundamental parametric properties that determine in what way the universally existing adhesive properties can be used are the glass transition temperature, the solubility parameter, the surface free energy and the viscosity. Added to these are the non-parametric qualities of microstructure or organization. Some of these properties are mainly involved in the mode of application of the adhesive to the substrate and play little direct part once intimate contact on a molecular scale has been achieved. The parametric properties are interlinked as several authors have demonstrated[95,96] and the secondary properties of strength and flexibility dependent on them.

Microstructure

Block copolymers are well known to possess microstructure in which phase separation has led to the formation of a hard and sometimes crystalline phase in a rubbery matrix or the reverse situation where a rubbery phase is discrete in a glassy matrix. This type of composite structure can be advantageous in reinforcing a soft, extensible rubber or improving the fracture toughness of an otherwise brittle resin. The scale of the two-phase structure is such as to be resolvable only in the electron microscope. These properties are exploited in adhesives formulation as also is the possibility of adsorbing preferentially one of the polymeric blocks to a substrate either by using high temperatures or by solution in a suitable solvent. An example of this is the use of Heveaplus, a grafted block copolymer of methyl methacrylate (MMA) to natural rubber, as a primer in securing adhesion between poly(vinyl chloride) (PVC) and natural rubber. Applied from a polar solvent to a PVC surface, the extended PMMA chains are adsorbed to the surface. When hot rubber is applied to the dried surface of the primer, molecular rearrangement releases and extends the rubber moiety allowing a diffusion of rubber chains to establish a link which is then strengthened by vulcanization.

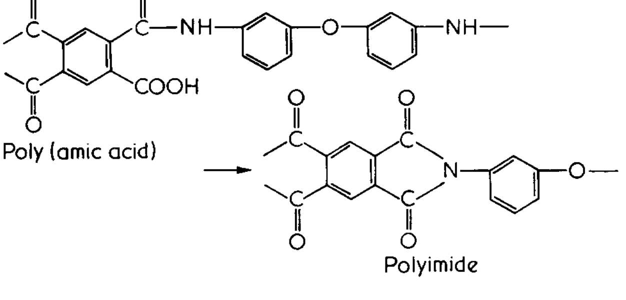
Styrene–butadiene–styrene block copolymers are used in both hot melt adhesives (HMA) and in solvents. In both cases the appropriate additives can associate with the styrene or the butadiene phase and hence modify the stress–strain curve of the material. Tackifying resins which are usually added in preparing contact adhesives which form good bonds immediately on contacting the coated surfaces of the two adherends, preferentially associate with the styrene phase and hence modify its T_g. Suitable choice of resin can result in a higher or lower T_g as is required. A second T_g is present associated with the butadiene component and this too can be shifted.

Polyurethane adhesives also have the reinforcing effect of the polar groups forming a pseudo-crystalline, hard domain in a softer continuous phase. The ratio of hard to soft material as well as their actual properties is determined by the length of the polyol chain which, in adhesives technology, is either a simple glycol or an hydroxy-terminated polyester. There are several chemically alternative routes and the polymer supplied as a single solution in a mixed hydrocarbon-ester mixture has been fully reacted so that no free isocyanate groups remain and is of moderately high molecular weight. Urethanes of high molecular weight are used in the coating industry where solvents such as dimethylformamide can be handled. Two part adhesive mixtures usually contain an hydroxyl-terminated prepolymer and are reacted immediately before use with either a polyisocyanate or an isocyanate-terminated prepolymer usually of low molecular weight. The technology when isocyanates are used for bonding textiles to rubber is different. The polyurethane adhesives, and this refers to fully reacted types, have in the urethane linkage the dual possibility of forming hydrogen bonds of either the donor or acceptor type and it is in this chemical property that their wide versatility as flexible adhesives most probably resides. Their strength properties are enhanced by the domain structure in much the same way as crystallization strengthens bonds made with grades of polychloroprene which have not been sulphur-modified, except that the process of crystal growth takes time and the maximum bond strength consequently takes a few days to develop.

Two-phase microstructures are not confined to flexible rubbery adhesives. One of the earliest and most successful of structural adhesives is a composite of poly(vinyl formal) with a phenol–formaldehyde (P/F) resin and here too a two-phase system exists though the present writer seems to be in a minority in regarding the P/F resin as the disperse phase. Early disappointments with epoxy resins as structural adhesives have led to material of improved ductility and it is customary to specify given peel adhesion behaviour as well as lap-shear tensile strength. The most recent epoxy materials appear to contain carboxyl-terminated rubbers which may be polybutadiene or acrylonitrile–butadiene copolymers. The latter would be more compatible with the epoxy resin and would be expected to give rubbery inclusions in a resinous matrix. They could therefore be described as toughened rather than flexible epoxide resins. Recent patents[97] cover the reaction product of a polyepoxide with a minor amount of a polymer containing a reactive carboxyl group and 1,5-dihydroxynaphthalene or 2,2-bis (4-hydroxy-phenyl) sulphone. The claimed modulus of the amine-cured material is almost twice that obtained with a bis-phenol A resin with triethylene tetramine so that it can scarcely be called a flexible material even though its peel performance is superior. Another patentee[98] claims a polymeric composition in which a second polymeric phase is added, finely divided and is a vinyl polymer or copolymer but this is likely to be a physical blend without, as in the previous case, chemical linkage of the two components.

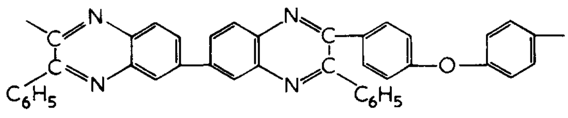
Structural adhesives for high temperatures

Of course, the microstructures described above, dependent as they are on dual ductile/brittle phases, are no use in adhesives designed to operate at high temperatures although nitrile–phenolic adhesives are most probably two phases and would seem to belie this statement. Unsaturated rubbers such as acrylonitrile–butadiene copolymers can be crosslinked by reaction with a resole stage phenol–formaldehyde resin, the phenol group, methylol group and the double-bond of the butadiene coming together to form a 6-membered chroman ring. Nitrile–phenolics can be used over a wide range of conditions as they are toughened with the butadiene inclusion and hence show high peel as well as impact strength. They will endure extended service up to about 130°C and in the very short term appreciable joint strength is retained to about 200°C. The straight epoxy adhesives show a steep drop in joint strength with increasing temperature and even with immediate rise of temperature lose all strength by 120°C but if crosslinked with phenol–formaldehyde instead of with amine, appreciable bond strength is retained up to about 280°C on a short term basis. However, with aircraft speeds greater than Mach 3 contemplated, skin heating brings the integrity of honeycomb panels into question. The problem is compounded by the loss in strength of aluminium at higher temperatures and honeycomb construction of titanium alloy or stainless steel becomes necessary. Although there is clearly an upper limit to the temperature any polymer depending on carbon–carbon linkages can stand this has not yet proved to be the practical limitation and polycyclic, nitrogen-containing polymers such as the polyimides and polybenzimidazoles have been used. The problem encountered with these materials are those associated with preparing polymers sufficiently irregular to exhibit some flow properties at elevated temperatures to enable the substrate to be properly wetted without introducing too much sensitivity to temperature; i.e. conflicting aims. Polyamides with symmetrical precursors such as *p*-phenylene diamine and pyromellitic dianhydride are intractible. The problem of wetting the substrate is overcome by using a solution of the partly condensed poly(amic acid), removing the solvent after applying the solution to the two substrates, closing the joint under pressure and heating to complete ring closure thus:



The practical difficulty is that of removing all the solvent without starting cyclization. Additionally, the present author believes chain branching or crosslinking appears at this stage by the carboxylic group of one chain reacting with the secondary amide of another. This together with hydrogen bonding accounts for the complete insolubility of the product and its lack of flowing under even high pressure. Attempts made to prepare a copolymer of imide and amide gave a very successful film-forming polymer but, unfortunately with greatly reduced temperature resistance, adhesion to steel falling catastrophically above 200°C.

Polyquinoxalines are the most recent recruits to commerically available high-temperature adhesives and a recent survey[99] quotes a tensile shear test with stainless steel as giving 23 MN/m^2 at room temperature, 15.7 MN/m^2 at 315°C after remaining at this temperature for 200 hr and 9 MN/m^2 after 10 min at 538°C. The repeat unit of the polymer is given as:



Structural features will be noticed connecting it to remarks made about the need for bulk and flexibility of polyimides.

Environmental problems

It is embarrassingly difficult to write any review article without considering the effect of the environment, hacknied though the subject is. The adhesives industry has relied in the past on solvents to obtain good contact with substrates but the climate of opinion and impending legislation is likely to ban or at least severely to restrict their use in the near future. Solvent cements are easily compounded, by using two-part compositions the polymers can be crosslinked to give good temperature and creep resistance without the use of heat or pressure and liquids are easily dispensed and spread. The alternatives are present but do not necessarily afford complete or convenient replacements and it is not merely an economic problem though the newer materials are more expensive than the ones they will replace. The possibilities are given below.

(i) *Hot-melt adhesives*: these require placement devices ('guns') or if used as sheets then heated presses. No HMA available at the present time will crosslink on application. They cannot therefore replace two-part solvent adhesives. This does not imply that HMA are poor replacements; they are widely used for many purposes in many industries particularly where high speed operations are involved, e.g. edge veneering at 100 m/sec.

(ii) *Aqueous emulsions*: as replacements for solvent adhesives they may show disadvantages in slower drying particularly with a lack of immediate bonding. There is a major problem in that it is difficult to adjust formulations to start from a polymer latex instead of from a polymer already mixed with necessary additives. The action of a tackifier in admixture with a polymer involves mutual solution. Mixing a polymer latex with an aqueous suspension of the tackifying resin keeps the two components completely separated until the film is dry. At this stage, although contact is made solution does not follow. Mixing polymer and tackifier before emulsification imposes extra stages apart from the difficulty of obtaining a good, stable emulsion under these conditions without the excessive use of soaps and other hydrophilic material.

(iii) *Monomeric adhesives*: these have their specific and very important place in the industry but it is difficult to ban solvents on the grounds of toxicity and replace them with the bulk use of monomers which are but solvents under a different name even though the amount evaporated is kept low rather than encouraged.

(iv) *Solventless liquid adhesives*: epoxy–polyamide formulations come into this category and operate very efficiently. Rubbery materials are available but would need to be used with chain extension and crosslinking chemicals before they could replace existing rubbery solutions. This implies two-part formulations in which one part, most likely to be a polyisocyanate, has its own handling problems even if it is relatively involatile. Additionally, although such materials are available or could become so, the setting process, a matter of chemical kinetics, would be slow at room temperatures and the necessity for jigging increased.

All four alternatives to the release of solvents to the environment thus pose considerable technical difficulties.

Additives

It is difficult to think of the use of polymeric materials without additives. Apart from the antidegradative agents and fillers familiar to all polymer technologists, there is a wide range of chemical additives which are of special concern when formulating adhesives. The most important of these now being investigated are tackifying resins and coupling agents. Additionally, though not to be discussed, are film forming agents and freeze–thaw stabilizers for emulsions, anti-skinning and anti-slump agents for sealants, chemicals to modify rheological properties before setting, catalysts for crosslinking reactions of epoxies and polyurethanes besides the usual vast armoury of chemicals for vulcanizing rubbers.

Tackifying resins. Those used in conjunction with pressure-sensitive adhesives were originally α and β pinene resins of natural origin. They are still regarded as among the best but are now expensive. Synthetic replacements supplied by the petroleum industry tend to be highly branched linear polymers, somewhat removed from the very bulky short chains of bicyclic terpenes made by polymerizing the pinenes. Other naturally occurring materials extensively used are the various ester derivatives of abietic acid in which there are three fused benzene rings and a number of small branched alkyl substituents round the boundary of the molecule. Polymerization is through the conjugated double-bond spanning two of the benzene rings. Their replacement involves pentaerythritol or glycerol esters.

For more polar materials such as polychloroprene contact adhesives, novolak resins of *p*-tert-butyl phenol are universally used and for heat resistance are reacted with magnesium oxide before incorporation into the elastomer.

Coupling agents. The most commonly used coupling agents are trialkoxy siloxanes with the fourth valency of the silicon attached through a short alkyl chain to some functional group reactive with the adhesive polymer. There have been claims for the addition of the siloxane to an epoxide resin whence it is supposed to migrate to the interface but most have been made with the siloxane applied as a priming coat. There is then no doubt that it is at the interface. The condensed siloxane resin must, of course, be present as a layer of finite thickness and forms, as might be expected a rather brittle layer if cast as a film. It undoubtedly protects the interface from attack by water and, although it does hydrolyse the process is very slow at ordinary temperature. There are however a number of puzzling features to which Patrick has drawn attention[92]. When γ-aminopropyltrimethoxysilane was applied in a series of concentrations in solvent to an aluminium substrate in the form of a tapered cantelevered beam to enable crack-growth measurements to be made in the manner already described, in the presence of water interfacial failure was only prevented when the silane had been applied over a very narrow range of concentration. Above or below this concentration stress–corrosion occurred. Clearly, lower concentrations could imply imperfect coverage of the substrate or perhaps fissiparous films but it is difficult to understand what is happening with films thicker than a minimum particularly as, in technological practice such finess is not observed but the coupling agent provides protection. Other coupling agents have been recommended and include chromium complexes, titanes, alkyl phosphates, alkyl and aryl phosphonates and phosphites[100].

CONCLUSION

Adhesion science is multidisciplined but is strongly influenced by polymer science as its materials basis and its growth points coincide with certain growth aspects of polymers. These are the growing realization that supermolecular structure is important with precipitated hardening phases and that these are best achieved by block copolymers either by specific preparation or by grafting on to existing polymers. The most fundamental parameters governing adhesion are those which can be manipulated by polymerization technique. Adhesives are used to make joints and joints are stressed and sometimes fail; hence the need to turn to the research engineer with his finite element analysis and the physicist with fracture mechanics. Industry, in general, lacks these specialists as it has concentrated on chemists to produce the materials. This is now being rectified.

ACKNOWLEDGEMENTS

Thanks are due to the following individuals who permitted reproduction of the following figures: Figure 4, Dr D. Packham, University of Bath; Figure 5, D. J. James, Rubber and Plastics Research Association; Figure 7, S. Dean, The City University and D. Sheppard, the Materials Quality Assurance Directorate, Ministry of Defence, Woolwich. UK.

REFERENCES

(N.B. Some of these references are to reviews in which adhesion aspects of the particular subject receive prominence. In these cases, to emphasize that the reference is to a review, the title has been given. Other references have been selected to illustrate the points made in the article without necessarily implying the origin of the work.)

1 Norman, R. H., Stone, M. H. and Wake, W. C. Resin–Glass Interface, 'Glass Reinforced Plastics', (Ed. B. Parkyn) Iliffe, London, 1970, Ch. 15

2 Rumpf, H. Die Wissenschaft des Agglomeriens *Chem. Ing. Tech.*, 1974, **46**, 1

3 Curtis, A. S. G. Cell Adhesion *Prog. in Mol. Biol.* 1973, **27**, 317; Cell Adhesion, *Adhesion-2.* (Ed. K. W. Allen), Appl. Sci. Publ., London, 1978, In press

4 Crisp, D. J. 'Mechanisms of Fouling Organisms', *Proc. 3rd Int. Conf. Marine Corrosion and Fouling in the Sea,* (Ed. R. F. Acker, B. F. Brown, J. R. DePalma, and W. P. Iverson) Gaithersburg, Maryland, USA 1972. Publ. U.S. Dept. of Commerce, Nat. Bur. Stand., 1973, pp. 691–709

5 Wilson, A. D. 'Current Research in the Laboratory of the Government Chemist' *Chem. Ind.* 1975, 490–2

6 Grimley, H. 'van der Waals Forces and their Role in Adhesion', 'Aspects of Adhesion, 7', (Eds. D. J. Alner and K. W. Allen), Transcripta Books, London, 1973, pp 11–29
7 Lifshitz, E. M. *Dokl. Akad., Nauk. SSSR* 1954, **97**, 643
8 Briscoe, B. J. and Tabor, D. Surface Forces in Friction and Adhesion *Faraday Special Discuss. Chem. Soc. No. 2. 'Solid/Solid Interfaces'*, Chem. Soc., London, 1972, pp 7–17
9 Roberts, A. D. and Thomas, A. G. *Wear* 1975, **33**, 45
10 Bailey, A. 'Physics of Adhesion', (Eds. R. Polke and P. Hohn) Institut Mechanische Verfahrenstechnik, Karlsruhe, 1969, pp 1–9
11 Good, R. J. 'Adsorption at Interfaces', (Ed. K. L. Mittal) ACS Symp. Ser. 8, Am. Chem. Soc., Washington, 1975, pp 28–47
12 Girifalco, L. A. and Good, R. J. *J. Phys. Chem.* 1957, **61**, 904
13 Fowkes, F. M. 'Recent Advances in Adhesion', (Ed. L-H. Lee) Gordon and Breach, New York, 1973, pp 39–43
14 Fowkes, F. M. Surface Chemistry, 'Treatise on Adhesion and Adhesives, Vol I' (Ed. R. L. Patrick) Marcel Dekker, New York, 1967, Ch. 9
15 Greenwood, L. and Wake, W. C. 'Adhèsion des Elastomères', Assoc. Francaise des Ingenieures Caout. Plast., Paris, 1970, pp 19–26
16 Zisman, W. A. see 'Contact Angle, Wettability and Adhesion', (Ed. R. F. Gould) Adv. Chem. Ser. No 43, Am. Chem. Soc., Washington, 1968. (Essays in honour of Dr W. A. Zisman on his 60th birthday)
17 Baszkin, A. and Ter-Minassian-Saraga, L. *J. Polym. Sci. (C)* 1971, Polymer Symposium No 34, 243
18 Shafrin, E. G. 'Handbook of Adhesives', 2nd Edn, (Ed. I. Skeist) van Nostrand Reinhold, New York, 1977, pp 67–71
19 Zisman, W. A. *Ibid.* pp 33–66
20 Good, R. J. Intermolecular and Interatomic Forces, *loc. cit.* ref 14, Ch. 2
21 Lee, L-H. *J. Appl. Polym. Sci.* 1968, **12**, 719
22 Zhukov, I. I. and Talmud, S. L. *Kolloid. Zh.* 1935, **1**, 5
23 Voyutskii, S. S. 'Autohesion and Adhesion of High Polymers' (Translated S. Kaganoff) Interscience, Wiley, New York, 1963
24 Wake, W. C. *loc. cit.* ref 14, Vol 2, Ch. 4
25 Voyutskii, S. S. *J. Adhes.* 1971, **3**, 69
26 Skewis, J. D. *Rubber Chem. Technol.* 1966, **39**, 217
27 Campion, R. P. *J. Adhes.* 1975, **7**, 1
28 This question, with a review of Anand's work and references, is discussed in the 28th Foundation Lecture of the Institution of the Rubber Industry. *J. Inst. Rubber Ind.* 1973, **7**, 242
29 Bister, E., Borchard, W. and Rehage, G. *Kautsch. Gummi Kunstst.* 1976, **29**, 527
30 Deryaguin, B. V. and Krotova, N. A. *Dokl. Akad. Nauk. SSSR* 1948, **61**, 849
31 Deryaguin, B. V., Krotova, N. A., Karassev, V. V., Kirillova, Y. M. and Aleinikova, I. N. Proc. 2nd Int. Congress Surface Activity, 1957, BP 595–603
32 Schnabel, W. *loc cit.* ref 10, pp 102–6
33 Krupp, H. *J. Adhes.* 1972, **4**, 83
34 Donald, D. K. *Ibid.* pp 233–45
35 Weaver, C. 'Adhesion: Fundamentals and Practice', (Ed. UK Ministry of Technology) Maclaren, London, 1969, pp 46–57
36 *Idem., loc. cit.* ref 8, pp 18–25
37 Fowkes, F. M. Remarks at a lecture, 1972, unpublished
38 Gent, A. N. and Schultz, J. *Proc. Int. Rubber Conf. Brighton*, 1972, Inst. Rubber Industry, London, 1972, Paper C1
39 Buchan, S. and Rae, W. D. *Trans. Inst. Rubber Ind.* 1946, **20**, 205
40 Zentler-Gordon, H. E. and Hillier, K. W. *Sci. J. Roy. Coll. Sci.*, 1944, **14**, 140
41 Lewis, A. F. and Forrestal, L. J. *ASTM Spec. Tech. Publ.* 1964, **360**, 59
42 Zhurkov, S. N. *Int. J. Fract. Mech.* 1965, **1**, 311
43 Lewis, A. F. and Saxon, R. 'Epoxy Resins', (Eds. C. A. May and Y. Tanaka) Marcel Dekker, New York, 1973, Ch. 6
44 Lewis, A. F. and Forrestal, L. J. 'Treatise on Adhesion and Adhesives Vol 5' (Ed. R. L. Patrick) Marcel Dekker, New York, in press
45 Allen, K. W. and Shanahan, M. R. *J. Adhes.* 1975, **7**, 161; 1976, **8**, 43
46 Brenman, M. and Lerchenthal, C. H. *Polym. Eng. Sci.* 1976, **16**, 747
47 Pike, M. and Watson, W. F. *J. Polym. Sci.* 1952, 9, 229; Angier, D. J. and Warton, W. F. *J. Polym. Sci.* 1955, **18**, 129
48 Baremboim, N. K. 'The Mechanochemistry of Polymers', (Translated R. J. Moseley from Russian of 1961) Maclaren, London, 1964
49 DeLollis, N. J. 'Adhesives for Metals', Palmerston, New York, 1970, p 37
50 Salomon, G. 'Adhesion and Adhesives', 2nd Edn. (Eds. R. Houwink and G. Salomon) Elsevier, Amsterdam, 1965, Vol 1, p 6
51 Borroff, E. M. and Wake, W. C. *Trans. Inst. Rubber Ind.* 1949, **25**, 199
52 Bikerman, J. J. *Adhesives Age*, 1959, **2**, 23
53 Schonhorn, H. *J. Polym. Sci. (B)* 1964, **2**, 464
54 Hanson, R. H. and Schonhorn, H. *Ibid.* 1966, **4**, 203
55 Sykes, J. M. and Hoar, T. P. *J. Polym. Sci. (A-1)* 1969, **7**, 1385
56 Bright, K. and Malpass, B. W. *Eur. Polym. J.* 1968, **4**, 431
57 Packham, D. E., Bright, K. and Malpass, B. W. *J. Appl. Polym. Sci.* 1974, **18**, 3237
58 Eley, D. D. and Rudham, R. *loc. cit.* ref 35 pp 91–102
59 Packham, D. E., Bright, K. and Malpass, B. W. *J. Appl. Polym. Sci.* 1974, **18**, 3249
60 Perrins, L. E. and Pettett, K. *Plast. Polym.* 1971, **39**, 391
61 Allen, K. W., Alsalim, H. S. and Wake, W. C. *loc. cit.* ref 8 pp 38–45
62 Volkersen, O. *Luftfahrt forsch.* 1938, **15**, 41
63 Goland, M. and Reissner, E. *J. Appl. Mech.* 1944, **2**, A17–A27
64 Sneddon, I. N. 'The Distribution of Stress in Adhesive Joints', 'Adhesion', (Ed. D. D. Eley) Oxford University Press, London, 1961, Ch 9
65 Adams, R. D. and Peppiatt, N. A. *J. Strain Anal.* 1973, **8**, 134
66 *idem, ibid.*, 1974, **9**, 185
67 Adams, R. D., Chambers, S. H., Del Strother, P. J. A. and Peppiatt, N. A. *Ibid.* 1973, **8**, 52
68 Greenwood, L., Boag, T. R. and McLaren, A. S. *loc. cit.* ref 35 pp 273–279
69 Coppendale, J. *Thesis* Bristol University, Department of Mechanical Engineering; Adams, R. D. and Coppendale, J. to be published
70 Kaelble, D. H. *Trans. Soc. Rheol.*, 1959, **3**, 161; 1960, **4**, 45
71 Inoue, Y. and Kobatake, Y. *Appl. Sci. Res (A)* 1959, **8**, 321
72 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
73 Kaelble, D. H. *Adhes. Age*, 1960, **3**, 37
74 Gent, A. N. and Petrich, R. P. *Proc. Roy. Soc. (A)* 1969, **310**, 433
75 Aubrey, D. W., Welding, G. N. and Wong, T. *J. Appl. Polym. Sci.* 1969, **13**, 2193
76 Andrews, E. H. and Kinloch, A. J. *Proc. Roy. Soc. (London)* 1973, **332**, 385
77 Dahlquist, C. *loc. cit.* ref 35, 143
78 Wetzel, F. H. *ASTM Bull.* 1957, **221**, 61
79 Stefan, J. *Sitzungsber. Akad. Wiss. Wien (Math. Naturwiss. Kl Abt. 1)*, 1874, **69**, 713
80 Aubrey, D. W. Pressure-sensitive adhesives–principles of formulation, in 'Developments in Adhesives', (Ed. W. C. Wake), Applied Science, 1977, Ch 5
81 Kamagata, K., Kosaka, H., Hino, K. and Toyamo, M. *J. Appl. Polym. Sci.* 1971, **15**, 483
82 Whitehouse, R. S., Counsell, P. J. C. and Lewis, G. *Polymer*, 1976, **17**, 699
83 Rogger, J. S. *Adhäsion* 1967, **10**, 521
84 Matting, A. and Draugelates, U. 'Die Schwingfestigkeit von Metallklebverbindungen', *Ibid.* 1968, **11**, 5–22, 110–132, 161–176
85 Hockney, M. G. D. 'Effect of outdoor exposure on stressed and unstressed adhesive bonded metal-to-metal joints'. Trial 1, Part 2. *Four Year Summary*, Royal Aircraft Establishment, Farnborough, 1973
86 Kerr, C., Macdonald, N. C. and Orman, S. *J. Appl. Chem.* 1967, **17**, 62
87 Butt, R. I. and Cotter, J. L. *J. Adhes.* 1976, **8**, 11
88 Patrick, R. L., Brown, J. A., Verhoeven, L. E., Ripling, E. J. and Mostovoy, S. *Ibid*, 1969, **1**, 136
89 Ripling, E. J., Mostovoy, S. and Bersch, C. *Ibid* 1971, **3**, 145
90 Mostovoy, S. and Ripling, E. J. *J. Appl. Polym. Sci.* 1969, **13**, 1083

91 Irwin, G. R. Fracture Mechanics Applied to Adhesive Systems, *loc. cit.* ref 14, Ch 7
92 Patrick, R. L. 'The Use of Scanning Electron Microscopy', *loc. cit.* ref 14, Vol 3, Ch 4
93 Gledhill, R. A. and Kinloch, A. J. *J. Adhes.* 1974, 6, 315
94 Skeist, I. 'Handbook of Adhesives', 2nd Edn, van Nostrand Reinhold, New York, 1977
95 Lee, L-H. *J. Appl. Polym. Sci.* 1968, 12, 719
96 Hobin, T. P. *J. Adhes.* 1972, 3, 237
97 The Dexter Corporation, US Pat. 3 678 130, 3 678 121 (1970
98 Ciba–Geigy, Ltd, Br. Pat., 1 370 782 (1970)
99 Aponyi, T. J. 'Other High Temperature Adhesives', *loc. cit.* ref 94, Ch 38
100 Cassidy, P. E. and Yager, B. J. 'Reviews in Polymer Technology I', (Ed. I. Skeist) Marcel Dekker, New York, 1972, pp 1–49