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Review
The science of adhesion
Part 1 *Surface and interfacial aspects*

A. J. KINLOCH
Ministry of Defence (P.E.), Propellants, Explosives & Rocket Motor Establishment, Waltham Abbey, Essex, UK

The present paper, Part 1, reviews surface and interfacial phenomena, including mechanisms of adhesion, which are relevant to the adhesive joining of materials with the aim of outlining the current philosophies, and relating them, where possible, to the practice of adhesive bonding. Part 2 will examine the mechanics of adhesive joint fracture and the effects of various operating environments on joint performance.

1. Introduction

An adhesive may be defined as a material which when applied to substrate surfaces can join them together and resist separation. Adhesive is the general term and includes cement, glue, paste, etc. These terms are all used essentially interchangeably. Various description adjestives are often applied to the term adhesive to indicate certain characteristics, for example, its physical form, e.g. liquid adhesive, film adhesive; its chemical form, e.g. epoxy adhesive; to indicate the materials bonded, e.g. metal-to-metal adhesive, paper adhesive; or to show the conditions of use, e.g. cold-setting adhesive, solvent-based adhesive.

As a means of joining materials, the use of adhesives offers many advantages when compared to other, more conventional methods such as brazing, welding, riveting, bolting, etc. The advantages include:

(a) the ability to join dissimilar materials, for example, metals to plastics and rubbers,

(b) the ability to join thin sheet material efficiently,

(c) an improved stress distribution in the joint which imparts, for example, an increase in fatigue resistance to the bonded component,

(d) an increase in the design flexibility,

(e) the fact that, frequently, it is the most convenient and cost effective technique.

These advantages have led to a continuing increase in the use of adhesives and a widespread appreciation of adhesives technology. However, our fundamental knowledge concerning the nature of the forces of attraction between bodies, determination of the magnitude of such intrinsic forces, and their relation to measured adhesive joint strengths, namely the "science of adhesion", has undoubtedly lagged behind the applied technology. Indeed, for many adhesive/substrate interfaces of considerable practical importance there are still unresolved debates concerning the detailed mechanisms of adhesion and the mechanics of joint rupture.

One of the main reasons why the theory has followed behind the technology is that the science of adhesion is a truly multi-disciplined subject. The adhesion scientist often needs to consider aspects of surface chemistry and physics, rheology, polymer chemistry, stress analysis, polymer physics, and fracture phenomena, to interpret fully his data. The many texts [1–12] on the topic of adhesion and adhesives illustrate this statement and the reader is referred to these for more detailed treatments than can be presented here.

This and a subsequent paper will present a critical assessment of recent published works on those aspects of adhesion science which are relevant to the adhesive joining of materials, with the aim of outlining the current philosophies and relating them, where possible, to the practice of adhesive bonding. Part 1 of the review will consider surface and interfacial aspects, including mechanisms of adhesion, while Part 2 will examine the mechanics of adhesive joint fracture and the effects of operating environments on joint performance. The relationships between the surface and interfacial aspects and the measured joint strength and durability will be emphasised wherever possible.

2. Interfacial contact

It has been recognised for many years that the establishment of intimate molecular contact at the interface is a necessary, though sometimes insufficient, requirement for developing strong adhesive joints. This means that the adhesive needs to be able to be spread over the solid substrate surface, and needs to displace air and any other contaminants that may be present on the surface. An adhesive which conforms ideally to these conditions must [13]:

(a) when liquid, exhibit a zero or near zero contact angle,

(b) at some time during the bonding operation have a viscosity that should be relatively low, e.g. no more than a few centipoises,

(c) be brought together with the substrate with a rate and manner that should assist the displacement of any trapped air.

In order to assess the ability of a given adhesive/substrate combination to meet these criteria it is necessary to consider wetting equilibria, to ascertain values of the surface free energies of the adhesive and substrate and the free energy of the adhesive/substrate interface and to examine the kinetics of the wetting process.

2.1. Wetting equilibria

Surface tension is a direct measurement of intermolecular forces. The tension in surface layers is the result of the attraction of the bulk material for the surface layer and this attraction tends to reduce the number of molecules in the surface region resulting in an increase in intermolecular distance. This increase requires work to be done, and returns work to the system upon a return to a normal configuration. This explains why tension exists and why there is a surface free energy. The most common type of physical surface attractive forces are the van der Waals forces, and can be attributed to different effects: (a) dispersion (or London) forces arising from internal electron motions which are independent of dipole moments and (b) polar (or Keesom forces) arising from the orientation of permanent electric dipoles and the induction effect of permanent dipoles or polarizable molecules. The dispersion forces are usually weaker than the polar forces but they are universal and all materials exhibit them. Another type of force that may operate is the hydrogen bond, formed as a result of the attraction between a hydrogen atom and a second, small and strongly electronegative atom such as a fluorine, oxygen or nitrogen.

Wetting may be quantitatively defined by reference to a liquid drop resting in equilibrium on a solid surface as shown in Fig. 1. The tensions at the three phase contact point are indicated such that LV is the liquid/vapour point, SL is the solid/liquid point and SV is the solid/vapour point. The Young equation [14, 15], relating these tensions to the equilibrium contact angle θ, may be written as

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta . \quad (1)$$

The term γ_{SV} represents the surface free energy of the solid substrate resulting from adsorption of vapour from the liquid and may be considerably lower in value than the surface free energy of the solid in vacuo, γ_S. This reduction in the surface free energy of the solid when covered by a layer of vapour has been defined by the concept of equilibrium spreading pressure, π_S, such that when the vapour obeys the ideal gas law [16]

$$\pi_S = \gamma_S - \gamma_{SV} = RT \int_0^{p_0} \Gamma \, d(\ln p), \quad (2)$$

where p is the vapour pressure, p_0 is the equilibrium vapour pressure, R is the gas constant, T is the absolute temperature and Γ is the surface concentration of the adsorbed vapour. Thus Equation 1 may be rewritten as

$$\gamma_S = \gamma_{SL} + \gamma_{LV} \cos \theta + \pi_S . \quad (3)$$

When $\theta > 0^\circ$ the liquid is nonspreading but

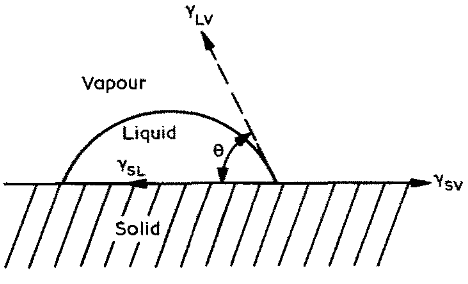


Figure 1 A liquid drop resting at equilibrium on a solid surface.

when $\theta = 0^\circ$ the liquid wets the solid completely and spontaneously and spreads freely over the surface at a rate depending on the liquid viscosity and solid surface roughness. Thus for spontaneous wetting to occur

$$\gamma_{SV} \geqslant \gamma_{SL} + \gamma_{LV}, \tag{4}$$

or

$$\gamma_S \geqslant \gamma_{SL} + \gamma_{LV} + \pi_S. \tag{5}$$

It is also possible for a liquid to spread and wet a solid surface even when $\theta > 0^\circ$ but this requires the application of a pressure or force to the liquid to forcibly spread it over the solid surface. However, before these concepts may be of use in adhesives technology the surface and the interfacial free energies need to be evaluated and the kinetics considered.

2.2. Surface and interfacial free energies

A distinction may be made between low-energy and high-energy solid surfaces. Organic compounds, such as polymers, belong to the first group and their surface free energies are usually less than $100\,\mathrm{mJ\,m^{-2}}$. Metals, metal oxides, and ceramics belong to the second group and their surface free energies are typically greater than $500\,\mathrm{mJ\,m^{-2}}$.

The first approach to the characterisation of low-energy, polymeric solid surfaces was an empirical one developed by Zisman. He and his co-workers [17–21] established that, for low-energy solids and a series of liquids, a rectilinear relationship frequently existed between the cosine of the contact angle, $\cos\theta$, and the surface tension of the wetting liquid, γ_{LV}. Zisman defined a critical surface tension of wetting, γ_c, by the value to which γ_{LV} extrapolated as $\cos\theta$ tends to unity, i.e. as θ tends to zero degrees. Thus γ_c is the surface tension of a liquid which will just spread on the surface giving a zero contact angle. Zisman and subsequent workers [19] have found a similar behaviour for a wide range of homologous series of liquids and solid surfaces. Indeed, Zisman found that even when $\cos\theta$ was plotted against γ_{LV} for a series of non-homologous liquids the points fell close to a straight line, although some deviations were observed for solid surfaces having very low values of γ_c (where $\gamma_c < 20\,\mathrm{MN\,m^{-1}}$). Some typical relationships are shown in Fig. 2 and experimental details are given in the original papers [17–21].

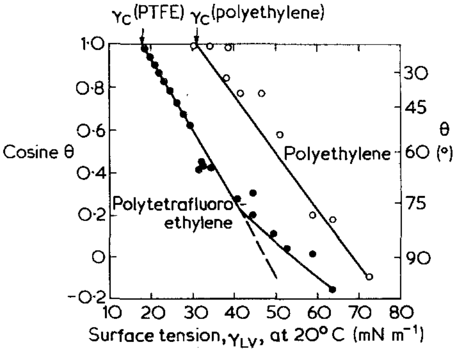


Figure 2 Wettability of polytetraflouroethylene and polyethylene.

The widespread occurrence of the rectilinear relationship between $\cos\theta$ and γ_{LV} led Zisman to use the critical surface tension to characterize and compare the wettabilities of a variety of low-energy surfaces. Some typical values of γ_c for polymeric solids are shown in Table I. The critical surface tension has been an extremely useful parameter for the surface characterisation of low-energy solids, and Lee [22] has even derived an empirical relationship between γ_c and glass transition temperature. However, Zisman has always emphasised that γ_c is not the surface free energy of the material, but only an empirical parameter the relative values of which act as one would expect the surface free energy to behave. Many subsequent authors have assumed that these two parameters are equal without comment. The relationships between γ_c, γ_{SV} and γ_S for a low-energy solid are discussed later.

More recently Dann [23] has re-examined the empirical observations of Zisman and, by measuring the contact angles of homologous and non-homologous series of liquids on a number of polymeric surfaces, he found that different liquid series gave different values of critical surface tension, γ_c, for a particular polymeric surface. In fact Fox and Zisman [19] had also previously observed this result for paraffin and for hexatriacontane. Dann also recorded that the relationship between the cosine of the contact angle and the surface tension of the wetting liquid was normally a curve of a power form, rather than a linear one, and employed the theoretical concepts of Good, Girifalco and Fowkes [24, 25, 35] to explain this feature. The reasons why Zisman observed a linear relationship were that for the hydrocarbon liquids he studied only a narrow range of surface tensions were involved and only dispersion (or London) force components contributed to their total surface tension (no polar contribution). The non-homologous liquids used by Zisman have the unusual feature that the

TABLE I Values of surface free energies of polymers at room temperature obtained by various methods

Solid surface	Critical surface tension[*] γ_c(mN m^{-1})	γ_S^D from Equation (13)[†] (mJ m^{-2})	Values from Equation (15) (mJ m^{-2})			Surface tension from molten polymers[‡] (mN m^{-1})
			γ_S^D	γ_S^P	γ_S	
Polyhexafluoropropylene	16.2 – 17.1	18.0	11.7	0.7	12.4[§]	
Polytetrafluoroethylene	18.5	19.5	14.5	1.0	15.5[§]	26.5
Styrene–butadiene rubber			27.8	1.3	29.1[¶]	
Polychlorotrifluoroethylene	31.0	30.8	31.4	2.1	33.5[¶]	31.1
Polyethylene	31.0	35.0	31.3	1.1	32.4[§]	35.7
Polystyrene	32.8	44.0	38.4	2.2	40.6[§]	40.7
Polychloroprene	38.0					
Nylon 66	42.5		33.6	7.8	41.4[§]	
Polyethyleneteraphthalate	43.0		41.8	3.3	45.1[¶]	
Typical amine-cured epoxy			41.2	5.0	46.2[‖]	
Phenol–resorcinol resin	52.0					
Urea–formaldehyde	61.0					

[*] see [59]

[†] see [38]

[‡] see [61, 62]

[§] see [60]

[¶] see [70]

[‖] see [54]

dispersion force component decreases as the total surface free energy increases, and it was this that caused the plot of $\cos\theta$ against γ_{LV} to approximate to the linear relationship observed in Zisman's work. Finally, Dann demonstrated that when a liquid series possessing only dispersion forces is used, the critical surface tension equals the dispersion force component of the surface free energy of the solid and consequently provides a method for determining the surface free energy of the solid.

Good and Firifalco [24, 15] have expressed the interfacial free energy in terms of the surface free energies of the pure phase by an analogy to the Berthelot relation [26]. This relation is for the attractive constants between like molecules A_{aa} and A_{bb} and that between unlike molecules A_{ab} such that

$$\frac{A_{ab}}{(A_{aa}A_{bb})^{1/2}} = 1. \tag{6}$$

For generality, Good and Girifalco set their relationship equal to Φ so that Φ possessed a maximum value of unity and was defined in terms of molecular geometrics and forces of interaction across the adjacent phases [27]. Thus when expressed in terms of surface free energies for two phases a and b, the interfacial free energy between the phases, γ_{ab}, is given by

$$\gamma_{ab} = \gamma_a + \gamma_b - 2\Phi(\gamma_a\gamma_b)^{1/2}, \tag{7}$$

where γ_a and γ_b are the surface free energies of the phases a and b. This geometric mean average has previously been used successfully by Hildebrand [28] for predicting the intermolecular energy of solutions. Equations (3) and (7) may be combined to yield

$$\gamma_S = \frac{[\gamma_{LV}(1+\cos\theta)+\pi_S]^2}{4\Phi^2\gamma_{LV}}. \tag{8}$$

Various workers [29–33] have suggested that the spreading pressure, π_S, for a liquid on a surface with which it makes finite contact, is negligible, which means that a relatively high-energy liquid is not adsorbed and hence cannot reduce γ_S of a low-energy solid.

Thus Equation (8) becomes

$$\gamma_S = \frac{\gamma_{LV}(1+\cos\theta)^2}{4\Phi^2}. \tag{9}$$

Setting $\theta = 0°$ it is evident that the relation of γ_S to γ_c is

$$\gamma_c = \Phi^2\gamma_S. \tag{10}$$

Hence, from contact angle measurements, liquid surface tensions and a knowledge of Φ [32, 34], the value of γ_S may be ascertained and from Equation (7) the value of γ_{SL} may also be found.

Fowkes has developed a similar argument for the interfacial free energy but adopted a slightly different approach. Fowkes [35] first proposed that the surface free energy of a pure phase, γ_a, could be represented by the sum of the contributions arising from different types of force components. Fowkes [36] has identified at least seven components but Schultz *et al.* [37] have suggested that the surface free energy may be generally expressed by two terms, namely a dispersion and a polar component, such that

$$\gamma_a = \gamma_a^D + \gamma_a^P, \tag{11}$$

where γ_a^D is the dispersion force component and γ_a^P is the polar force component. Fowkes then proposed that the geometric mean of the dispersion force components is a reliable prediction of the interaction energies at the interface caused by dispersion forces. Thus, for interactions involving only dispersion forces,

$$\gamma_{ab} = \gamma_a + \gamma_b - 2(\gamma_a^D\gamma_b^D)^{1/2}. \tag{12}$$

Fowkes [38, 39] confirmed the validity of these equations by experimental and theoretical approaches, and has extended these concepts to solid–liquid systems by combining Equation (3) with Equation (12) to give

$$\cos\theta = \frac{-\gamma_{LV} + 2(\gamma_S^D\gamma_{LV}^D)^{1/2}}{\gamma_{LV}} - \frac{\pi_S}{\gamma_{LV}}, \tag{13}$$

where γ_S^D and γ_{LV}^D are the dispersion force components to the solid and liquid surface free energies, respectively.

Tamai, Makuuchi and Suzuki [40] and Dann [41] introduced an energy term, $-I_{ab}$, into Equation (12) to account for the stabilisation by non-dispersion forces. However, γ_S^P cannot be evaluated merely by the introduction of this term and consequently Owens and Wendt [42] and Kaelbe and Uy [43], by analogy with the work by Fowkes, have proposed that I_{ab} may be expressed by the relation $2(\gamma_a^P\gamma_b^P)^{1/2}$. This expression may be introduced into Equation (12) to give

$$\gamma_{ab} = \gamma_a + \gamma_b - 2(\gamma_a^D\gamma_b^D)^{1/2} - 2(\gamma_a^P\gamma_b^P)^{1/2}. \tag{14}$$

Considering a solid–liquid system, this relationship may be combined with Equation (3) to eliminate the interfacial free energy. Assuming the spreading pressure to be negligible, then

$$1 + \cos\theta = \frac{2(\gamma_S^D)^{1/2}(\gamma_{LV}^D)^{1/2}}{\gamma_{LV}} + \frac{2(\gamma_S^P)^{1/2}(\gamma_{LV}^P)^{1/2}}{\gamma_{LV}}. \quad (15)$$

Fowkes [39] and Dann [23] have evaluated γ_{LV}, γ_{LV}^D and γ_{LV}^P for many liquids using the concepts previously discussed. Consequently, if the contact angles of two liquids on a solid surface are measured, simultaneous equations may be formed from Equation (15) and solved to obtain values of γ_S^D and γ_S^P. The total surface free energy of the solid surface, γ_S, is then simply the sum of these components. This approach has been discussed in detail by Kaelble [44] and Sherriff [45]. Values of γ_S, γ_S^D and γ_S^P for various low-energy surfaces are given in Table I.

Although the results in Table I indicate that there is generally good agreement between the different approaches that have been adopted to evaluate the surface free energies of polymers, each approach has its critics. Fowkes [46], Wake [47] and Panzer [48] have objected to the use of a relation, such as the geometric mean, to predict the polar force interactions. Their criticisms are based upon experimental evidence and theoretical considerations. They consider that polar force interactions within liquids or solids cannot be predicted because of interaction energies observed between them. For example, water may form hydrogen-bonds with the π-orbitals of polystyrene but there are no hydrogen-bonds within polystyrene. They also comment that the flexibility of the macromolecular chains means that the polar groups will have specific orientations according to the polar nature of the liquid present on the surface of the polymer. The work of Baszkin *et al.* [108] provides evidence for this effect. Lipatov and Feinerman [49] agree with these objections but consider that these arguments are equally true for dispersion force interactions and thus invalidate the whole approach, as expressed in Equations (11) and (12). They also concur with Bikerman [50] who concluded that the additivity hypothesis contradicts both electrodynamics and interaction theory for liquids. Others [51, 52] have accepted the basic approach for deducing both the dispersion and polar force interfacial interactions but examined the possibility of using other relationships, such as the harmonic mean, rather than the geometric mean. However, the concept of employing the geometric mean for dispersion and non-dispersion forces has received experimental [37, 53] and theoretical [54] justification and while the theoretical basis for the concept may remain to be unequivocally established the concept has proved to be extremely useful [37, 53–58], as will be shown later.

Sharpe and Schonhorn [63] have emphasised the importance of wetting and proposed that the single most important factor influencing adhesive joint strength is the ability of the adhesive to spread spontaneously on the substrate when the joint is initially formed. They developed a criterion from Equation (4) for the case when the adhesive will spontaneously spread on the substrate and, by ignoring the interfacial free energy and using Zisman's critical surface tension concepts, proposed that the γ_c of the adhesive must be less than that of the substrate. By reference to Table I it can be seen that this means, for example, that high joint strength should not result, and has been observed not to result, when polyethylene substrates are bonded using an epoxy–amine adhesive but that polyethylene should, and does, adhere strongly when melted against a cured epoxy–amine solid substrate. This arises because, in the former case, γ_{LV}(epoxy–amine adhesive) $>$ γ_c(polyethylene substrate) and hence wetting is limited, while in the latter case γ_{LV}(polyethylene adhesive) $<$ γ_c(cured epoxy–amine substrate) and so spontaneous wetting occurs. Indeed, the requirement for the low surface free energy of polyethylene and similar substrates to be increased is a major reason why surface modification of such materials is often necessary prior to bonding [64]. Thus the Sharpe and Schonhorn [63] criterion essentially proposes that a mobile, liquid adhesive with small or zero contact angle, which will spread readily, flow into crevices, and achieve true contact with little opportunity for the voids which may act as stress concentrators, is of prime importance. Further work has since suggested that an additional requirement is that the interfacial free energy, γ_{SL}, should be as low as possible [65–68].

Schonhorn has since considerably modified his views (see Section 3.5), and Huntsberger's [69] analysis indicates that good adhesives are not necessarily those which exhibit low or zero contact angle with the substrate. Huntsberger's analysis stresses the importance of wetting as a kinetic process for, although the thermodynamics may indicate the establishment of intimate molecular contact, the kinetics of wetting may be the determining factor.

A variety of techniques have been employed [71–79] to ascertain the surface free energy of high-energy solids. Many involve the melting of the solid and hence the determination of the surface free energy at relatively high temperatures, but temperature coefficients of the surface free energy may have been reported [71, 77–79] to enable room-temperature values to be deduced. Fowkes [38] has combined Equations (2) and (12) to give

$$\gamma_S^D = (\pi_S + 2\gamma_{LV}^2)/4\gamma_{LV}^D. \qquad (16)$$

Hence, values of π_S from adsorption studies, and a knowledge of γ_{LV} and γ_{LV}^D for the adsorbate, enable γ_S^D for the high-energy surface to be deduced. Schultz *et al.* [37, 80] have recently proposed a more direct method for measuring γ_S^D and γ_S^P of a high-energy solid, which involves measurement of the contact angle of water on the solid under an n-alkane.

2.3. Kinetics of wetting

Bascom *et al.* [13, 81] have employed interference microscopy and ellipsometry to and show that if the contact angle is zero, surface tension gradients may exist at the spreading front which may assist or hinder spreading depending upon their direction. These surface tension gradients arise from thermal gradients or, in the case of liquids containing a more volatile component of different surface free energy, such as a trace impurity, they may arise from a concentration gradient. This effect is illustrated in Fig. 3 and at the leading edge of the spreading liquid there is a thin (either 1 or 2 monomolecular layers) primary film which is followed by a transition region in which thermal or concentration gradients create a surface tension gradient and thereby a surface flow that drags the underlying liquid forward. The rate of flow in the transition region may exceed the rate of gravity flow in the much thicker secondary film so that a ridge of liquid develops. Spreading rates resulting from this gradient effect are relatively low: typically about 0.1 μm s^{-1} for a polyisobutylene fluid on polished steel.

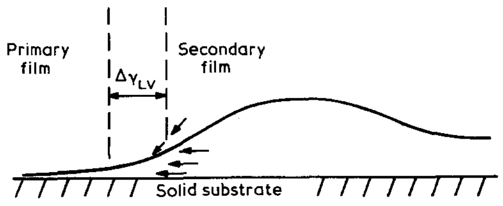


Figure 3 Schematic diagram of the surface and bulk flow patterns at the leading edge of a spontaneously spreading film. After Bascom and Patrick [13].

The topography of the substrate surface may also influence the kinetics of wetting.

Firstly, a liquid forming a contact angle of less than 90° with a solid surface may spread along fine pores, scratches and other inhomogeneities by capillary action, even though it may be non-wetting on a planar surface. Bascom *et al.* [81] have reported that random surface scratches increased the spreading rate of some liquids by as much as fifty per cent and that open capillaries filled well ahead of the diffusional advance of the primary film. Similar observations have been recorded by Cottington *et al.* [82]. Cheever [83] has studied zinc phosphate conversion coatings and treated the situation theoretically as a capillary matrix in which the capillaries assume the particular shape of slits. A mathematical and physical model was derived from Poiseuille's equation which adequately described the flow of liquid in zinc phosphated steel substrates, and gave the capillary pressure which was generated in the zinc phosphate coating to be about 0.7 MPa. However, spreading rates from this effect and surface tension gradients are not high and may be overshadowed when a liquid adhesive is forcibly spread over such a surface. Nevertheless Bascom and Patrick [13] have suggested that such effects may play a role in the redistribution of the adhesive after its initial application.

Secondly, Wenzel [84] has shown that another effect of surface roughness is to change the apparent contact angle, θ', observed for the rough solid, compared to the same angle, θ, observed for the smooth surface. This change in the apparent contact angle can be expressed by

$$\cos\theta' = r\cos\theta, \qquad (17)$$

where r is the roughness factor or the ratio of the actual area to the projection area of the solid. On a smooth surface, if θ is less than 90°, roughening the surface will result in θ' being even smaller, thus increasing the apparent surface free energy of the solid surface and consequently also the extent of wetting. However, if θ is greater than 90° on a smooth surface, roughening the surface will increase the contact angle θ' still further and decrease the degree of wetting. Other, more sophisticated models of substrate surface topography have since been developed [85–90] to take account of advancing and receding contact angles and contact angle hysteresis (i.e. the difference often observed in the value of these two angles).

Thirdly, de Bruyne [91] has modelled various types of substrate surface topography and obtained quantitative expressions for the relationship between the extent of wetting and the driving pressure. Fig. 4 shows the capillary penetration to be expected, under atmospheric pressure and against the back pressure of trapped air, as a function of the contact angle made on the solid by the penetrating liquid. The limited penetration into the "ink-bottle" pits is especially marked and this effect will be heightened if the liquid has a viscosity greater than a few tens of centipoises and is forced rapidly across the substrate surface. Under such circumstances the liquid near the surface cannot keep up with the advancing front so that a higher dynamic contact angle develops [13, 92, 93].

Various workers [94–96] have examined the kinetics of wetting of molten polymers on substrates by following the change in the contact angle of molten polymers as a function of time at different temperatures. Schonhorn *et al.* [94] have demonstrated that the ratios of the cosine of the contact angle, θ_t, at a time, t, to the cosine of the contact angle, θ_∞, at an infinite time, could be superimposed, using a time–temperature equivalence, to give a single master curve. Newman [97] and Cherry and Holmes [95] have reported that this time–temperature dependence may be expressed by

$$\cos\theta_t = \cos\theta_\infty[1 - a\exp(-ct)], \quad (18)$$

where a and c are constants and where [94]

$$c = \frac{\gamma_{LV}}{\eta L}, \quad (19)$$

where η is the viscosity of the polymer and L a parameter with dimensions of length [95, 98] and related to the adhesive/substrate interaction. Cherry and Holmes also concluded that the spreading of a molten polymer across a metal surface could be described in terms of an activated rate process in which the activation energy barriers were the same as those which oppose viscous flow, and the driving force for this derives from the action of surface forces during the replacement of a solid/vapour interface by the solid/liquid interface. In subsequent work [98] the parameter c was termed the "wetting constant" and joint strengths were thought to correlate better with a high wetting constant (except for very low values) than with a low contact angle.

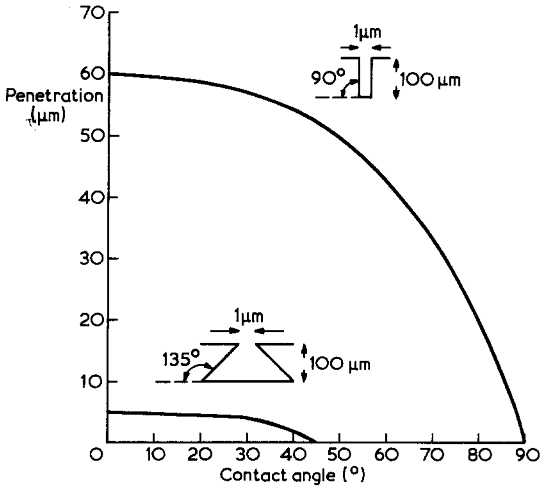


Figure 4 Comparison of the penetration of a film into cylindrical and "ink-bottle" pits. After de Bruyne [91].

2.4. The bonding operation

2.4.1. *Air entrapment*

Bascom and Cottington [99] have studied the mechanism and effects of air entrapment during the preparation of joints with structural film adhesives. Optical microscopy studies on glass/adhesive joints revealed that initially a thin film of air was trapped between the adhesive and glass substrate which usually extended over about half of the interfacial area. As the temperature was raised, to effect cure of the adhesive, this air drew up into bubbles that were eventually displaced into the adhesive layer. However, incomplete displacement occurred if the adhesive had a contact angle greater than zero on the substrate surface or did not become sufficiently fluid during the heat cure. Such air voids may be eliminated if the joint is bonded in any autoclave, where there is a hydrostatic pressure high enough to compress entrapped air to a negligible volume, or by employing a "vacuum release" technique [99]. This latter method simply involves starting the cure in vacuum (about 650 Pa) and subsequently releasing the vacuum at the temperature at which the resin's viscosity is at a minimum. Air voids may obviously act as stress raisers and, indeed, increases in the peel strength of aluminium/

epoxy adhesive joints of up to thirty per cent were reported upon complete void removal using the vacuum release technique.

2.4.2. The bonding environment

Other aspects of the bonding operation are the environmental conditions employed and these are particularly important when bonding metallic substrates which are usually, of course, covered by an oxide layer. Metals and metal oxides are usually classed as high-energy solids since in the ultra-clean state they have surface free energies, γ_S, typically greater than $500\,\mathrm{mJ\,m^{-2}}$. Thus, it would seem, at first, that such a surface would be readily wetted by organic adhesives having low surface free energies (typically less than about $70\,\mathrm{mJ\,m^{-2}}$, see Table I), once any machine oil, protective greases or other contaminants remaining from the materials production had been removed. However, even in the absence of these obvious impurities a high-energy surface adsorbs water vapour from the atmosphere [100, 101] and other contaminants such as nitrogen and organic adsorbates, such as hydrocarbons [102], which lower the surface free energy, γ_{SV}, of the substrate and may prevent spreading of the adhesive. Indeed Bennett and Zisman [103] determined the critical surface tension, γ_c, of various "clean", hydrophilic, high-energy surfaces at two extreme values of relative humidity, 0.6% r.h. and 95% r.h., and found that the surfaces were converted to ones of low γ_c (about 46 and $38\,\mathrm{mJ\,m^{-2}}$ respectively) and, further, that the γ_c values were almost independent of the actual underlying solid substrate.

Gledhill *et al.* [55] have recently extended this earlier work by examining the effect of a range of relative humidities on the wettability of the mild-steel surfaces of different rugosities and have considered the implications of such data on the strength of joints prepared under different humidities. From the contact angle measurements and, using Equations (15) and (11), the value of γ_{SV} for a polished and grit-blasted steel surface was deduced as a function of relative humidity. The results are shown in Fig. 5. For the polished surface there is a linear correlation and the results are in good agreement with values previously reported by Bennett and Zisman [103]. For the rougher, grit-blasted surfaces there is a considerably greater variation in the value of γ_{SV} with humidity and, as might be expected from Section 2.3, the value of γ_{SV}(rough) is greater than γ_{SV}(polished). From the values of γ_{SV}^D and γ_{SV}^P a wettability envelope may be constructed. For wetting to occur, Equation (4) revealed

$$\gamma_{SV} \geqslant \gamma_{SL} + \gamma_{LV}. \tag{4}$$

Substituting for γ_{SL} from Equation (14) into Equation (4) and re-arranging, then the condition for wetting just to occur becomes

$$\gamma_{LV} - (\gamma_{SV}^D\gamma_{LV}^D)^{1/2} - (\gamma_{SV}^P\gamma_{LV}^P)^{1/2} = 0. \tag{20}$$

Thus, knowing values of γ_{SV}^D and γ_{SV}^P for a solid surface enables Equation (20) to be solved to yield values of γ_{LV}^D and γ_{LV}^P for liquids which would just wet the solid surface and so allow a wettability envelope for the solid to be constructed. Wettability

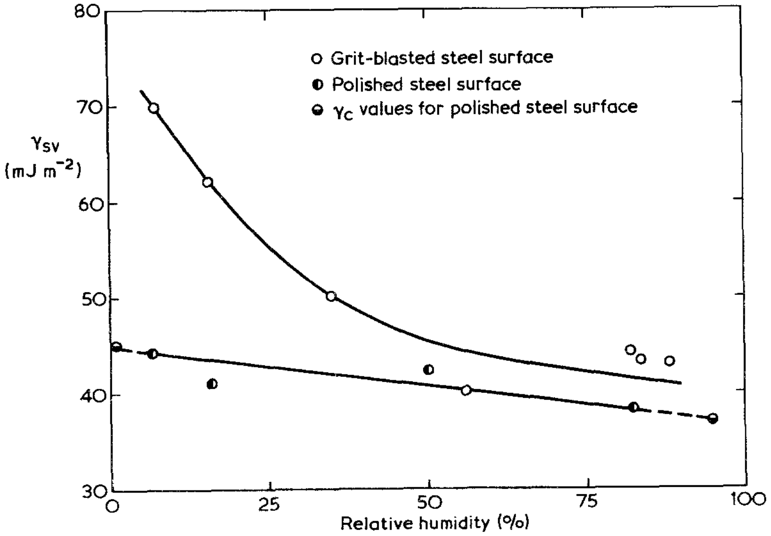


Figure 5 Surface free energy, γ_{SV}, of grit-blasted and polished mild-steel surfaces as a function of relative humidity. After Gledhill, Shaw and Kinloch [57].

envelopes for the grit-blasted mild-steel surfaces in 7% r.h. and 56% r.h. environments are shown in Fig. 6 with the typical γ^D_{LV} and γ^P_{LV} values for an amine-cured epoxide adhesive (Table I). As may be seen, the γ^D_{LV} and γ^P_{LV} values for this adhesive lie inside the 7% r.h. envelope but outside the 56% r.h. envelope, indicating wetting of the steel surface by the epoxide adhesive at the lower humidity but non-wetting at the higher humidity. When adhesive joints were prepared in these respective relative humidity environments the lower humidity resulted in significantly stronger joints. Thus the enhanced wetting of the steel surface by the adhesive at the lower humidity, as indicated by the wettability envelopes, was directly reflected in higher joint strengths.

Therefore it is important to ensure that the bonding environment is such that adsorbed contamination is kept to a minimum; the lower the extent of such contamination, the more readily will it be displaced by the adhesive which may then achieve intimate molecular contact with the solid substrate surface. If multilayer contamination is not displaced by the adhesive it will act as a "weak boundary layer" (see Section 3.5) and low joint strengths will result.

Finally, it is of interest to note that the presence of adsorbed hydrocarbons probably assists this displacement process since the common adhesives are usually relatively polar in character and thus will have a thermodynamic tendency to displace such non-polar contamination, especially if only physisorbed.

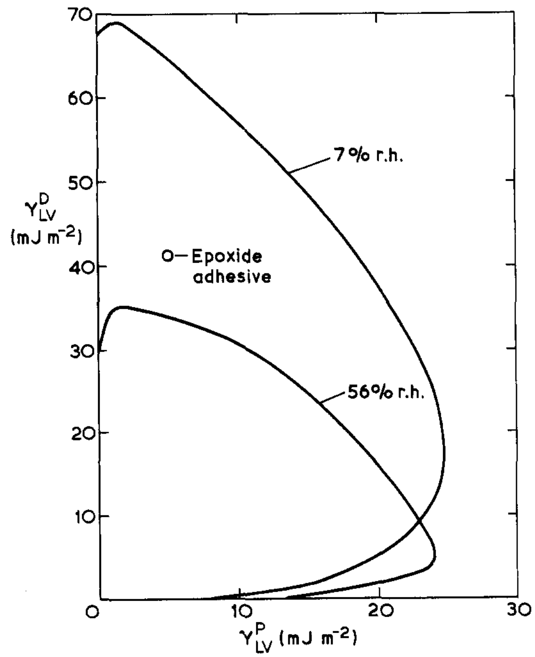


Figure 6 Wettability envelopes for grit-blasted mild-steel surfaces at various humidities. After Gledhill, Shaw and Kinloch [57].

2.5. Orientation at interfaces

Schonhorn [104] has shown that orientated *monolayers* of amphipathic molecules, such as stearic acid, may be employed as extremely effective adhesives in the bonding of polyethylene to aluminium; indeed, so effective are these adhesives, that joint strengths may exceed the cohesive strength of the polyethylene. Multi-layer adsorption lowered the joint strengths not because of less intrinsic adhesion of the amphipathic molecule to the substrate surface, but because the relatively thick layer possessed low cohesive strength and thus behaved as a weak boundary layer. While chemisorption was thought to occur for the stearic acid on the aluminium oxide [105, 106], Wake [107] has speculated that some diffusion occurs across the interface between the alkane chains of the acid and the polyethylene.

Recent elegant work by Baszkin, Nishino and Ter-Minassian-Saraga [53, 58, 108] has also demonstrated the effect that orientation at the interface may have upon measured joint strengths. They have quantitatively determined the surface densities of the polar sites on a polyethylene substrate as the surface is oxidised, employing a technique which is based upon the adsorption of radioactive calcium ions. They showed that as the temperature is raised to between about 80° C and 85° C there is a decrease in wettability, due to the increase of chain mobility, leading to the redistribution of polar groups into the bulk, and that the remaining surface density of polar groups depended upon the nature of the liquid in contact with the polyethylene. This loss of polar groups at elevated temperatures was mirrored by a loss in joint strength.

3. Mechanisms of adhesion

The mechanisms of adhesion are still not fully understood and many theories are to be found in the current literature. Often, the proponents of each theory offer their hypothesis as a comprehensive explanation of all adhesion phenomena and exclude all the alternative explanations. Much of this confusion undoubtedly arises because the test methods commonly employed to measure the strengths of adhesive joints are not well suited to theoretical analysis. They introduce geometrical factors and loading factors which are difficult to analyse, and the measured joint strength includes indeterminate contributions from rheological energy losses in the adhesive and substrate. Thus, although the intrinsic adhesion forces acting across the adhesive/substrate interface may affect joint strength they are usually completely obscured by other contributions, and information concerning the magnitude of such forces may only be indirectly obtained. This inability to measure the interfacial interactions has been the main obstacle to the development of a comprehensive theory of adhesion. The four main mechanisms of adhesion which have been proposed are:

(a) mechanical interlocking,
(b) diffusion theory,
(c) electronic theory,
(d) adsorption theory.

3.1. Mechanical interlocking

This theory proposes that mechanical keying, or interlocking, of the adhesive into the irregularities of the substrate surface is the major source of intrinsic adhesion. The attainment of good adhesion between smooth surfaces exposes this theory as not being of general applicability and the results shown in Fig. 4 must raise doubts as to whether any significant penetration of adhesive into some configurations of irregular cavities suitable for forming a mechanical key, for example, an "ink-pot" type cavity, would normally occur. However, there are some instances where mechanical interlocking has been demonstrated to contribute significantly to the intrinsic adhesion forces.

The most notable example of such a significant contribution is the adhesion of polymers to textiles. Many years ago Borroff and Wake [109–111] convincingly demonstrated that the most important single feature in the adhesion of a simple rubber to an uncoated fabric is the penetration of the protruding fibre ends of the spun yarn into the rubber. The degree of penetration necessary is such that, upon the rubber–textile structure being stressed, the length of fibre embedded is sufficient for the total shearing force on the fibre/rubber interface to exceed the breaking strength of the fibre. The intrinsic adhesion between fibre and rubber arises from primary or secondary forces, either chemical or van der Waals bonds, but is only of indirect importance since it will simply determine the length of fibre which is needed to be embedded before the interfacial shear strength exceeds the tensile strength of the fibre. If the fibre ends are removed by employing a fabric woven from continuous filament yarn then this mechanical interlocking mechanism can no longer operate. Hence, when using rayon, nylon or other continuous filament textiles, pre-treatments typically based upon isocyanates or resorcinol–formaldehyde are necessary to increase the contribution from primary and secondary interfacial forces to the intrinsic adhesion [12].

Another, but somewhat more contentious, example of where mechanical interlocking may contribute significantly to the intrinsic adhesion is the metal plating of polymers where a chemical pre-treatment of the polymeric substrate is employed prior to plating. Some workers [113–117] have argued that the adhesion of metal plating to polymeric substrates is a function of the surface topography. Others [117–120] have emphasised the role that increased oxidation of the polymer surface, commonly induced by the pre-treatments employed prior to plating, plays and thus the importance of surface force interactions. A balanced view emerges from the quantitative experiments of Perrins and Pettett [121] which enabled the contributions to the intrinsic adhesion arising from mechanical interlocking and surface force components to be separated out for the adhesion of electroplated copper to polypropylene. Following the theories of Andrews and Kinloch [70, 122] and Gent and Schultz [123], Wake [124] has suggested that the effects of mechanical interlocking and surface face components could be multiplied to give a result for the measured joint strength:

$$\begin{aligned}\text{Joint strength} &= (\text{constant})\\ &\quad\times(\text{mechanical component})\\ &\quad\times(\text{surface free components}).\end{aligned} \tag{21}$$

This equation reveals that the substrate should possess, simultaneously, the topography and surface chemistry necessary to produce the highest extent of mechanical interlocking and surface force contribution. Thus, this interaction results in the highest joint strengths.

Recent work by Packham and co-workers [125–130] provides further evidence for the importance of substrate surface topography when

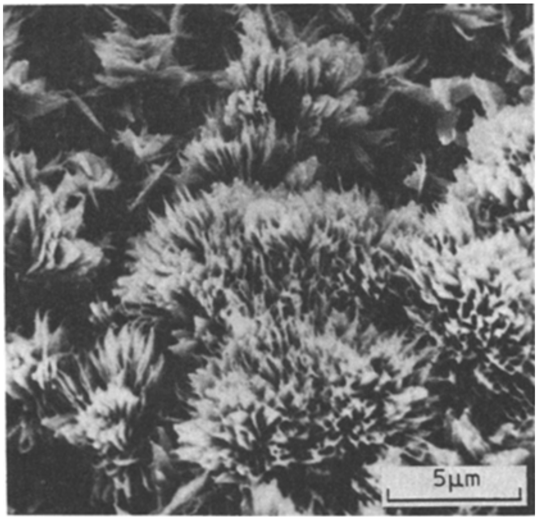


Figure 7 Fibrous copper (II) oxide prepated by immersion of copper in proprietary solution. After Evans and Packham [127].

considering the strength of certain interfaces. In their studies on the adhesion of polyethylene to metallic substrates they found that high peel strengths were obtained when a very rough, fibrous-type, oxide surface was formed on the substrate. Fig. 7 is a scanning electron micrograph of the surface of copper treated in a proprietary oxidizing solution which resulted in high joint strength. When the fibres were damaged to reduce the surface roughness, without detectably having changed the chemical nature of the substrate, the joint strength dropped markedly. However, if the chemical nature of the oxide was changed by electrolytic reduction, with a minimum change in topography, the strength was still substantial.

The enhancement of joint strength that may result from increasing the rugosity of the substrate surface, as detailed above by Packham and co-workers and previously by Jennings [131, 132], Bascom *et al.* [133] and Mulville and Vaishnav [134], need not necessarily arise either from a mechanical interlocking mechanism or indeed from an increase in surface area for bonding or from improved kinetics of wetting (see Section 2.3). The measured adhesive joint strength almost always reflects the value of two parameters: (a) the intrinsic adhesion and (b) the energy dissipated viscoelastically and plastically in the highly strained volume around the tip of the propagating crack and in the bulk of the joint. The latter term usually dominates the measured joint strength, and also gives rise to the rate and temperature dependence of joint strengths (see Section 3.4). Several workers [130, 135, 136] have suggested that the importance of high surface rugosity is to increase the energy dissipated viscoelastically and plastically during joint failure, and Evans and Packham [130] and Wang and Vazirani [136] have applied the theory of the strength of fibre reinforced composite material to the problem. Evans and Packham treated the polyethylene/fibrous oxide interfaces as a composite with discontinuous fibres in a resin matrix. When such a composite is stressed so that fibres and matrix are deformed elastically, stress is transferred from the fibres to the matrix in the region of the fibre ends and this leads to the build-up of high shear stresses at the fibre ends. Thus, by analogy, it is to be expected that the presence of fibres on the substrate would lead to high shear stresses around the fibre ends, giving failure by plastic deformation of the polymer, initially around the fibre tips, and then, as the stress concentration is relieved, further into the bulk of the polymer. Thus, a much larger volume of polymer will be plastically deformed during fracture, compared to that volume deformed when bonding to a chemically similar but smooth surface, and this large amount of plastic deformation accounts for the high joint strength.

Therefore, although in certain instances mechanical interlocking may contribute to the intrinsic adhesion forces, the frequently observed increase in measured joint strength with increasing surface rugosity may be attributable to other mechanisms.

3.2. Diffusion theory

Voyutskii [137] is the chief advocate of the diffusion theory of adhesion which states that the intrinsic adhesion of high polymers to themselves (autohesion), and to each other, is due to mutual diffusion of polymer molecules across the interface. This requires that the macromolecules or chain segments of the polymers (adhesive and substrate) possess sufficient mobility and are mutually soluble, that is that they possess similar values of the solubility parameter. The solubility parameter, δ, may be defined by

$$\delta = \frac{\Delta H_V - RT}{V}^{1/2}, \qquad (22)$$

where ΔH_V is the molar heat of vapourization, R is the gas constant, T is the temperature (K) and V is the molar volume.

Voyutskii's experimental evidence for his proposals are the effects of contact time, temperature, polymer type, molecular weight and viscosity on the measured joint strength. He argues that the functional dependence of joint strength on some of these parameters is similar to that expected for a diffusion process and therefore that adhesion is a result of diffusion. However, the dependence of measured joint strengths on parameters such as time-of-contact and polymer molecular weight, may be readily explained either by their effect on the kinetics of the wetting process in which intimate molecular contact is established between adhesive and substrate [138–142], or on the energy dissipative processes which may occur in the adhesive and the substrate during joint fracture. Vasenin [143–145] has adopted a more fundamental, theoretical approach to the diffusion theory and has derived an equation relating molecular characteristics of the polymer chain to measured joint strengths.

With regard to the autohesion of polyisobutylene, both experimental and theoretical relations for the measured joint strength as a function of the time-of-contact and polymer molecular weight are shown in Fig. 8. The agreement between the experimental results and the theoretical predictions is good although it should be noted that, since the values of two parameters in the theory could not be calculated, they were obtained by fitting to the experimental data. It is worthwhile to consider that, if the coefficient of diffusion is taken to be 10^{-14} cm^2 s^{-1}, Vasenin's theory predicts, for instance, that it takes one hundred hours (3.6×10^5 secs) for the molecular segments of one polyisobutylene sheet to penetrate 10 μm into the other. However, Voyutskii and Vasenin point out that a much smaller penetration can still result in high joint strengths and, for example, that an interpenetration of macromolecules between 10 and 20 Å may result in a five- to nine-fold increase in joint strength.

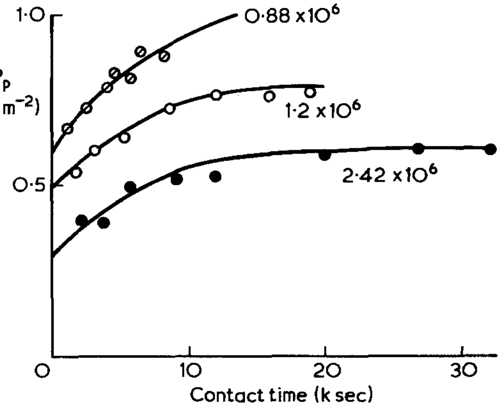


Figure 8 Relation between measured peeling energy, P_p, and contact time for the autohesion of polyisobutylenes of various molecular weights. The curves are calculated from diffusion theory and the points are experimentally determined. After Vasenin [143].

One criticism of this work is that, since peel tests introduce various geometric considerations and usually involve rheological properties of the adhesive and substrate, the results from such tests may be ambiguous. Campion [146, 147] has shown that the degree of autohesion of various elastomers may be correctly ranked from a consideration of the polymer's microstructure since this controls the ease with which cavities of space may form between chains, which directly affect the diffusion rate across the interface.

Direct evidence for inter-diffusion in compatible polymers does exist. Radiometric studies [148, 149] have demonstrated the presence of macromolecule diffusion. The diffusion constants were found to be of the order of 10^{-11} to 10^{-14} cm^2 s^{-1} which Voyutskii [150] argues is completely adequate for the formation of an intrinsically strong interface between the polymers after a contact time of only a few seconds, as discussed above. Further work [151, 152] using techniques of optical microscopy, including some under ultraviolet light employing luminescence analysis [153], has indicated that in compatible, non-polar polymers the zone of interfacial boundary dissolution due to diffusion may be about ten micrometres deep.

An area where inter-diffusion is of cardinal importance is the solvent-welding of plastics. This is a technique in which the adhesion of plastic components is promoted by the temporary presence of a solvent in the absence of an extraneous adhesive. A requirement of the solvent is that it strongly plasticises the surface of the polymers, which results in a large increase in free volume and hence in the chain mobility of the polymer in the interfacial region, increasing the rate and extent of inter-diffusion of the polymer chains. There should also be no major structural restriction on polymer chain movement such crosslinks and significant crystallinity, which confines this joining technique typically to glassy thermoplastics such as polystyrene, acrylic polymers, polysulphone, polycarbonate etc. [154].

In summary, the inter-diffusion of polymer chains across an interface requires the polymers (adhesive and substrate) to be mutually soluble and the macromolecules or segments to have sufficient mobility. These conditions are usually met in the autohesion of elastomers and in the solvent welding of compatible, amorphous plastics. In both these examples inter-diffusion does significantly contribute to the intrinsic adhesion. However, where the solubility parameters of the materials are not similar, or where one polymer is highly crosslinked, is crystalline or is above its glass transition temperature, then inter-diffusion is an unlikely mechanism.

3.3. Electronic theory

If the adhesive and substrate have different electronic band structures there is likely to be some electron transfer on contact to balance Fermi levels which will result in the formation of a double layer of electrical charge at the interface. The electronic theory of adhesion is due primarily to Deryaguin and co-workers [155–157] and they have suggested that the electrostatic forces arising from such contact or junction potentials may contribute significantly to the intrinsic adhesion. The controversy this theory has caused is due to this final statement that electrostatic forces are an important *cause*, rather than merely a *result*, of high joint strength.

Deryaguin's theory essentially treats the adhesive/substrate system as a capacitor which is charged due to the contact of the two different materials. Separation of the parts of the capacitor, as during interface rupture, leads to a separation of charge and to a potential difference which increases until a discharge occurs. Adhesion is presumed to be due to the existence of these attractive forces across the electrical double layer. This theory requires a variation of the measured work of adhesion with the pressure of the gas (governed by Paschen's Law, see for example [9]) in which the adhesive measurements are conducted ported no increase in the peel strength of pressure-sensitive tapes when tested in vacuum as opposed to atmospheric pressure. Further, Deryaguin has equated the measured work of adhesion, determined from peel tests, with the calculated electrical energy stored in a capacitor and reported good agreement between the two quantities. However, the majority of the measured work of adhesion is dissipated through viscous and visco-elastic responses of the materials and this energy should not have been included in the value equated with the electrical energy.

Skinner, Savage and Rutzler [159] have calculated the tensile strength of a metal/polymer/metal joint due to the existence of electrical double layers at the interfaces as a function of the volume charge density. For boundary charge densities of 10^{17}, 10^{19} and 10^{21} electrons cm^{-3} corresponding values of joint strength of 0.4 kPa, 40 kPa and 4 MPa were deduced, while the experimental measurements indicated that the maximum charge density was of the order of 10^{19} electrons cm^{-3} and the joint strength was of the order of 7 MPa. Roberts [160] has concluded that the maximum contribution to the thermodynamic work of adhesion for a natural rubber/glass interface is about 10^{-5} mJ m^{-2}, which is negligible compared to the contribution from van der Waals forces of about 60 mJ m^{-2}.

Graf Von Harrach and Chapman [161] have measured charge densities on a glass insulator substrate coated with a vacuum-deposited layer of gold, silver or copper and from such measurements deduced the electrostatic contribution to the work of adhesion. In Table II the values calculated are compared with the thermodynamic work of adhesion, W_A, deduced assuming only van der Waals interfacial attractions, and the measured adhesive peeling energy for removing the metallic coating. The contribution from electrostatic forces is usually much lower than that from van der Waals interactions.

Weaver [162–165] has employed the "scratch-test" to investigate the adhesion of various vacuum-deposited metallic films on a range of insulator, polymeric substrates. This test technique necessitates an extremely subjective interpretation and, although it has, as a consequence, been heavily criticised [166–169], the general trend of Weaver's results are intriguing. Weaver reported that upon ageing various metal/polymer interfaces large increases in the scratch resistance were found for copper, silver or gold coatings and smaller increases for aluminium. This appeared to be true irrespective of the nature of the polymeric substrates, although some polymers such as polypropylene and polytetrafluoroethylene exhibited much smaller effects than others like polycarbonate and polymethylmethacrylate. Previous work

TABLE II Electrostatic contribution to the adhesion of vacuum-deposited metals on glass substrates

Metal film	Work of Adhesion ($mJ\ m^{-2}$)		Adhesive peeling energy ($mJ\ m^{-2}$)
	Electrostatic contribution	Van der Waals contribution	
Gold	5	950	1400 ± 300
Copper	80	400	800 ± 200
Silver	115	800	1000 ± 200

[170, 171] on metallic coatings on glass had suggested that increases in scratch resistance upon ageing metal/glass interfaces were due to increased oxidation of the metal surface with time leading to stronger interfacial bonding, possibly due to an oxide bond between the metal and glass with an oxygen atom acting as a bridge [172]. However, Weaver considered that the inclusion of gold in the above list made any such analogous explanation unlikely for the metal/polymer interfaces. The key experiment was to deposit the metal onto the polymeric surface, age the specimen to increase the measured interfacial strength, and then to replace the coated polymer in a vacuum chamber and expose it to a glow discharge for a few minutes. The glow discharge has been found to produce no changes in the measured strength of copper coated onto glass, where primary chemical bonding via an oxide layer occurs, but for copper on polymethylmethacrylate the high interfacial strength which had developed on ageing was reduced to the initial level and started to build again on further ageing.

Weaver concluded that the way in which an ionizing discharge removed the increased adhesion confirmed the electrical nature of the increased adhesion, although the exact mechanism of charge transfer between the film and substrate remained unidentified. Deryaguin and others [173] have suggested that an electron transfer from the metal to the polymer so as to equalize the Fermi levels is responsible, but Weaver considered that this should be a fairly rapid process and although it might explain the initial adhesion it could not explain the slow build-up in adhesion that was observed upon ageing. Also if the electrons have to enter the conduction band, a metal electron would have to acquire extra energy of the order of 2–3 eV and Weaver considered the chances of this to be negligible. Finally, according to Deryaguin's mechanism the magnitude of the charge transferred, and therefore the adhesion, should depend directly on the height of the potential barrier at the metal/polymer interface but Weaver [162] found no correlation between the work function of the metal and the measured strength. In the light of these and other observations Weaver suggested that the Fermi level in the polymer was initially above that in the metal and thus the charge transfer producing adhesion might be due to positive hole injection, i.e. electron transfer from polymer to metal. Further, under these conditions the charge build-up would be slow since there are very few conduction electrons in any insulator and even these are likely to lie in electron traps which would greatly reduce the electron mobility and increase the time required for charge to build-up at the interface. The final charge concentration under these conditions might easily depend on the number of available electrons rather than the difference in energy levels and it would be impossible to trace any correlation between final adhesion and work function.

Several groups of workers [174–177] have investigated the improvement in the adhesion of thin metal films which is recorded if the insulator substrate is subjected to a low-pressure glow discharge prior to coating. Stoddart *et al.* [175] found no net surface electric charge on the substrate but found that the electron emission was altered, indicating that the surface electronic states of the substrate had been changed. The mechanisms of adhesion, and the relative importance of any electrostatic contribution, remain therefore somewhat vague. Recognising this, Wake [47] has recently suggested that, while the nature of the charge-carrying bodies in polymers is obscure, it is known that additives and impurities may drastically affect their ability to form electrical double layers and thus it would be extremely worthwhile to generate data on radiation polymerized material made from a highly purified monomer.

Finally, however, an interface where the influence of an electrostatic double layer has been clearly demonstrated is Zr-coated gold spheres on CdS single crystal substrates [178, 179]. The adhesive force was measured by a centrifuge technique as the intensity of the illumination on the adhesive system was varied. This changed the electronic properties of the photoconducting CdS substrates and hence the electrostatic double layer force at the interfaces could be varied leaving the other forces, e.g. van der Waals forces, unaffected. Qualitatively the experimental results were in agreement with a simple model of the metal–semiconductor contact.

It should be noted that most workers have described their results in terms of the bulk electronic properties of the materials. However, since, for example, most metals are covered by an oxide layer which has its own electronic states which may well influence the electron transfer mechanisms, the possibly greater relevance of the surface electronic states should not be overlooked.

3.4. Adsorption theory

The adsorption theory of adhesion is the most generally accepted theory and has been discussed in depth by Kemball [180], Huntsberger [69], Staverman [181] and Wake [182]. This theory proposes that, provided sufficiently intimate intermolecular contact is achieved at the interface, the materials will adhere because of the surface forces acting between the atoms in the two surfaces; the most common such forces are van der Waals forces and are referred to as secondary bonds. In addition, chemisorption may well occur and thus ionic, covalent and metallic bonds may operate across the interface; these types of bonds are referred to as primary bonds. The terms primary and secondary are in a sense a measure of the relative strength of the bonds as may be seen from Table III where the types of bonds are shown with estimates of the range of magnitude of their respective bond energies.

3.4.1. Secondary force interactions

Huntsberger [69, 185] and others [186, 187] have calculated the attractive forces between two planar bulk phases due solely to dispersion forces and have showed, for example, that even at a separation of one nanometre the attractive force would be approximately 100 MPa. This is considerably higher than the experimental strength of most joints. This discrepancy between theoretical and experimental joint strengths is attributed to air voids, cracks, defects or geometric features acting as stress raisers when the joint is loaded, causing rupture of the joint at stresses very much below the theoretical value. However, this calculation does indicate that high joint strengths may result from the intrinsic adhesion arising from solely dispersion force interactions.

The thermodynamic work of adhesion required to separate a unit area of two phases forming an interface, W_A, may be related to the surface free energies by the Dupre equation. In the absence of chemisorption and inter-diffusion the reversible work of adhesion, W_A, in an inert medium may be expressed by

$$W_A = \gamma_a + \gamma_b - \gamma_{ab}. \tag{23}$$

This equation only applies strictly to a solid/liquid or liquid/liquid interface but, by assuming that the surface energy of a liquid does not change significantly when it solidifies isothermally and ignoring any shrinkage stresses, it may be applied to solid-adhesive/substrate interfaces. By using Equation (14) to eliminate the interfacial free energy, γ_{ab}, then gives

$$W_A = 2(\gamma_a^D \gamma_b^D)^{\frac{1}{2}} + 2(\gamma_a^P \gamma_b^P)^{\frac{1}{2}}. \tag{24}$$

It is a recurrent hypothesis in the literature that the measured strengths of adhesive joints may be correlated with the thermodynamic work of adhesion, W_A, [64–66, 188–192]. Indeed, shortly after Zisman introduced his concept of the critical surface tension of wetting, γ_c, Levine *et al.* [188] reported a correlation between the strength of joints prepared from an epoxy adhesive bonding various polymeric substrates and the γ_c of the substrate, as shown in Fig. 9. However, while some subsequent authors [189–191] have confirmed such correlations others [98, 192] have found none. The main cause for this conflict is that the test methods commonly employed for measuring the strengths of adhesive joints are not well suited to theoretical analysis, as will be shown in detail in Part 2 of this review. Furthermore, such a correlation would only be expected when the locus of joint failure is interfacial. Thus, although the thermodynamic work of adhesion may affect joint strength it is often completely obscured by other contributions.

By adopting a continuum fracture mechanics approach, the work of Andrews and Kinloch [70, 122, 194, 195] and Gent and Kinloch [193] defined a geometry independent measure of joint strength, the adhesive failure energy, *P*. Model joints were prepared between a crosslinked amorphous (a-styrene-butadiene-rubber) and rigid poly-

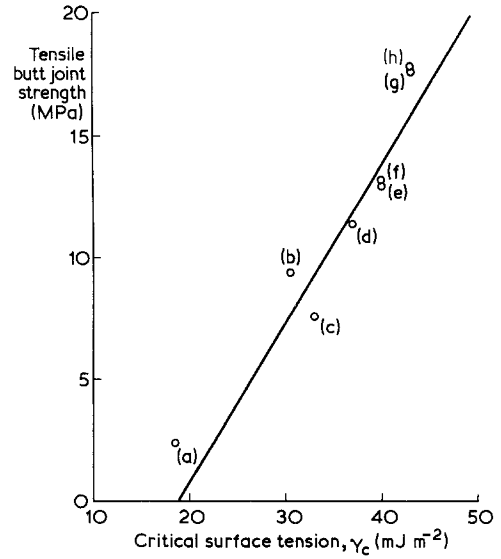


Figure 9 Relation between measured joint strength and critical surface tension, γ_C, of the substrate for an exoxy adhesive bonding various polymeric substrates: (a) polytetraflouroethylene; (b) polyvinylflouride; (c) polystyrene; (d) polyvinylalcohol; (e) polyvinylidenechloride; (f) polyvinylchloride; (g) polyethyleneteraphthalate; (h) poly (1, 4-cyclohexylenedimethyleneteraphthalate). After Levine, Ilkka and Weiss [188].

meric substrates and the adhesive failure energy, P, was determined for a wide range of temperatures, T, and rates of crack propagation, $\dot{c}$. For any given rubber–substrate joint the results yielded a single master curve when normalised to a reference temperature by means of the Williams-Landel-Ferry rate-temperature-equivalence for simple viscoelastic materials. The results so obtained are shown in Fig. 10, where the observed rate of crack propagation, $\dot{c}$, has been transferred into a reduced rate, $\dot{c}\,a_T$, using the glass transition temperature, T_g, of the rubber as the reference temperature [196, 197]

$$\mathrm{Log}_{10}\,a_T = \frac{17.4\,(T-T_g)}{51.6+T-T_g}. \qquad (25)$$

There are several noteworthy features of Fig. 10. Firstly, the relations for the adhesive failure energies and cohesive fracture energy are strictly parallel. This suggested, initially, that purely interfacial failure could not occur, and that cohesive failure must take place in the adhesive, albeit close to the interface. However, this reasoning was considered to be fallacious since the rubbery adhesive in the vicinity of the crack was subjected to stresses (and thus energy losses) whether the crack travelled within the rubber or along the interface. Secondly,

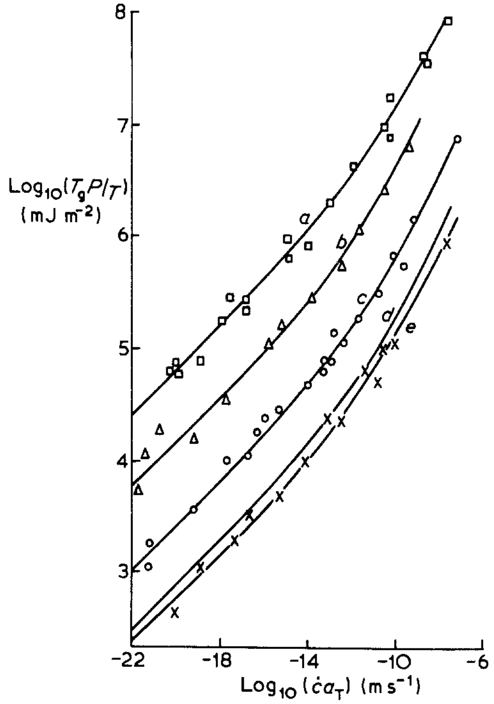


Figure 10 Adhesive failure energy, P, shown against reduced rate of crack propagation, $\dot{c}a_T$ for various styrene–butadiene–rubber/polymeric substrate joints: (a) cohesive fracture energy, τ, for the rubber; (b) adhesive failure energy, P, for rubber/etched fluorinated ethylene-propylene copolymer substrate; (c) adhesive failure energy, P, for rubber/treated fluorinated ethylene-propylene copolymer substrate; (d) adhesive failure energy, P, for rubber/polyethyleneterephthalate substrate; (e) adhesive failure energy, P, for rubber/nylon 11 substrate. After Andrews and Kinloch [70].

the relation between P and $\dot{c}a_T$ for a given rubber/substrate joint could be described by a single master curve which embodies all the individual measurements. This dependence of P upon the rate of propagation and temperature, in agreement with the Williams-Landel-Ferry relation for simple viscoelastic materials, clearly demonstrated the importance of the viscoelastic response of the rubbery adhesive in determining the magnitude of the observed failure energy. Indeed, the energy dissipated viscoelastically at the propagating crack tip was usually the dominant term in the observed failure energy, but the value of P did approach the expected value for the thermodynamic work of adhesion, W_A, at low rates and high temperatures when the viscoelastic energy losses were relatively small. Further experimental and theoretical considerations [70, 122, 123, 195] demonstrated that the adhesive failure energy, P, for a crosslinked rubbery adhesive/rigid plastic substrate interface could be divided into two major components:

(a) The energy required to propagate a crack through unit area of interface in the absence of viscoelastic energy losses, i.e., an intrinsic adhesive failure energy, P_0;

b) The energy dissipated viscoelastically within the rubbery adhesive at the propagating crack, again referred to unit area of interface.

The intrinsic adhesive failure energy, P_0, was evaluated and found to be virtually independent of rate and temperature, since its value depended upon the type and strength of bonding forces at the interface (or in the adhesive or substrate depending upon the locus of failure). The energy dissipated viscoelastically was usually the dominant term and was, by definition, rate, $\dot{c}$, and temperature, T, dependent. Thus, it was shown that

$$P = P_0 \mathbf{F}(\dot{c}, T), \qquad (26)$$

where **F** is a viscoelastic loss function dependent upon the rate and temperature (and strain at points remote from the crack [198]). P_0 was then expressed as a weighted average of the various failure modes,

$$P_0 = iI_0 + r\mathscr{T}_0 + sS_0, \qquad (27)$$

where I_0, $\mathscr{T}_0$ and S_0 are the intrinsic failure energies for interfacial, cohesive-in-rubber and cohesive-in-substrate failure respectively, and i, r and s are the respective area fractions of interfacial failure, failure in adhesive and failure in substrate. For those joints which exhibited a solely interfacial locus of failure and in which only secondary bonding was established across the interface then $i = 1$, $I_0 = W_A$ and therefore P_0 should be equal to the thermodynamic work of adhesion, W_A. The value of P_0 was ascertained from these mechanical property studies and compared to values of W_A calculated from Equation (24) and the two parameters were found to be in good agreement, as may be seen from Table IV.

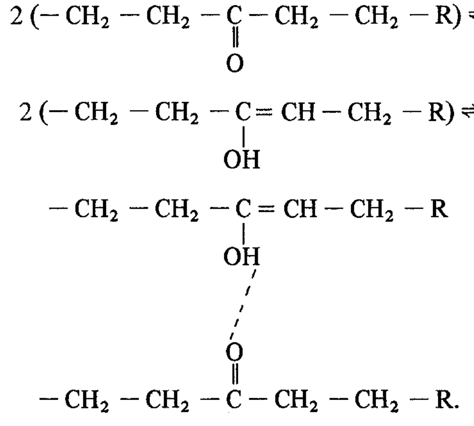
TABLE III Bond types and typical bond energies [183, 184]

Type	Bond energy (kJ mol^{-1})
Ionic	590 – 1050
Covalent	63 – 710
Metallic	113 – 347
Permanent dipole-dipole interactions	
Hydrogen bonds involving fluorine	Up to 42
Hydrogen bonds excluding fluorine	10 – 26
Other dipole-dipole (excluding hydrogen bonds)	4 – 21
Dipole-induced dipole	Less than 2
Dispersion (London) forces	0.08 – 42

TABLE IV The intrinsic adhesive failure energy, P_0, and thermodynamic work of adhesion, W_A, for a styrene-butadiene-rubber adhering to various substrates [70]

Substrate	P_0 (mJ m^{-2})	W_A (mJ m^{-2})
Fluorinated ethylene–propylene co-polymer	22	48
Plasma-treated fluorinated ethylene–propylene co-polymer	69	57
Polychlorotfifluorethylene	75	63
Nylon 11	71	71
Polyethyleneterephthalate	79	72

As may be seen from Table III, the strength of the hydrogen bond lies between that of the van der Waals forces and the primary bonds, and the formation of hydrogen bonds across the interface may certainly increase the intrinsic adhesion as has been discussed by Pritchard [199]. He cites the dipping of nylon cords into a complex adhesive mixture of rubber and resorcinol–formaldehyde, as used in the production of tyres, as an example where hydrogen bonding may play an important role; the resorcinol–formaldehyde being adsorbed onto the nylon surface via hydrogen bonds through the phenolic groups. Another example where hydrogen bonding has been shown to play an important role is in the autohesion of polymers which have been subjected to surface oxidation by immersion in certain acids [57, 200] or exposure to an electrical ("corona") discharge [201–203]. In the case of polyethylene, the formation of hydrogen bonds has been suggested to be the result of tautomerization according to a series of the following transformations:

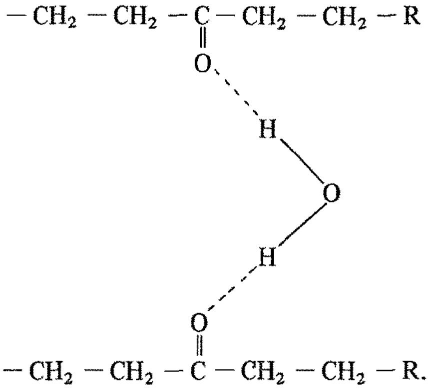


$$2(-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-R) \rightleftharpoons$$

$$2(-CH_2-CH_2-\underset{\underset{OH}{|}}{C}=CH-CH_2-R) \rightleftharpoons$$

$$\begin{array}{c} -CH_2-CH_2-\underset{\underset{OH}{|}}{C}=CH-CH_2-R \\ \vdots \\ -CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-R. \end{array} \qquad (28)$$

Here the carbonyl group at the surface of the oxidized polyethylene may first undergo the tautomerization of the ketone to the enolic form. The enolic form then exhibits an acidic character and may form a hydrogen bond with a carbonyl group of adjacent surface. A second possible mechanism of hydrogen bond formation is via a water molecule [53]



(29)

Some supporting evidence for these schemes comes from the studies of Blythe *et al.* [203] who have employed X-ray photoelectron spectroscopy to analyse the surface of oxidized polyethylene. However, their results also indicate that several other hydrogen bonding mechanisms should be considered.

It has also been suggested [46, 204] that acid–base interactions across an interface may contribute to intrinsic adhesion forces. The analysis presented by Bolger and Michaels [204] attempts to identify many of the distinguishing features of acid–base interactions in terms of the ionic character of a hydroxylated metal oxide substrate and the organic functional group provided by the adhesive.

3.4.2. The role of primary interfacial bonding

Although it is evident that intrinsic adhesion arising from secondary bonding forces alone may result in adequate and high joint strengths, many adhesion scientists, including the author, believe that the additional presence of primary bonding may often increase the measured joint strength and is certainly a necessary requirement for securing environmentally stable interfaces. However, although there is considerable indirect evidence [195, 205–216] emphasizing the importance of interfacial chemical bonding, studies which directly confirm its role are scarce. The use of sophisticated, surface-specific, analytical techniques such as Laser-Raman spectroscopy [217], X-ray photoelectron spectroscopy [218] and secondary-ion mass spectroscopy [219, 220] has produced definitive evidence that primary interfacial bonding may occur in certain circumstances and may make a significant, indeed often vital, contribution to the intrinsic adhesion.

One of the most controversial areas for the role of primary interfacial bonds has been when adhesion promotors, or coupling agents, are employed to enhance the joint strength or, more commonly to enhance the environmental resistance of the interface to attack by moisture. The various types of adhesion promotors that have been employed have been the subject of many papers [221–228] and it is sufficient to note here that the most common type are the silane coupling agents which have the general structure $X_3Si(CH_2)_nY$, where $n = 0$ and 3, X is a hydrolysable group on silicon and Y is an organofunctional group selected for compatibility with a given resin. They are widely used as a surface finish on glass fibres prior to forming a glass fibre reinforced composite, as an additive in adhesive formulations and as a primer applied to the substrate prior to adhesive bonding.

The silane films usually employed on the substrate have been shown to be polymeric [229, 230]; indeed, the films were found to be much thicker than a monolayer of silane monomer and appeared to be composed of a strongly held polysiloxane network along with some hydrolysed or partially hydrolysed silane and small polysiloxane molecules.

Until recently there has been little known of the mechanism by which the intrinsic adhesion of the interface is enhanced, especially with respect to environmental attack. The generally, but not universally, accepted mechanism by which the durability of the joint is increased is the formation of strong, primary interfacial bonds. For the polysiloxane/substrate interface this arises from the formation of Si–O–substrate bonds. For the adhesive/silane interface this arises from the reaction of the Y-group on the silane with reactive groups in the adhesive. Alternatively, other features such as wetting [225] and the possible formation of a boundary layer in the adhesive differing in chemical and physical properties to that of the bulk resin [13] have been suggested to be of importance.

Recent studies by Koenig and Shih [217], employing Laser-Raman spectroscopy have clearly established the presence of $\equiv$Si–O–Si$\cdot\cdot$ bonding across a polysiloxane/glass interface, and the presence of such bonds most probably accounts for the increased water resistance of glass fibre composites and glass joints, bonded with structural adhesives [231] when a silane primer is present. Also Gettings and Kinloch [219, 220] have employed secondary ion mass spectroscopy (SIMS) to investigate the interfacial interactions between a γ-glycidoxypropyltri-methoxy silane primer deposited onto a mild- or stainless-steel substrate. With the SIMS technique, ionized particles ejected from the surface by the action of an argon beam are mass-analysed. As the current densities used in SIMS are low (of the order of $10^{-10}\,\mathrm{A\,cm^{-2}}$) the first one or two monolayers of the surface can be investigated. Either atoms or molecules can be ionized and thus details of the chemical state of the atoms in a surface can be inferred. This technique revealed that good interface stability was associated with the presence of $\mathrm{FeOSi^+}$ radicals from the primer-coated mild steel surface and $\mathrm{FeOSi^+}$ and $\mathrm{CrOSi^+}$ radicals from the coated stainless steel surface. Thus providing firm evidence for the formation of primary interfacial bonding, probably –Fe–O–Si$\equiv$ and –Cr–O–Si$\equiv$ respectively between the metal oxide and polysiloxane primer.

Somewhat different examples of instances where strong interfacial bonding has been confirmed come from the use of inelastic electron tunneling spectroscopy [232–234] and attenuated total reflectance infra-red spectroscopy [235]. In these studies organic molecules were found to chemisorb onto metal oxides and the bonding was found to be almost purely ionic in character. Inelastic electron tunneling spectroscopy is an exciting new technique for investigating the vibrational spectra of organic molecules adsorbed onto solid surfaces [232, 236–238]. It is based upon quantum-effect tunneling of electrons through a thin insulating layer sandwiched between two metal films. The insulating layer should be about 2 to 3 nm thick for optimum resolution but it can be composed of two parts, typically the oxide of one metal substrate and a superimposed monolayer of the organic material of interest. Small voltages are applied across the insulating layer and the vibrational spectra of its components are determined by the energy lost by tunneling electrons. Data is generally obtained in terms of the second derivative ($\partial^2 I/\partial V^2$) of the tunneling current, I, as a function of the applied voltage, V, since this is the analog of an infra-red spectrum. Chu *et al.* [232] examined the adsorption of 4-hydroxybenzoic acid on aluminium oxide and concluded that the bonding was ionic in character ($-\mathrm{COO^-Al^+}$) with the phenyl ring orientated perpendicular to the surface. These new, surface-specific techniques should provide much interesting information on the nature of interfacial bonding and considerably assist in the identification of mechanisms of adhesion.

3.5. Weak boundary layers

The topic of weak boundary layers is included in this section since it has been the subject of considerable controversy in discussions of the mechanisms of adhesion, especially with respect to low-energy substrates which are usually subjected to various surface pretreatments prior to bonding in order to improve their adhesion.

Bikerman [5] initiated the debate when he stated that even though failure might appear to be interfacial, with the separation appearing to be exactly along the adhesive/substrate interface, a cohesive break of a weak boundary layer is the real event. Bikerman has proposed many classes of weak layers and offered two basic premises to explain why joints never fail interfacially.

Firstly, he considered the probability of a crack situated at the interface, between an adhesive molecule and a substrate molecule, proceeding along the interface. Considering a two-dimensional structure, the crack must propagate either between two molecules of the adhesive or between two molecules of the substrate, or between a molecule of the adhesive and a molecule of the substrate. If these three paths are equally probable, the probability of the crack propagating along the interface is $\frac{1}{3}$. Thus the probability of the crack propagating along the interface between $(n + 1)$ pairs of dissimilar molecules is $(\frac{1}{3})^n$, and this probability of course decreases even further if a three-dimensional structure is considered. Therefore, when the formation of a crack between any two molecules is equally probable, the fracture can never occur only along the adhesive/substrate interface for purely statistical reasons. Secondly, he considered the forces of attraction between two dissimilar gases and showed that the attraction between two dissimilar molecules is smaller than between two identical "strong" molecules, but greater than between two "weak" molecules. Thus, by analogy to adhesive systems, molecules favour rupture in cohesion in the weaker phase.

Huntsberger [239] and Voyutskii [240] have critically examined these premises and have shown that the simplifying assumptions made by Bikerman do not hold for most practical systems. They have pointed out that Bikerman has failed to take into account the structure of real adhesives which are invariably polymeric. Structural features such as chain entanglements, crystallinity, and orientation of chains and cross-links will result in the cohesive fracture stress often being much greater than that required for interfacial failure where often only secondary intermolecular forces are involved. Experimentally, also, much evidence [122, 239, 241–245] has been published to show that interfacial failure can occur and does so fairly frequently. The new techniques of Auger and X-ray photoelectron spectroscopy have confirmed instances of interfacial failure beyond any doubt [102, 246, 247]. Further, even if the locus of joint failure is cohesive in the adhesive or substrate, close to the interface, this does not necessarily imply the presence of a weak boundary layer. Several authors [133, 248] have recently suggested that the stress distribution in the joint and around the tip of a crack propagating close to the interface causes "mechanical focusing" of the failure path close to the interface.

More recently Bikerman's ideas on weak boundary layers have been revitalised by the conclusions drawn by Schonhorn and co-workers. In 1966 Schonhorn and Hansen [249] reported a highly effective treatment for the surface preparation of low surface energy polymers to enhance adhesive bonding. Essentially the technique consisted of exposing the polymer surface to an inert gas plasma at reduced pressure generated by an electrodeless glow discharge (i.e. radio-frequency field). For polyethylene only very short treatment times were necessary and Schonhorn and co-workers [249–252] reported that, whilst this treatment did not change the wettability of the polyethylene, as measured by the critical surface tension, gel permeation chromatography showed that some highly crosslinked polymer was formed after treatment and the weight- and number-average molecular weights, M_w and M_n, increase from 86 000 to 135 000 and from 1 800 to 4 000 respectively. Also, attentuated total reflectance infra-red spectroscopy showed only the formation of transethylenic unsaturation after treatment and a thin intractable skin was readily observed by melting the polymer. However, attentuated total reflectance infra-red spectroscopy is not a true surface technique. The technique has a sampling depth, typically about 1 μm, that is relatively large compared to the likely depth of affected polymer, and care must therefore be taken to avoid possible misinterpretation of the results. Notwithstanding this, Schonhorn concluded that wettability was not the sole criterion for the formation of an adhesive joint and that the enhancement of the cohesive strength of a weak surface might be a factor of greater importance. He suggested that many melt-crystallized polymers possess an inherently weak boundary layer, between about 0.02 and 0.10 μm thick, which is composed of amorphous low molecular-weight materials rejected by the crystallization process. (The crystallization process was assumed to start in the bulk and proceeds outwards.) It was therefore concluded that the increases in joint strength achieved by this technique were primarily due to increasing the cohesive strength of the polymer in the surface regions by the introduction of crosslinks. The surface treatment was therefore called CASING (Crosslinking by Activated Species of Inert Gases).

Schonhorn and co-workers [253–255] have examined the effect of similar gas plasma treatment on improving the joint strengths of many polymeric substrates and have also investigated other methods [254, 256–259] for increasing the strength of any weak boundary layer which may be present.

A major criticism of Schonhorn's proposal that a weak amorphous surface is produced when polymeric films are melt crystallized in air is that his evidence is mainly inferred. Indeed, recent work by Briggs and co-workers [246, 247] using X-ray photoelectron spectroscopy found no evidence of joint failure occurring in the surface regions of a polyethylene substrate. Furthermore, many workers [64, 70, 260–267] have established that the surface free energy of the polymer substrate may be increased by the glow discharge treatment, and by some of the other treatments, investigated by Schonhorn. Thus, surface energetics and the production of chemically active species, to which grafting may occur, may account for the observed increased adhesion.

Therefore, while certain classes of weak boundary layers are well established, for example surface contamination (Section 3.4.2), their presence in joints where low strengths are recorded should not be automatically assumed.

4. Concluding remarks

The present paper, Part 1 has reviewed the reasons why materials adhere together with the role that surface and interfacial forces take in joint formation and rupture. Part 2 of this review will examine the mechanics and mechanisms of adhesive joint fracture and the effects of various operating environments on joint performance.

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