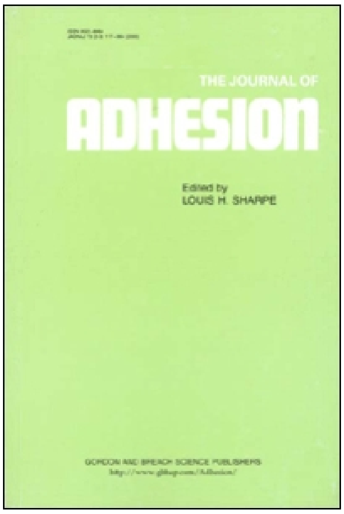

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# Some Contributions of Surface Analysis to the Development of Adhesion Theories

D. E. Packham[a]
[a] Centre for Materials Research, University of Bath, Claverton Down, Bath, UK

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# Some Contributions of Surface Analysis to the Development of Adhesion Theories

**D. E. Packham**
Centre for Materials Research, University of Bath,
Claverton Down, Bath, UK

*A concise historical account of the development of adhesion theories and a critical discussion of their contemporary relevance are given.*

*The pioneering work of McBain and Hopkins in 1925 led to the development of the modern adsorption and mechanical theories of adhesion. Somewhat later, there were important contributions from Russia where workers introduced the electrostatic theory (Deryaguin) and the diffusion theory of adhesion (Voyutskii).*

*Recent developments in contact mechanics, molecular dynamics, and, in particular, surface analysis have provided considerable insight into the nature of the interface and interfacial region in adhesive joints. These suggest that adsorption, mechanical, and even diffusion effects cannot be completely isolated from one another. It is argued that each theory is best regarded as emphasising a different aspect of a more comprehensive model which, in principle, relates molecular dispositions in the region of the interface to macroscopic properties of an adhesive joint.*

**Keywords:** Adhesion theories; Contact mechanics; Interdiffusion; Molecular dynamics; Segregation; Surface analysis

## 1. INTRODUCTION

Recent decades have seen a great clarification in our understanding of theories of adhesion, of the relationship between models of mechanisms on the molecular level, and the failure stresses and energies of

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Address correspondence to David E. Packham, Centre for Materials Research, University of Bath, Claverton Down, Bath, BA2 7AY, UK. E-mail: d.e.packham@bath.ac.uk

adhesive joints and of adhesively bonded structures. The development of surface analytical techniques have played a significant part in this clarification, and it is largely through the application of such techniques to adhesion problems that John Watts has established his reputation as a leading research scientist in the field. It seems appropriate then for a short review of some recent strands in the development of adhesion theories to form part of a collection of papers produced to Mark John Watts' work.

## 1.1. Newton's Challenge

The successful use of adhesives goes back many millennia, and so too must the tacit knowledge necessary for their successful use. In the upper palaeolithic era (between 40,000 and 10,000 years ago) stone and bone points were glued with resin to wooden shafts to produce spears. In the fifth millennium B.C., bitumen was being used as an adhesive to bond stone bladelets set obliquely in wooden handles of sickles in Mehrgarh on a tributary of the Indus [1]. By the first dynasty of ancient Egypt (*ca.* 3000 B.C.) natural adhesives were used to attach inlays to furniture [2].

By the seventeenth century Galileo, who was aware of the significance of surface roughness in adhesion and knew that rough surfaces required "the introduction of some sticky, viscous or gluey substance" for adhesion to occur [3], was placing the phenomenon of adhesion within the then traditional scientific paradigm, arguing that the Aristotelian principle of nature's abhorrence of a void provided the resistance to separation of the materials joined [4].

Further development came with Newton, who, in the 1730 s, having abandoned the Aristotelian paradigm, was arguing that adhesion was a result of "very strong attractions" between the particles of bodies. After mention of gravitational, magnetic, and electrical attractions, he postulated, "Some force [between particles], which in immediate contact is exceeding strong,... and reaches not far from the particles with any sensible effect." What these attractions were, Newton did not speculate, but left the challenge: "It is the business of experimental philosophy to find them out!" [5]. To what extent has modern science risen to Newton's challenge?

## 1.2. Structure of This Article

In this article an answer to this question will be suggested which first traces the development of the "classical" adhesion theories to the middle decades of the last century (Section 2), then some more recent work will be cited with emphasis on results obtained by surface analysis (Section 3).This suggests a modest reassessment of the relationship between these theories (Section 4).

## 2. CLASSICAL THEORIES OF ADHESION

### 2.1. McBain and Hopkins: Specific and Mechanical Adhesion

Most historical surveys treat the work of McBain and Hopkins in 1925 as the earliest application of modern scientific investigation to the study of adhesion [6]. McBain and Hopkins considered that there were two kinds of adhesion, specific and mechanical. Specific adhesion involved interaction between the surface and the adhesive: this might be "chemical or adsorption or mere wetting," Specific adhesion has developed into the model we today describe in terms of the adsorption theory. We now recognise that when adhesive and substrate come into contact (*i.e.* the substrate is wetted) adsorption of some sort will necessarily occur. The forces involved, which may range from secondary van der Waals forces (physical adsorption) to primary chemical bonding (chemisorption), play a crucial part in adhesion.

In contrast, mechanical adhesion was only considered possible by McBain and Hopkins with porous materials. It occurred "whenever any liquid material solidifies in situ to form a solid film in the pores." They cite as examples adhesion to wood, unglazed porcelain, pumice, and charcoal. For McBain and Hopkins mechanical adhesion was very much a common sense concept, "It is obvious that a good joint must result when a strong continuous film of partially embedded adhesive is formed in situ."

Despite its "obvious" nature, the mechanical theory of adhesion fell out of favour, and was largely rejected by the 1950s and 60s. This rejection was prompted by observations that the roughening of surface in some instances lowered adhesion and by the tendency to rationalise examples of increased adhesion to rough surfaces in terms of the increased surface area available for "specific adhesion" to take place [7].

However, by the 1970s the mechanical theory was again being taken seriously. This was in part a result of the realisation, brought by advances in electron microscopy, that some interesting and effective substrates were microporous or microfibrous in nature [7]. Since this period there have been innumerable examples in the literature of surfaces with roughness ranging from the macro to the nano and molecular scale associated with enhanced adhesion [8–10]. The enhancement of adhesion is generally a result of a more subtle mechanism than that suggested by a mere increase in surface area, leading to proportionately more interactions across the surface. The roughness will often alter the stress distribution in the joint when loaded, so as to involve larger volumes of adhesive in plastic deformation during the fracture process. This increases plastic losses during fracture: the increased energy loss is reflected in a higher practical adhesion to the rough surface.

## 2.2. Voyutskii and Deryagin: Diffusion and Electrostatic Theories

Two other theories of adhesion, which are still featured in contemporary discussions, have their origins in the mid years of the last century: these are the Diffusion theory and the Electrostatic theory, which were largely developed in Russia and became widely known in the 1960s.

### *2.2.1. Diffusion Theory*

This was originally associated with Voyutskii and other Russian workers [11]. Much of Voyutskii's original work was done on the self-adhesion (called autohesion) of unvulcanised rubber. It was extended to polymer adhesion, more generally, and to even the adhesion of polymers to metals. The theory postulates that the molecules of the two parts of the specimen interdiffuse, so that the interface becomes diffuse and eventually disappears. It was argued that the development of adhesion with time, the effects of molecular weight, of polarity, and of cross-linking all proved that the adhesion was associated with the interdiffusion of polymer chains.

### *2.2.2. Electrostatic Theory*

This was put forward by Deryagin and Krotova [12] in 1948. The interface is seen as analogous to the plates of an electrical condenser across which charge transfer occurs. Electrical phenomena (*e.g.* sparking) can often be demonstrated to accompany the destruction of an adhesive bond. Some indirect evidence for electrical mechanisms has been found. Many critics pointed out examples where a change of filler or of polymer might lead to the absence of electrical phenomena, despite there being similar levels of measured adhesion: most cases of conventional adhesion, it was argued, could be explained without recourse to the electrostatic theory [13–16].

Electrostatic forces are still considered to be of relevance in adhesion of small particles. Kendall cites electrostatic precipitation as an example where particles become charged and are deposited on an electrode surface [17,18]. Rimai and Quesnel acknowledge that electrostatic charges will affect particle adhesion, but argue that their effect has not been satisfactorily integrated into particle adhesion theory [19].

## 2.3. Wetting and Contact Angle: Work of Adhesion

The development of McBain and Hopkins' specific adhesion, which involved interaction between the surface and the adhesive, concentrated attention on the importance of contact angles ($\theta$) and wetting, leading to the modern adsorption theory of adhesion. However, significant contact between the two parts of the adhesive joint (*i.e.* wetting of the substrate by the adhesive) is obviously a necessary condition for adhesion, whether the mechanism is explicable in terms of the adsorption, mechanical, diffusion, or electrostatic theory of adhesion.

The importance of contact angles to adhesion immediately, via Young's equation [20], points to the importance of surface energies, $\gamma$:

$$\gamma_{\mathrm{sv}} = \gamma_{\mathrm{s}l} + \gamma_{l\mathrm{v}} \cos\theta, \tag{1}$$

where v refers to the vapour present in equilibrium with the solid (s) and liquid ($l$).

Surface energies are also associated with failure of an adhesive bond, because failure involves forming new surfaces and the appropriate $\gamma$ have to be provided. The $\gamma$ term may be the work of adhesion, $\mathrm{W_A}$, or the work of cohesion, $\mathrm{W_C}$, depending on whether the failure is adhesive or cohesive. For Phases 1 and 2, these are defined as follows [21]:

$$\mathrm{W_A} = \gamma_1 + \gamma_2 - \gamma_{12} \tag{2}$$

and

$$\mathrm{W_C} = 2\gamma_1. \tag{3}$$

Two serious problems associated with these relationships caused considerable difficulty. The first was practical: how can interfacial energies of solids be measured? This is outside the scope of this review, but it is appropriate to comment that considerable ingenuity has been used and much controversy generated in attempting to answer it [22]. The second problem concerned the theoretical relationship between practical, measured adhesion and the thermodynamic work terms $\mathrm{W_A}$ and $\mathrm{W_C}$. This is in many ways at the heart of adhesion theory.

## 2.4. Practical Adhesion and $\gamma$

It is generally found that practical adhesion failure energies are much larger than the $\gamma$ involved [*cf.* Equations (2) and (3)], and that failure is cohesive within the weaker phase. This led to the view, widely-advocated in the 1960s, that interfacial forces were irrelevant to the practical strength of adhesive joints. Bikerman was a determined proponent of this position [14]. He argued on theoretical grounds—now accepted as unconvincing—that adhesive failure (*i.e.* interfacial failure) was impossible. Where apparent adhesive failure was observed, Bikerman insisted that failure was actually cohesive in a weak boundary layer (WBL) formed at the interface.

However, it increasingly became recognised that the practical adhesion, for example, fracture energy (G), will comprise a thermodynamic surface energy term $G_0(W_A$ or $W_c)$ to which must be added a term $\psi$ representing other energy absorbing processes—for example plastic deformation—which occur during fracture:

$$G = G_0 + \psi. \tag{4}$$

Usually $\psi$ is very much larger than $G_0$. This is why practical fracture energies for adhesive joints are almost always orders of magnitude greater than $W_A$ or $W_C$. However, a modest increase in $G_0$ may result in a large increase in practical, measured adhesion as $\psi$ and $G_0$ are usually coupled. For some mechanically simple systems where $\psi$ is largely associated with viscoelastic loss, a multiplicative relation has been found:

$$G = G_0\{1 + \phi(c,T)\} \approx G_0 \times \phi(c,T), \tag{5}$$

where $\phi(c,T)$ is a temperature and rate dependent viscoelastic term. In simple terms, stronger bonds (increased $G_0$) may lead to much larger increases in fracture energy because they allow much more bulk energy dissipation (increased $\psi$) during fracture. Much of this clarification came from the work of Gent, Kinloch, and Andrews [23,24], who were able to relate $\gamma$ and practical adhesion for a mechanically simple system consisting of styrene butadiene rubber (SBR) bonded to various rigid substrates. Most bonds are mechanically complex and the quantitative elucidation of the various energy terms is still not possible.

## 3. SOME MORE RECENT WORK

There have been important experimental and theoretical advances in recent decades which should refined our understanding of the “very strong attractions" between the particles of bodies to which Newton referred. In this article, some reference is made to consequences of developments in contact mechanics and in understanding of the dynamics of molecular chains, but more emphasis is given to advances associated with the use of surface analysis, with which John Watts has been closely associated.

## 3.1. Contact Mechanics

Developments in contact mechanics have given new methods of studying the magnitude of adhesion forces over very small areas. The surface forces apparatus (SFA) uses surfaces of defined geometry, such as crossed cylinders of molecularly smooth, cleaved mica, between which forces may be measured with a sensitivity of $10^{-8}$ N ($10^{-6}$ gf). The basic experiment, which enables the SFA to deduce surface energy values, involves bringing the two surfaces concerned into contact and observing either the load necessary to cause them to separate, or the relationship between the radius of the contact zone and the applied load.

Notionally related to the SFA are some scanning probe microscopy (SPM) techniques, particularly AFM and chemical force microscopy (CFM) which have provided not only surface images but also composition data and adhesive force measurements with nanometre spatial resolution [25–27].

Using these techniques, it has been shown that the distribution of adhesion force over a sample surface is often very non-uniform, even over a small area of a mica surface [25]. By studying the effect of contact time on the adhesion between two surfaces, hysteresis is sometimes observed as a result of reorganisation of the surfaces after they are brought into contact. This may occur at a macroscopic, microscopic, or molecular level. Using model systems representative of functionalised polymer chains, adhesion promoters, or additives, it is argued that interdigitation or interpenetration occurs, roughening the interface at the molecular level [8].

## 3.2. Molecular Dynamics

Theoretical developments in molecular dynamics have given us through reptation theory a greater understanding of the adhesive interactions between different polymers. When two polymers are brought into contact, even with thermodynamically incompatible polymers, there is some tendency for the interface to blur and for some interdiffusion to occur. More extensive roughening of an interface between incompatible polymers can be obtained by use of various types of copolymer, introduced at the interface as putative compatibilisers. The interface may be strengthened, as a result of interdiffusion and roughening on a nanoscale.

With suitable copolymers, roughening of the interface between two incompatible polymers by interdiffusion can lead to a range of values for fracture toughness (G). Diblock copolymers act in this way but random copolymers can sometimes be more effective, providing the polymers are not too incompatible [28]. The important parameters are the surface density and length of the copolymer chains. Toughening of the interface—increase of adhesion—may occur as a result of pull-out or scission of the connector chains, or of fibril or craze formation in a matrix. This last mechanism gives the highest G and tends to occur at high surface density of chains.

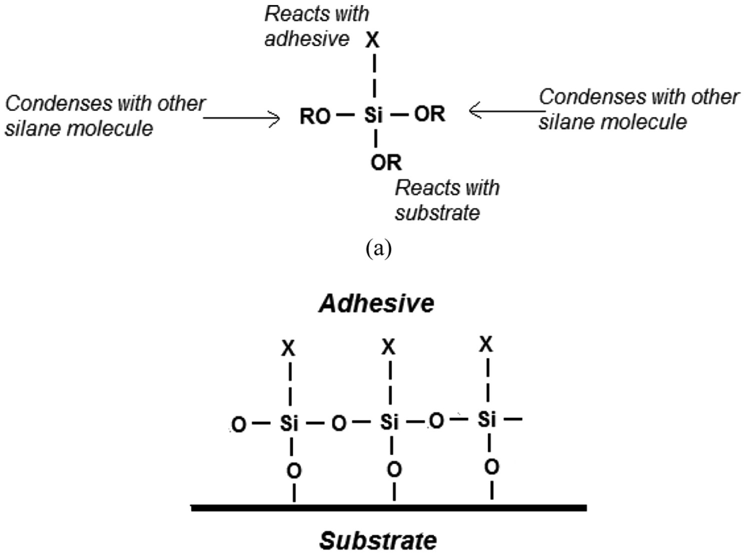
## 3.3. Surface Analysis

Surface analysis, particularly XPS and high resolution Secondary Ion Mass Spectroscopy (SIMS) using time of flight mass spectrometers, has enabled detailed information to be obtained about the chemical nature of surfaces involved in adhesion, both prior to bonding and after failure. Use of depth profiling techniques can provide similar information about regions of a bond remote from the ideal interface. Bikerman has been proven partly right: weak boundary layers are often, but not always, the cause of poor adhesion; cohesive failure is common, but not universal. Much more detailed information about the nature of bonding at an interface and the structure of interfacial regions is now available, and some of this is now discussed.

### *3.3.1. Bond Types*

The crucial importance of adsorption of the adhesive onto the substrate has been discussed since the days of McBain and Hopkins. However, until the advent of surface analysis, it had rarely been possible to demonstrate experimentally the type of bonding—primary or secondary—or even to establish which functional groups were involved.

The importance of organosilane compounds as adhesion promoters has been known for many years. A typical silane has a structure shown in Fig. 1(a). Three hydrolysable alkoxy groups are attached to the silicon atom: the fourth silicon bond leads (usually *via* a short alkyl chain) to a group X which is chosen for its affinity with the adhesive in question. It has long been supposed that that the silane hydrolyses is adsorbed onto the surface by covalent bond formation with surface OH groups [Fig. 1(b)].



(a)

(b)

**FIGURE 1** Organosilane adhesion promoter: (a) typical structure; (b) simplified mode of action.

An early success of surface analysis was Gettings and Kinloch's use of SIMS to give direct experimental evidence of the formation of a covalent bond formed between an organosilane adhesion promoter and a steel surface [29]. An $Fe{-}O{-}Si^{+}$ fragment was detected coming from a steel surface which had been treated with $\gamma$-glycidoxypropyltrimethoxysilane (GPS). The identification of this fragment was possible with an instrument of relatively low resolution because there are no other candidate ions close to the mass value of $Fe{-}O{-}Si^{+}$. More recently, the use of high resolution SIMS has similarly found evidence for metal-silane covalent bonding with aluminium and zinc [30].

Another feature of the classic model of silane action is the postulated reaction between functional groups on the silane and on the adhesive system. This too has been demonstrated by SIMS for GPS used with an epoxy resin. Watts *et al.* detected fragments characteristic of the reaction product of the amine curing agent [2,4-toluene diisocyanate urone (TDI urone)] with the epoxy (oxirane) ring on the organosilane [31].

Surface analysis has also produced evidence of the significance in adhesion of other types of bonding, in particular of donor-acceptor (Lewis acid-base) bonding. In the study just cited, Watts *et al.* found that, in the absence of GPS, hydrogen bonding (*i.e.* electron donor-acceptor bonding) between the amine curing agent and surface OH groups on the aluminium occurred. The SIMS spectrum showed a protonated amine curing agent fragment, *i.e.* a cation of one mass unit greater than the molar mass of the amine itself. They suggest that this was formed by the rupture of a hydrogen bond between a hydroxyl group on the aluminium surface and a nitrogen (or possible a carbonyl oxygen) in the curing agent, *e.g.* $\text{–NH–} \rightarrow \text{–N}^{+}\text{H}_2\text{–}$.

With monochromated X-ray sources, the chemical shifts observable in high resolution XPS enable small changes to be detected in the molecular bonding of a chemical group. This may allow the conformation and bonding of a molecule adsorbed on a substrate surface to be deduced. Leadley and Watts have studied the adsorption of polymethylmethacrylate (PMMA) and polyacrylic acid onto an oxidised metal or silicon surface [32,33]. They argue that the ester groups in PMMA are adsorbed in different ways, depending upon the acid and basic nature of sites on the substrate surface. Thus, for an acid surface (*e.g.* oxidised silicon) adsorption involves a hydrogen bond between the carbonyl oxygen and the hydrogen of surface OH groups (Fig. 2). For a strongly basic substrate, adsorption is *via* the positive end of the carbonyl dipole in the ester group, *i.e. via* the carbon atom of the carbonyl group. For weakly basic surfaces the spectra are interpreted as indicating hydrolysis of the ester and adsorption through the carboxylate anion so formed (Fig. 2).

The spectra of these different structures are sufficiently distinct to enable the use of PMMA or polyacrylic acid to estimate the nature and density of the different acidic and basic sites on a substrate surface. Leadley and Watts found both acidic and weak basic sites on the surface oxides of aluminium and iron but only basic sites (both weak and strong) on copper and nickel.

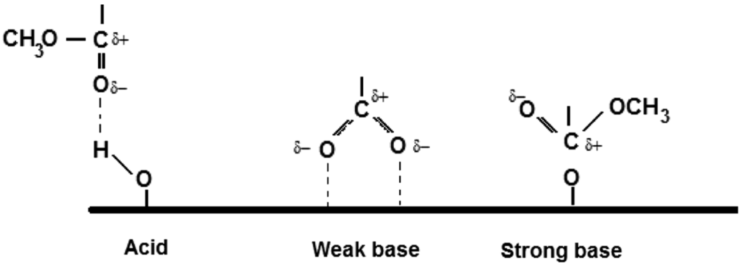


**FIGURE 2** Adsorption of PMMA onto surfaces of differing acidic and basic nature (after Leadley and Watts [32]).

### 3.3.2. Segregation and Interdiffusion

An understanding of the nature of the adsorption of the adhesive at a substrate surface is an important step towards understanding the structure-property relationships which determine the practical adhesion of a bond. However, as was explicit in the discussion of the significance of Equations (4) and (5) above, an adhesive joint must be regarded as a composite [34], the properties of which depend not just on the interface, but on the properties of the phases joined. Surface analysis experiments which have shown the occurrence of interdiffusion and segregation point to the complexity of the structure of interfacial regions in an adhesive bond.

As the previous discussion showed, surface analysis has produced results supporting two key features of the traditional model for the mode of action of silane adhesion promoters (Fig. 1): reaction with the substrate *via* Si–O–R and reaction with the adhesive *via* group X. This, however, is not the complete story, because the structure of the silane layer is complex, and a model of a silane monolayer linking substrate to adhesive [*cf.* Fig. 1(b)] is naïve. Although Davis and Watts observed a 1.7 nm layer of adsorbed silane (GPS) at an iron surface, they showed by depth profiling using SIMS that the structure of the silane deposit was complex. Both the silicon and epoxy ends of the GPS were detected in the outer layers, showing that the silane molecules are not highly orientated [35].

The complexity of the interfacial regions in silane-treated aluminium has been further demonstrated by Abel *et al.* in a study of bond durability on the effect of various silane deposition conditions, such as solvent type, solution concentration, pH, and hydrolysis time [36]. They applied GPS to grit blasted aluminium and used the Boeing wedge test to study durability of bonds with a toughened epoxy adhesive which were exposed to 96% relative humidity at 50°C for 7 days. Under these conditions failure was apparently interfacial, *i.e.* to the naked eye it seemed that the adhesive was on one failure surface with bare aluminium substrate on the counter surface. However, XPS demonstrated aluminium and silicon, as well as carbon and nitrogen from the adhesive on *both* sides of the failure surface. This implies that there is not a sharp interface with oxidised aluminium on one side and silane and epoxy on the other, but a complex "diffusion zone" in which silane and epoxy as well as aluminium oxide are present.

This self-roughening of an interface, producing what is sometimes called a diffusion zone or interphase is by no means confined to silanes: it is quite common. Watts and colleagues have also studied interfaces using ultra-low-angle microtomy, enabling depth profile information to be obtained [37,38]. Essentially a low angle taper section, less than 0.05°, is cut through the interface using a microtome with a tungsten carbide knife, and is then examined by XPS or SIMS. When a poly(vinylidene difluoride) (PVdF) coating on a polyurethane primer were examined in this way, XPS showed the diffusion of fluorine into the top nanometers of the polyurethane, despite the thermodynamic incompatibility of the two polymers.

A further example of the complex nature of an interface, and how this can exert a strong influence on the performance of the adhesive bond, is shown in work of Kinloch *et al.* on bond durability [39]. They used surface analysis in a study of the effect of pretreatment on the durability of bonds to aluminium made with a hot-cured toughened epoxy adhesive.

Cyclic fatigue experiments were done in wet and dry environments. Below a critical loading, characterised by a threshold value ($G_{th}$) of strain energy release rate, no crack growth occurred. Values of $G_{th}$ are given in Table 1 for aluminium with a phosphoric acid anodising pretreatment. This pretreatment produces a micro porous surface [40], consisting of cylindrical pores a few tens of nanometres in width, which run typically for hundreds of nanometres from the outer surface, almost to the base metal.

When tested in the wet environment in the absence of a primer, the anodized aluminium gave a low value of $G_{th}$. To simple visual inspection, failure appeared to be at the oxide-adhesive interface, but XPS clearly showed that failure is actually within the oxide itself. However, when a low viscosity epoxy primer was used, prior to applying the toughened epoxy adhesive, a much higher value of threshold energy was obtained. The examination of thin sections through the interface by transmission electron microscopy showed that differences in interfacial structure were responsible for these differences.

Ultramicrotomed cross-sections, about 5–20 nm in thickness, were examined using energy-filtered transmission electron microscopy (EFTEM). The high carbon signal from the pores when the primer was used showed that they were substantially penetrated by the

**TABLE 1** Cyclic Fatigue of Phosphoric Acid Anodized Aluminium Bonded with Epoxy Resin $G_{th}$ of Strain Energy Release Rate (J/m$^2$) for the Start of Crack Growth [39]

| Environment | Dry | Water at 28°C |
|---|---|---|
| No primer | 200 | 50 |
| Primer | 240 | 245 |

primer. Without the primer, the absence of this signal showed that the adhesive used was of too high viscosity to penetrate the pores [8]. The unfilled pores provided a route for the easy ingress of water which attacked and weakened the anodic oxide.

## 4. ADHESION THEORIES: A CONTEMPORARY PERSPECTIVE

A theory in science is a model which aims to comprehend the experimental results in a field and, for a fruitful theory, to suggest new experiments and their outcomes.

The value of adhesion theories has been shown in their use in the design of adhesive joints. Thus, recognition of the importance of wetting (Sect 2.3 *supra*) has led to the introduction of innumerable procedures aimed at raising surface energy of a substrate and, thence, improving adhesion. The re-emergence of the mechanical theory in the late 1960 s was followed by much development work on forming porous anodic oxides on aluminium and other metals as pretreatments giving strong, durable bonds. An example is given in Section 3.3.2 which recognises the importance of penetrating the porous layer and avoiding the formation of a WBL. More recently, greater understanding of the interactions between different polymers (Section 3.2) has stimulated work on block and random copolymer compatibilisers.

Despite all this, we need to be clear that theories are models: we do not look to them for immutable truths. We expect them in time to be modified and discarded [41,42]. The Aristotelian paradigm largely gave way to a mechanical Newtonian model which has yielded to new paradigms of quantum theory and relativity.

In the light of our present understanding of adhesion, what can be said about the classical adhesion theories—adsorption, mechanical, diffusion, and electrostatic? On one level it could be said that they maintain their importance undiminished. It is still acknowledged that adsorption plays a vital role, that there are examples where electric fields are crucial, and so forth. However, the classic theories originated at a time when there were few, if any, experimental techniques available to study surfaces and interfaces at the nanometre level. We now benefit from several decades of results from scanning probe technologies and surface analysis and theoretical advances in contact mechanics and molecular chain dynamics. We have direct evidence for the presence of particular groups on a surface, for the effects of variations of topography, and chemical nature over small distances both along a surface and into the materials joined. Consequently, in many cases we have a much clearer understanding of what is happening in the interfacial region and of how it affects adhesion.

One consequence of this understanding is that we can often make plausible suggestions about adhesion mechanisms without having to hide behind broad-brush statements about mechanical effects or chemical activation. We should also recognise now that the mechanisms characteristic of classical theories are not completely distinct. This is our contemporary answer, no doubt provisional, to Newton's challenge [5].

It is recognised that the practical surfaces used in adhesion are always to a degree rough: the only question is "How rough?" As the roughness of a surface changes, so must the chemical environment of its surface atoms and molecules. Thus, changing the roughness changes the local chemistry which will affect the adsorption properties of the surface and also the Fermi levels which may be relevant to electrostatic attraction. The scale of roughness of surfaces encountered in adhesive joints varies from the macroscopic through to the nano- and molecular scale, from the classic realm of the mechanical theory to that of the diffusion theory. In principle, the range of types of force which may act between adsorbate and adsorbed molecule on a nominally flat surface are the same as those which may act between diffusing molecules.

Moreover, the way in which adhesion is enhanced is essentially the same whether we think in terms of adsorption, diffusion, or roughening. These provide mechanisms whereby the energy dissipation ($\Psi$ in Equation (4)) is enhanced. It is common to find that strong chemical interaction leads to plastic or viscoelastic losses, interdigitation to crazing, and roughening to increasing the volume of plastically deformed material.

Of course, there are circumstances where the concepts associated with one particular theory are most significant, but perhaps we should avoid giving the impression that each of the classical theories is distinct and separate. They are best regarded as emphasising a different aspect of a more comprehensive model which, in principle, relates molecular dispositions in the region of the interface to macroscopic properties of an adhesive joint. It would be a mistake today to lay too much emphasis on the distinctions between classical theories, however valuable this might have been at various times during the last 80 years in stimulating the development of new concepts and in suggesting fruitful experiments.

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