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Adhesive Bonding: The Importance of Polymeric Interfaces

Anthony J. Kinloch*

1. Introduction

Modern adhesives are increasingly being used in advanced technology applications and are based upon macromolecules. Thus, all interfaces between adhesives and substrates may be said to constitute a 'polymeric interface'. In the formation of an adhesive joint three important stages may be identified [1]: Firstly, the adhesive must establish intimate interfacial molecular contact with the substrate – often termed 'wetting'. Some form of intrinsic adhesion forces then need to be established between the adhesive and the substrate, and such intrinsic adhesion forces will hold the materials together throughout the service-life of the adhesive joint. Secondly, to attain the above requirements, the adhesive had to be in a 'liquid' form at some stage during the bonding operation. However, the adhesive almost invariably now has to harden in order to be able to withstand the stresses and strains that may be applied to the joint. Thirdly, it must be appreciated that the details of the design of the joint, the way in which loads are applied to it, and the service environment that it must withstand, will all affect its mechanical performance and life expectancy.

The importance of the polymeric interface is to be found throughout all these different aspects of the science of adhesion and adhesives, and this will be illustrated by examples drawn from the bonding of elastomers to plastic substrates, the bonding of thermoplastic composites, and the environmental attack of moisture upon steel and aluminium-alloy bonded joints.

2. The Bonding of Elastomers to Plastic Substrates

The thermodynamic work of adhesion, W_A, required to separate a unit area of a solid and a liquid phase forming an interface across which secondary forces are acting may be related to the surface and interfacial free energies by the *Dupre* equation:

$$W_A = \gamma_a + \gamma_s - \gamma_{as} \qquad (1)$$

where γ_a is the surface free energy of the adhesive, γ_s that of the substrate, and γ_{as} that of the adhesive/substrate interface.

Now by adopting a fracture mechanics approach the work of *Andrews, Gent* and *Kinloch* [2–5] defined a geometry-independent measure of joint strength, the adhesive fracture energy, G_c. From experimental and theoretical considerations, it was demonstrated that G_c, for a cross-linked elastomeric adhesive/rigid plastic interface could be divided into two major components: *a*) The energy required to propagate a crack through a unit area of interface in the absence of viscoelastic energy losses, *i.e.* an intrinsic adhesive fracture energy, G_0, which is a direct measure of the bonding forces. *b*) The energy, ψ dissipated viscoelastically within the elastomeric adhesive at the propagating crack, again referred to unit area of interface.

The values of G_0 were ascertained for various joints from studies of the crack propagating along the elastomeric/substrate interface. When interfacial failure occurred, the values of G_0 were compared to corresponding values of W_A calculated from *Eqn. 1*. The results are shown in *Table 1* and, as may be seen, the values of the two parameters are in good agreement. Thus, the nature of the intrinsic adhesion forces acting across these interfaces was secondary interfacial bonds.

An important general point emerges from the above work. Namely, that although the energy, ψ, which is dissipated viscoelastically and plastically is usually far greater than W_A, the value ψ is dependent upon the value of W_A. Indeed, for the model joints described above, the value of ψ is directly proportional to the value of W_A. Hence, designing to maximise the interfacial bonding forces is not a trivial pursuit. Obviously, this has long been recognised in industry as evidenced by most adhesives being polar in character and often having the capability to establish H-bonds, and possibly even chemical bonds, to the substrate.

Table 1. *Values of the Intrinsic Fracture Energy (G_0) and the Thermodynamic Work of Adhesion, (W_A) for a Cross-linked Styrene-Butadiene Rubber Adhering to Varios Substrates*

Substrate	G_0 [mJ/m^2]	W_A [mJ/m^2]
Fluorinated ethylene-prophylene copolymer	22	28
Plasma-treated ethylene-prophylene copolymer	69	57
Poly(chlorotrifluoroethylene)	75	63
Nylon 11	71	71
Poly(ethylene terephthalate)	79	72

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3. Bonding of Thermoplastic Fibre-Composites

3.1. Introduction

Fibre-composites, such as carbon-fibre composites, based upon thermoplastic polymeric matrices offer several advantages when compared to those based upon thermosetting resins. Such advantages include the ability to readily form the fibre-composite materials into complex shapes, greater resistance to impact damage and higher temperature resistance. However, many technical and economic problems have yet to be resolved before thermoplastic fibre-composites can be used by industry. One such problem is the adhesive bonding of thermoplastic fibre-composites using conventional structural adhesives technology [6] [7]. One of the most commonly employed thermoplastic fibre-composites is the poly(ether-ether ketone) matrix containing carbon-fibres, marketed by *ICI* plc as *'APC-2'*.

3.2. Surface Pretreatment

It was found that, for thermoplastic fibre-composites bonded using conventional epoxy or acrylic structural adhesives, the usual treatment employed for thermosetting-based composites, namely a simple abrasion/solvent wipe pretreatment, was inadequate for obtaining high joint strengths. This arose from the crack growth which causes joint failure occurring along the adhesive/thermoplastic composite interface, which is relatively weak, when such a pretreatment is employed. We proceeded to demonstrate that a corona treatment could be a most effective treatment for thermoplastic fibre-composites. Indeed, the treatment is so effective that the crack now propagated either through the adhesive layer or through the composite substrate, depending upon the relative stresses acting in the composite compared to its transverse tensile strength.

3.3. Surface-Chemistry Studies

Surface-chemistry studies were undertaken to examine the detailed mechanisms whereby the corona-discharge so effectively modified the surface of the *'APC-2'* and similar composites. The contact angle studies enabled the surface free energies to be deduced as a function of the level of corona pretreatment and a dramatic increase in the polar, γ^p, force component to the surface free energies after treatment was observed.

Analysis of the surface regions regions using X-ray photoelectron spectroscopy (XPS) revealed that no significant differences existed in the concentrations of elements which may be associated with contaminants, such as silicon and fluorine, between the thermoplastic and thermosetting composites. The analysis did confirm, however, that the surface regions of the thermoplastic composite had been chemically modified by the corona treatment. This is shown in *Figs. 1* and *2* where the increased type and concentration of oxygen groups are clearly evident. Furthermore, a detailed analysis was conducted to evaluate the concentration of the polar groups on the surface of the composites. The concentration of the polar groups from XPS, the polar surface free energy from the contact analysis and the joint strength results have all been correlated to the energy of the corona pretreatment employed.

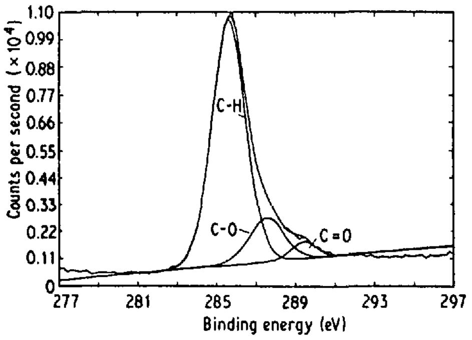

Fig. 1. *A narrow XPS scan of the carbon peak of the untreated* 'APC-2' *thermoplastic composite, showing the three species which make up the carbon peak*

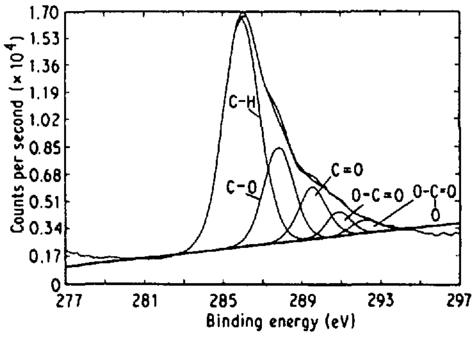

Fig. 2. *A narrow XPS scan of the carbon element of a corona treated* 'APC-2' *thermoplastic composite* (corona energy level is 25 J/mm²), *showing the five species which make up the carbon peak.* Note the increase of oxidation and the extra two species on the right-hand side of the carbon peak.

4. Environmental Attack Upon Adhesive Joints

4.1. Introduction

Adhesives are being increasingly used in structural engineering applications, but a problem frequently encountered is that the mechanical performance of the joint may deteriorate upon exposure of the bonded component to its service environment. Unfortunately for the adhesion scientist, one of the most aggressive environments is also one of the most common, namely water. For example, the loss of strength in a hot-dry climate is usually minimal whilst that in a hot-wet tropical environment may be extremely high [1] [8].

4.2. Mechanisms of Environmental Attack

It is generally observed that the locus of joint failure of well prepared joints is invariably by cohesive fracture in the adhesive layer. However, by using advanced surface analytical techniques, such as XPS [9] [10], it has been clearly demonstrated that after environmental attack, it is *via* interfacial failure between the adhesive (or primer) and the substrate (typically a metal oxide) or *via* failure in an oxide layer.

4.2.1. Interface Stability

The intrinsic stability of the adhesive/substrate interface in the presence of any liquid environment may be assessed from thermodynamic considerations [11]. If only secondary (*e.g. van der Waals*) forces are acting across the interface, then the work of adhesion, W_A, in an inert medium may be expressed by *Eqn. 1*. However, in the presence of a liquid (denoted by the suffix 'L') the work of adhesion, W_{AL}, is:

$$W_{AL} = \gamma_{aL} + \gamma_{sL} - \gamma_{as} \qquad (2)$$

where γ_{as} and γ_{sL} are the interfacial free energies between the adhesive/liquid and substrate/liquid, respectively. Some examples of W_A and W_{AL} are shown in *Table 2*. For those interfaces where there is a change from a positive to a negative work of adhesion then, this provides a driving force for the displacement of adhesive on the substrate surface by the ingressing liquid. It is, therefore, to be expected that, if the joint is subjected to such an environment, there will be a progressive encroachment into the joint of debonded interface.

Table 2. *Values of* W_A *and* W_{AL}

Interface	W_A [mJ/m²]	W_{AL} [mJ/m²]	Environmental interfacial attack observed?
Epoxy/ferric oxide	291	EtOH: 22 H_2O: –255	No Yes
Epoxy/silica	178	H_2O: –57	Yes
Epoxy/CFRP	90	H_2O: 44	No
Vinylidene chloride-methacrylate Copolymer/polypropylene	88	H_2O: 37 Salt Soln: –0.8	No Yes

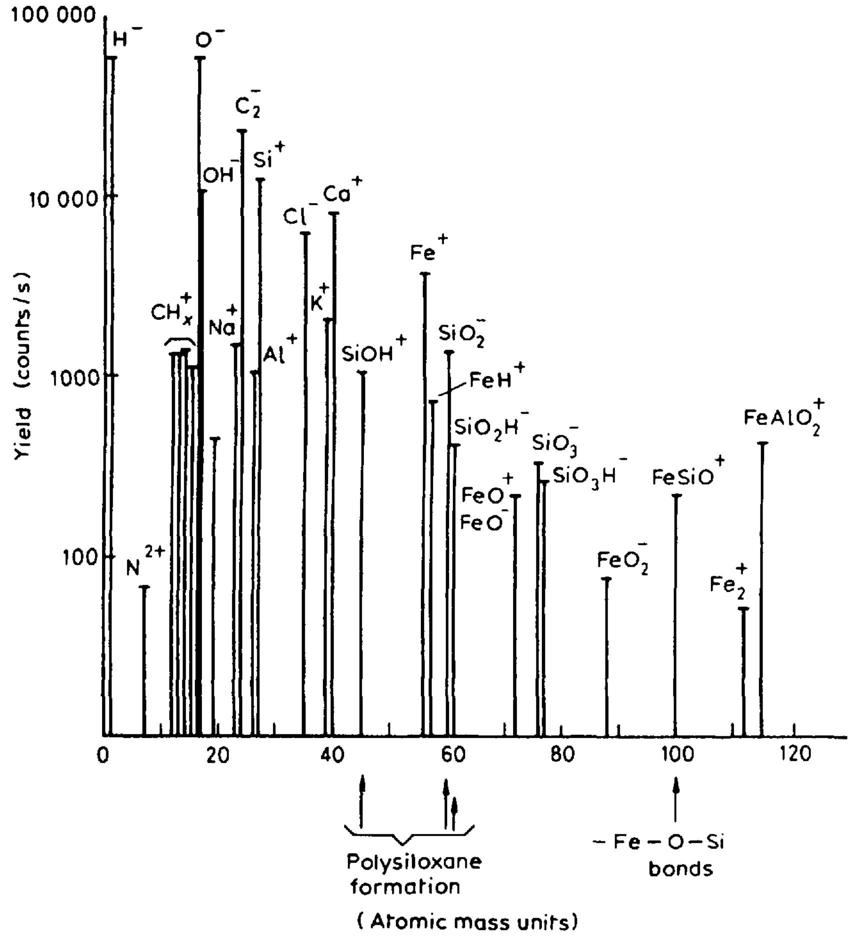

Fig. 3. *Positive and negative static SIMS from a mild steel substrate coated with a γ-glycidoxypropyltrimethoxysilane primer*

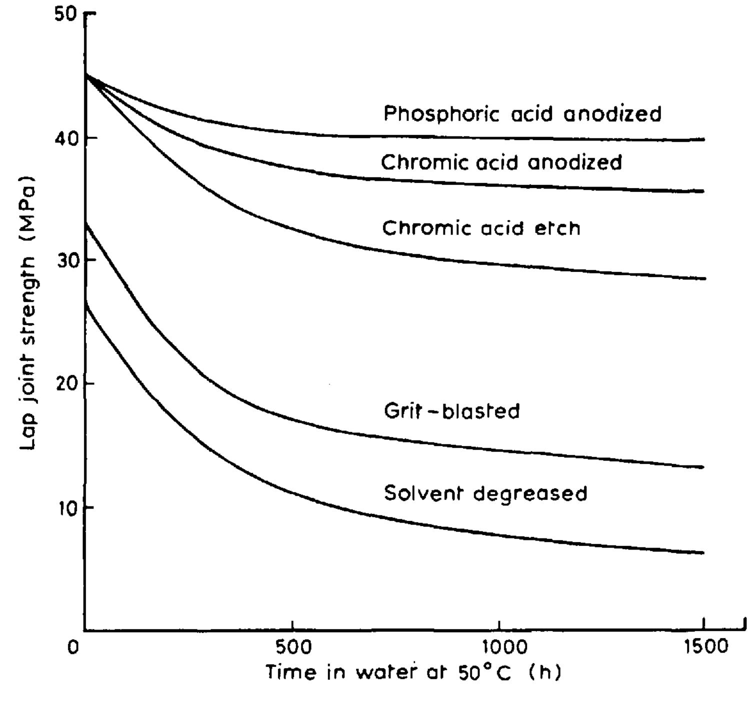

Fig. 4. *Effect of surface pretreatment on the durability of aluminium alloy/toughened epoxy joints subjected to accelerated ageing at 50°*

This will have the effect of progressively reducing the joint strength and also of progressively changing the locus of joint failure to interfacial between adhesive and substrate. This is exactly what has been observed in practice.

The thermodynamics demonstrate that to attain more environmentally stable interfaces, one needs to establish stronger interfacial forces than solely secondary bonds. In structural bonding, the formation of primary bonds across the interface has largely been achieved by the use of organometallic and, possibly, phenolic primers. A typical organometallic primer is γ-glycidoxy-propyltrimethoxy silane, and *Fig. 3* shows [12] the secondary-ion mass spectrum (SIMS) of this primer adsorbed onto a mild steel substrate, and the presence of the $FeSiO^+$ radical provides strong evidence for the formation of a chemical bond, probably Fe—O—Si, between the metal oxide and the polysiloxane primer. Indeed, only for the silane primer where there was evidence of chemical, rather than purely secondary, bonding between the primer and the metal oxide was there observed any improvement in joint durability.

4.2.2. Oxide Stability

As we have identified the stability of the 'interphase' as a key parameter in influencing joint durability, then obviously the choice of surface pretreatment for the substrate prior to adhesive bonding is of major importance. This is particularly marked in the case of aluminium alloys and there is considerable evidence [1] [8] that the importance of the surface treatment arises from its influence on the surface chemistry, thickness and morphology of the aluminium oxide generated. *Fig. 4* illustrates the effects of surface pretreatments on the durability.

For example, the original 'free' oxide generated by the chromic-acid etch treatment has been found to be largely amorphous but upon exposure to moisture becomes hydrated and changes to crystalline, pseudo-boehmite. This hydrated oxide may be readily distinguished by its distinctive morphology which consists of irregular-shaped platelets; dubbed by *Venables* and coworkers [13] a 'cornflake structure'. This structure is relatively weak, however, and only loosely bound to the underlying oxide. If the hydrated oxide can be formed *in situ* in the joint, it, therefore, represents a weak boundary layer with failure occurring in this loosely-bound oxide layer. However, recent work by *Davies* and *Kinloch* [14] has suggested that such relatively large-scale hydration does not form in the joint, but that a more subtle hydration process may possibly proceed.

Now the phosphoric-acid anodising pretreatment leaves an oxide which is thicker and more porous, and so may allow the formation of a 'micro-composite' at the interface [14]. However, possibly of greater importance is the presence of PO_4^{3-} ions in the outermost layers of the oxide which inhibits any hydration of the oxide. Indeed, the oxide surface produced by the chromic-acid etch treatment may have its hydration resistance greatly increased, if phosphonic-acid based inhibitors are adsorbed onto the oxide prior to adhesive bonding. This significantly increases the durability of the subsequent adhesive joint [15].

4.3. Kinetics of Environmental Attack

Kinloch and coworkers [16] have undertaken quantitative predictions for the durability of unstressed butt (tensile) joints consisting of mild-steel substrates loaded with a simple epoxy adhesive. Firstly, from diffusion data for the adhesive, concentration profiles for water ingressing into the adhesive joint were calculated as a function of time and temperature. For this joint, environmental attack occurs by truly interfacial failure, as discussed above, and the kinetics of failure are governed solely by the rate of water diffusion. Secondly, therefore, by assigning a constant, critical water concentration for debonding, the interfacial environmental crack length as a function of time the joint spent in water at a given temperature was deduced. Thirdly, this crack length was combined into a continuum fracture mechanics model to predict the failure stress of the environmentally-aged joints. The predictions, over a wide range of times and temperatures were in excellent agreement with the experimentally-determined values.

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Improvement of Adhesion on Automotive Top Coats by Corona Discharge

Kurt Jud*

Abstract. A highly automated *Corona Discharge* treatment transforms a nonpolar, not bondattractive top coat surface into a polar, adhesively suitable substrate for structural bonding, *i.e.* for automotive windscreen fastening (*Fig. 1*). This cost-effective, secure purely physical procedure replaces the expensive, manual, wet pretreatment in applying solvent containing inflammable primers.

Investigations have shown an excellent adhesion of particularly polyurethane adhesives to Corona-Discharge-treated current automotive topcoats, independent of the type and amount of many top-coat additives. Adhesion experiments and the determination of surface energy have shown an insensitive resulting performance towards changing process parameters.

Scientific examinations with IR and ESCA analysis as well as electron microscopy provide valuable explanations for the efficiency of the *Corona Discharge* treatment.

The Problem

In the Automotive Industry many coated materials are bonded frequently and in great extent together with glass, plastics, and textiles today. Examples are: direct glazing, fastening of plastic parts, spoilers and friezes, bonding of SMC panels to the load bearing frame.

All paints and coatings contain additives, which ease the compounding or the application or even provide some finishing properties to the paint surface. The most important properties amongst those are as follows: dispersion, self leveling, antifoaming, pigment wetting, conductivity, brilliance, and dust repulsion.

These additives are non-volatile surface-active agents, which also migrate to the surface of the finished paint coating. Additives at the surface of electrocoats, surfacer, primer, and base coats become dissolved in the next wet system applied and migrate to the surface of the top coats, *i.e.* the clear coats. Most additives are derivatives of silicone oils containing methyl and phenyl groups. They create a hydrophobic layer on the surface and reduce the surface energy to less than 30 mN/m (*Table 1*). As a result, they have poor wettability characteristics when used with adhesives possessing higher surface tensions. In contrast to top coats, these surface-active agents contain no functional groups for powerful interaction or chemical reaction with conventional adhesives (*Fig. 3*).

Table 1

Surface Energy [mN/m]			
Glass	73	Water	73
Phosphatised Steel	43–46	Glycerine	63
Cathodic E-Coat	32–40	Ethyleneglycol	48
Polyethylene	22	Dioxane	33
Polypropylene	28	Butanol	23
Polytetrafluorethylene	19	Xylene	29
Alkyd Resin	33–60	Butylacetate	25
Alkyd Melamine		Diisobutylketone	22
Top Coat	30	Solvent Naphtha	18–22
Polyvinylchloride	39–42		
Polymethacrylate	32–41		
Epoxy Resin	45–60		
2 pt Epoxy Adhesive	39–44		
2 pt PUR Adhesive	44		
Polyamide	46		
Polydimethylsiloxane	22		
Togocoll FH 500	33		
Togocoll FH 500 DI	32		

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