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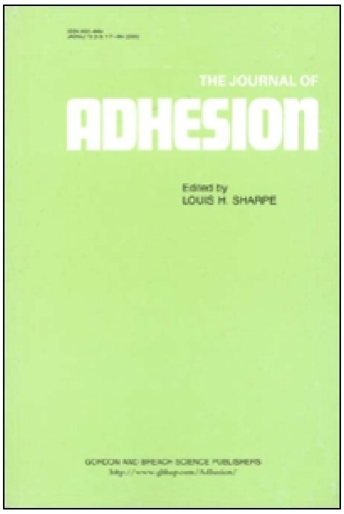

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Engineering the Interface in Composites and Bonded Components*

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In this paper, various ways in which the interfaces in composites and bonded structures may be modified are surveyed. Direct pretreatment before bonding may be effective by altering the chemical nature of the surface or by altering its topography. Indirectly, the presence of one surface may alter the properties of an adjacent phase. This may occur by chemical reaction, by preferential adsorption of an additive or residue or by providing nuclei for the formation of a transcrystalline layer.

KEY WORDS Fibre composites; interface; transcrystalline layer; Griffith-Irwin theory of fracture; pretreatment; wedge test.

1. INTRODUCTION

Much of the interest in adhesion science is a result of its obvious applicability to solution of engineering problems. It is sometimes forgotten that *engineering* comes from *ingenium* and is cognate with ingenious. An increased understanding of adhesion science should enable engineers to develop ingenious ways in which interfacial regions can be modified in order to effect significant changes in properties of bonded components and composite materials. The internationally renowned work of Jim Wightman and his colleagues at Virginia Polytechnic Institute and State University on surface treatment and adhesion has shown engineers various subtle ways of doing this. This paper provides a survey of methods by which surfaces can be controlled so as to affect the performance of bonded structures and composite materials: it is appropriate that it should form part of a collection of papers honouring Jim Wightman.

2. CRITICAL EFFECT OF THE INTERFACE

The word "surface" and "interface" literally imply a two-dimensional area of contact between two volumes. As such, an interface may exist in geometry, but does not in technology. The gradual change of properties that occurs passing from one phase to

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* One of a Collection of papers honoring James P. Wightman, who received the 13th Adhesive and Sealant Council Award at the ASC's 1993 Fall Convection in St. Louis, Missouri, USA, in October 1993.

another has long been recognised, and is taken into account in the arbitrary definitions of a surface used in classical thermodynamics.[1] "Interface", then, is used to designate an "interfacial region" within which properties differ from those of the bulk phases. The terms "interphase," or "mesophase," have recently been employed to emphasise the three dimensional nature of this region.[2]

This emphasis is valuable because it directs attention, which may be excessively focused on the forces across the interface, towards the influence of the interfacial regions on the bonded structure or composite material as a whole. Even a simple bonded joint can usefully be regarded as a composite in the sense that its properties are the result of the interaction between those of the phases joined and of the interface between them. Good brought this out when he applied the Griffith-Irwin theory of fracture to a joint comprising a bond between two phases.[3] The fracture stress, σ_f, is given by

$$\sigma_f = k(EG/l)^{1/2} \tag{1}$$

where k is a constant, l is the length of the critical crack and EG is the product of modulus and fracture energy. The important point that Good made was that EG is a semi-local property, and that fracture will occur where this product is lowest. High adhesion may not be optimum for all bonds under all conditions. It may lower the joint strength by reducing the energy-absorbing capacity (G) in the interfacial regions. Controlled debonding at or near a strongly stressed interface can produce increased toughness in a composite either by fibre-matrix debonding at right angles to the direction of crack growth[4,5] or by fibre pull-out.[5] Control of the interface is also necessary in the context of degradation of properties in aqueous and other adverse environments, where it is the durability, rather than the absolute value, of the interfacial adhesion that is significant.[6]

The ability to control an interface is central to successful applications of adhesion. The first examples considered are those which involve direct pretreatment of a surface of a component material. Other examples are then discussed in which the interface affects the properties of the adjacent phases extending some way into the bulk, or in which the interface is indirectly modified by the surface activity of minor components of the materials joined.

3. PRETREATMENT OF SURFACES

In controlling the interface in composites and in adhesive bonding, the surface pretreatment is an important stage. There are a number of different ways in which pretreatment may be effective. In some examples its function is best regarded as a cleaning, removing weak boundary layers. In others the pretreatment is designed to raise the surface energy of the substrate so that the resin will better wet it.[7] These methods can be regarded as changing the chemical nature of the surface. Other treatments aim at the development of a rough substrate topography. This is often referred to as acting as a "mechanical key".[8] The topography modifies the way the stresses are transmitted across the interface and consequently the properties of the adhesive bond.[7]

3.1 Chemical Modification

Polyethylene provides a good example of a polymer where changes in surface chemistry are needed to achieve good adhesion. It is a notoriously difficult substrate to bond. When applied to a solid as a hot melt, it is usually necessary for oxidation of the polymer to occur, if a good bond is to be obtained.[9,10] The results in Table I illustrate this. Where oxidation is inhibited, peel strengths less than 1N/mm are found: under these experimental conditions they represent very low adhesion.

Polyethylene has a low surface energy and sometimes a weak boundary layer of additives come to its surface during moulding.[10] Techniques have been developed for overcoming these problems when forming adhesive bonds to solid polyethylene. They involve surface treatment by such means as chemical oxidation, flaming or corona discharge treatment. These introduce reactive functional groups into the surface.[11] Some of these methods have been adapted by Ward and Ladizeski for treatment of ultra-high modulus polyethylene fibres for use as a reinforcement in polyester and epoxy composites.[12] Chromic acid treatment and plasma etching of the fibres were employed to achieve a range of values of both monofilament pull-out adhesion and inter-laminar shear strength, as shown in Table II. This work provides an example of an adverse effect of high fibre-matrix adhesion. Enhanced adhesion resulting from oxygen plasma treatment prevented delamination during impact, and so reduced the impact strength.[13]

Ward *et al.* investigated the effect of the oxygen plasma on the polyethylene fibre surfaces. At short treatment times, general oxidation of the surface occurred. With intermediate times, surface cross-linking predominated. Long treatments produced a rough surface "which could give rise to a mechanical keying effect".[14]

TABLE I

Adhesion of polyethylene applied as a hot melt coating to etched mild steel: effect of suppressing oxidation of the polymer.[9]

Antioxidant in polymer	Coated in air or vacuum	Peel strength N/mm
none	Air	3.0
5 ppm	Air	1.9
540 ppm	Air	0.4
none	Vacuum	0.8

TABLE II

Epoxy resin reinforced with polyethylene fibres: effect of fibre treatment on inter-laminar shear strength (ILSS) and impact energy (after Ref. 12)

Treatment	ILSS MPa	Charpy energy $kJ\,m^{-2}$
None	15	158
Chromic acid	20	–
Plasma etching	27	119

As Chin and Wightman have shown, a pretreatment for a polymer that introduces polar functional groups into the surface and improves wettability, does not necessarily lead to improved adhesion.[15,16]

They used plasma treatment (in oxygen, argon or ammonia) to effect such changes in both high density polyethylene (HDPE) and in an aromatic polyimide. When adhesion to an acrylate-based pressure sensitive tape was measured, the peel strength was found to increase for the HDPE surfaces after plasma treatment, but to fall for the treated polyimide, as noted in Table III.

XPS results from the peeled surfaces showed that the plasma treatment had increased the polyimide surface polarity, but had also weakened the surface regions. Chin and Wightman emphasise the point that the "physical as well as the chemical characteristics of plasma-treated surfaces play an important rôle in adhesion".[16]

3.2 Modification of Topography

Polyethylene adhesion also provides a paradigm of adhesion where mechanical factors are significant. It is possible to prepare the surfaces of a number of metals with microfibrous topography: adhesion of polyethylene to these surfaces does not depend upon the oxidation of the polymer, in contrast to those discussed above.[17] The results in Table IV show good adhesion, in the absence of oxidation, to a steel surface covered by a blade-like oxide layer.

The good adhesion to these microfibrous surfaces is associated with energy absorption by extensive plastic deformation of the polymer during failure. The interfacial region can be regaded as a discontinuous fibre composite in which the stress concentrations at the fibre tips lead to the plastic drawing of the polymer.[18]

These microfibrous surfaces on steel were produced by a hydrothermal oxidation.[17] Hollenhead and Wightman compared this pretreatment with grit blasting for steel

TABLE III
Peel strengths[N/m] of pressure sensitive tape stripped from polyethylene and polyimide surfaces.[16]

Surface treatment:	None	Oxygen plasma-1 min
Polyimide	470	250
HDPE	90	690

TABLE IV
Adhesion of polyethylene applied as a hot melt coating to mild steel with a microfibrous surface oxide.[17]

Antioxidant in polymer	Peel strength N/mm
None	2.7
2000 ppm	2.2

bonded with a thermoplastic polysulphone.[19] Lap shear strengths for the grit blasted surfaces were 40% lower than those for microfibrous surfaces pretreatments: by increasing the strength of the interfacial region, failure is directed into the polymer where dissipation of fracture energy (high local G, equation 1) leads to a higher fracture stress. Although bonds with both pretreatments deteriorated with exposure to humid environments, those with the microfibrous surfaces were more durable.

Somewhat analogous to these microfibrous surfaces are microporous anodic oxide films which can be produced on several metals, for example aluminium and titanium. Here the polymer penetrates into the pores to give a bond of high initial strength. A useful property is that the bonds to porous anodic films generally show good durability in a humid environment.[10]

The potential of this particular type of "interfacial engineering" for aluminium was shown in the late '60s,[9] and has been widely exploited for adhesive bonding in the aircraft industry. Ko and Wightman[20] have demonstrated its effectiveness for aluminium-lithium alloys. Anodising in either sulphuric acid or phosphoric acid produced a porous surface oxide into which a polysulphone adhesive penetrated giving a "mechanical means of adhesion". By "engineering" the interface in this way, bonds were obtained which were much more durable in high humidity than comparable ones made to surfaces without this high porosity.

Some recent results which further illustrate this are shown in Figure 1.[21] Prior to bonding with epoxy resin and exposure to a humid environment, aluminium strips were treated either in a sulphuric acid/ferric sulphate solution (P2 etch) alone, or in P2 followed by anodising in phosphoric acid. The latter specimens, with the very porous surface topography, exhibited improved crack resistance.

Filbey and Wightman[22] have clearly demonstrated the applicability of analogous principles in the bonding of epoxies to titanium alloys. They found that anodising in either chromic acid or sodium hydroxide was capable of producing a surface with pores of 40 to 50 nm diameter. Surface analysis showed the penetration of resin into these pores and wedge test results demonstrated the superior durability of these anodic pretreatments, compared with others which did not give a microporous surface.

Surface roughness also plays a part in the engineering of surfaces in fibre composites. Ward's work on plasma etched polyethylene was discussed above. Moyer & Wightman

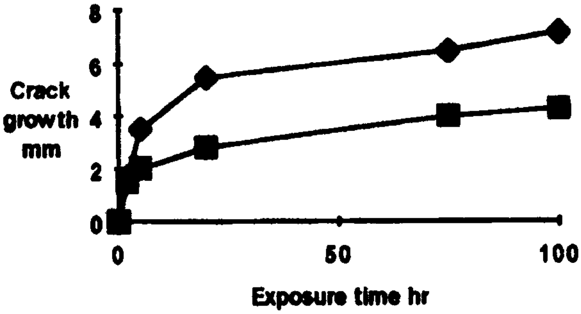

FIGURE 1 Aluminium bonded with epoxy resin: effect of pretreatment on growth of a performed crack during exposure to 96% relative humidity at 50 °C.[21] (P2 diamonds; P2 + anodise squares).

have reported the surface roughening of a carbon fiber-polyimide composite by treatment with an oxygen plasma.[23] Anodising has been shown by King *et al.*[24,25] to produce surface roughness on pitch-based carbon fibre. They used XPS and chemical probes in order to understand better the reasons for the improved properties of an epoxy composite made from the treated fibres. They concluded that the increased interfacial shear strength resulted primarily from improvements in mechanical interlocking rather than chemical interactions between fibre and matrix.

Marshall and Price[26] also claim to have found evidence of mechanical interlocking in composites made from treated carbon fibre. They talk of graphite sheet edges which "increase the number of potential bonding sites", and also present a "jagged surface profile [which may] increase mechanical keying." Unfortunately the value of their work is limited, as they give no detail whatever of the surface treatment they used!

4. OTHER INFLUENCES OF SURFACE ON MATERIAL PROPERTIES

In the previous section the emphasis was on the direct modification of the surface of the substrate or reinforcement in order to affect the properties of the composite. In other instances of interface engineering, the surface may exert an influence over the matrix phase in the adjacent region, or the surface may be modified by adsorption phenomena.

4.1 Crystalline Morphology

The morphology of a crystalline material depends on the relative rates of nucleation and of growth of the crystals.[27] A surface may provide a high density of nucleation sites, favouring the columnar growth of crystals from the surface into the melt. Such layers are well-known in metals, and often occur in polymers where the term "transcrystalline layer" (TCL) is used to designate them.

A recurring theme in adhesion is the influence of the substrate on the formation of a "transcrystalline" layer, and the influence of the layer on adhesion. Some early reports suggested that a TCL was formed only if the polymer solidified against a high energy substrate, and improved adhesion to the TCL morphology was claimed.[28,29] It was soon realised that its formation was largely controlled by the temperature gradient when the polymer solidifies, as would be expected from theory of nucleation and growth.[30,31] Examples have been quoted where the formation of a TCL was sporadic with adhesion not being affected by its presence.[27,32]

Fibres also may nucleate transcrystalline layers. In 1971 Bessell, Hull and Shortall reported TCL's formed on glass and carbon fibres when caprolactam was polymerised *in situ*.[33] In the same year Hobbs showed a similar effect when isotactic polypropylene crystallised in the presence of graphite fibres.[34] These was speculation that such surface nucleation would give high adhesion and improved composite properties. In 1974 Hull expressed the opinion that although some improvement could be demonstrated, other factors usually have an overriding effect.[35] Folkes writing a decade later broadly supported this conclusion.[36]

The present position seems not to be very different. TCL's are reported, especially around carbon fibres and in polyether-ether ketone (PEEK).[37–39] There is evidence that the surface structure of the fibres is significant, high modulus fibres, having a highly graphitised structure, being more efficient at nucleation than high strength fibres.[38] The temperature gradient and temperature of crystallisation are also acknowledged to be influential, and can override the effect of the particular surface.[39] The presence of a TCL is associated with modest improvements in some composite properties,[38,39] but its influence is often swamped by that of other factors such as pretreatment level.[38] The differences in flexural strength given in Table V are for carbon reinforced PEEKs which differ principally in the higher surface nucleation of the high modulus fibre. For comparison, it should be noted that the flexural strength for a composite, similar to HS/PEEK, but with "optimised" fibre surface pretreatment (not specified by the authors), was 152 MPa.[38]

4.2 Surface Activity and Syneresis

A surface active molecule migrates to an interface to reduce surface energy. Syneresis, strictly, is exudation of a liquid from a gel as it contracts;[1] the word is applied, by extension, to the migration of components from a polymer as it solidifies. In practice it is not always possible to distinguish surface activity from syneresis. Many polymers used in adhesives and composites are multicomponent, or even multiphase, systems and these phenomena enable control to be exerted over the composition of interfacial regions and of bulk properties.

For example during the moulding of nitrile butadiene rubber (NBR) a complex interlayer is formed between the rubber and the mould surface: the composition of this layer largely determines the level of adhesion obtained. Residues of carboxylic acid derivatives constitute an important part of this interlayer. There may be two sources of these derivatives in a NBR compound, emulsifier residues from the polymerisation and fatty acid added to the compound as part of the cure system. It is possible to control the composition of the interlayer, and to alter the adhesion accordingly.[40] The results shown in Table VI refer to the same base NBR, polymer A, and to two compounds detailed in Table VII. The mould adhesion (mould sticking index)[41] varies from 136kPa to 313kPa, depending on whether the base polymer is extracted before compounding (A *cf.* A-Ex), whether the compound contains added fatty acid (compound 2 *cf.* 1), whether the added acid is stearic or lauric (2 *cf.* 2L).

Stearic acid is also used to modify the interface in composites. The poor low temperature impact resistance of polypropylene may be improved by incorporation of a rubber phase such as EPDM. This lowers the modulus of the composite, and this, in

TABLE V
Influence of TCL on strength of carbon fibre reinforced PEEK.[38]
(HS-high strength, HM-high modulus carbon fibre.)

Composite	Surface nucleation	Transverse flexural strength MPa
HS/PEEK	Weak	53.6
HM/PEEK	Strong	76.4

TABLE VI
Influence of fatty acid on mould sticking index (kPa) of N.B.R. compounds, containing the same base polymer A, moulded against EN8 steel.[40]

Polymer	Compound	Mould sticking index
A	1	271
A	2	136
A-Ex	1	313
A-Ex	2	201
A	2L	288

Ex – base polymer extracted before compounding
L – lauric in place of stearic acid

TABLE VII
N.B.R. formulations (parts by weight).

	1	2
Polymer	100	100
GPF black	30	30
ZnO	2.5	2.5
Stearic Acid	–	1.0#
TMTD	3	3

In compound 2L the stearic acid is replaced by lauric acid at a molar equivalent level

turn, may be improved by addition of calcium carbonate filler. As a consequence of the surface energies of the three phases the filler tends to reside within the elastomer phase thereby obviating the desired effect. When small amounts of stearic acid are added to the composite, the desired improvement in modulus is achieved, as the fatty acid is adsorbed onto the surface of the mineral filler reducing its surface energy so that it becomes encapsulated within the polypropylene phase.[42]

The principles here of modifying the interfacial energy by adding a "compatibiliser" to achieve a desired phase structure and adequate interfacial adhesion is widely used, for example in polyethylene blends with polystyrene[43] and with polybutylene terephthalate.[44]

The toughening of glassy polymers by incorporation of a discrete rubbery phase is critically dependent upon achieving the appropriate phase structure in the composite. In rubber-toughened epoxies carboxy-terminated acrylonitrile butadiene rubber (CTBN) forms spherical inclusions, about a micron in diameter, within an epoxy-rich matrix.[45,46] The carboxy end groups are considered to act rather like a grafted-on compatibiliser, ensuring appropriate adhesion between the two phases.

In the examples just discussed, the presence of a polar molecule, such as a fatty acid, modified the adhesion by interfacial adsorption. A common practical adhesion problem is associated with the presence of oils or greases on the surface of a metal to be bonded. Many pretreatments are designed to remove such weak layers, but in some engineering situations grease-free metals are not practicable. Commerçon and Wightman[47] investigated adhesion to galvanised steel, such as that used for making car bodies. With certain epoxy adhesives they found similar lap shear strengths whether the metal had been degreased or deliberately oiled before bond formation. They comment that the adhesive was able to "displace or absorb the oil". This, then, is another example of modification of an interface by adsorption, the adhesive being more strongly adsorbed as the galvanised surface displaces the contaminating oil.

4.3 Chemical Interaction

Sometimes the surface of one phase may produce chemical changes in a contiguous phase. The high adhesion to steel of polyethylene without antioxidant, shown in Table I, is a result of the catalytic oxidation of the polymer by the adjacent iron.[10] In contrast to this, a nickel powder filler in polypropylene has been shown to enhance thermal stability compared with the unfilled polymer.[48] In NBR moulding the mould alloy can, depending on its composition, exert a catalytic effect on the cure reaction of rubber close to the mould surface. This is turn alters mould adhesion.[49]

An unwelcome example of chemical interaction of a substrate was observed when bonding copper with CTBN-toughened epoxy resin.[50] The fracture energy of the joints with copper was much lower than that with bonds with other metals, such as steel. Microscopic examination showed that gross phase separation had occurred in the adhesive producing two intermingled phases in the region of its interface with the copper substrate. It was speculated that the copper reacted with components of the adhesive system, altering the complex relations responsible for the usual form of phase separation. Direct evidence of reactions between a copper surface and an epoxy resin has since been published.[51]

CONCLUSIONS

The interface in a composite or bonded structure is crucial to its practical performance. An understanding of the interface, and of the ways in which the surface of one material may alter the properties of another, opens up the possibility of "engineering" an interface to achieve desired properties. The interfacial region may be altered by direct pretreatment of one of the surfaces or indirectly as a result of preferential adsorption of residues or additives or of chemical reaction at the interface.

At the beginning of this paper it was emphasised that the properties of a composite or of a bonded structure reflect the interaction between the various parts, the bulk phases and the interfacial region between them. The implications of equation (1) are that the strength of a bonded structure is determined by the lowest value of the product EG, modulus times fracture energy, which may occur in one of the bulk phases or at or near an interface. Modification of the interfacial region provides one way of moving the locus of failure, and so of altering the properties. Of course, the relationship between engineering properties of composites and interfacial structure is a very complex one which is not fully understood. Often a modification which improves one property will have an adverse effect on another. It is for the practising engineer to use ingenuity in making a judgement of what will best address what may be the conflicting claims of toughness and strength, of ease of manufacture and durability, of profit margins and environmental damage.

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