

## Review

# Adhesively-bonded joints and repairs in metallic alloys, polymers and composite materials: Adhesives, adhesion theories and surface pretreatment

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In the present paper, the following topics are reviewed in detail: (a) the available adhesives, as well as their recent advances, (b) thermodynamic factors affecting the surface pretreatments including adhesion theories, wettability, surface energy, (c) bonding mechanisms in the adhesive joints, (d) surface pretreatment methods for the adhesively bonded joints, and as well as their recent advances, and (e) combined effects of surface pretreatments and environmental conditions on the joint durability and performance. Surface pretreatment is, perhaps, the most important process step governing the quality of an adhesively bonded joint. An adhesive is defined as a polymeric substance with viscoelastic behavior, capable of holding adherends together by surface attachment to produce a joint with a high shear strength. Adhesive bonding is the most suitable method of joining both for metallic and non-metallic structures where strength, stiffness and fatigue life must be maximized at a minimum weight. Polymeric adhesives may be used to join a large variety of materials combinations including metal-metal, metal-plastic, metal-composite, composite-composite, plastic-plastic, metal-ceramic systems. Wetting and adhesion are also studied in some detail in the present paper since the successful surface pretreatments of the adherends for the short- and long-term durability and performance of the adhesive joints mostly depend on these factors. Wetting of the adherends by the adhesive is critical to the formation of secondary bonds in the adsorption theory. It has been theoretically verified that for complete wetting (i.e., for a contact angle  $\theta$  equal to zero), the surface energy of the adhesive must be lower than the surface energy of the adherend. Therefore, the primary objective of a surface pretreatment is to increase the surface energy of the adherend as much as possible. The influence of surface pretreatment and aging conditions on the short- and long-term strength of adhesive bonds should be taken into account for durability design. Some form of substrate pretreatment is always necessary to achieve a satisfactory level of long-term bond strength. In order to improve the performance of adhesive bonds, the adherends surfaces (i.e., metallic or non-metallic) are generally pretreated using the (a) physical, (b) mechanical, (c) chemical, (d) photochemical, (e) thermal, or (e) plasma method. Almost all pretreatment methods do bring some degree of change in surface roughness but mechanical surface pretreatment such as grit-blasting is usually considered as one of the most effective methods to control the desired level of surface roughness and joint strength. Moreover, the overall effect of mechanical surface treatment is not limited to the removal of contamination or to an increase in surface area. This also relates to changes in the surface chemistry of adherends and to inherent drawbacks of surface roughness, such as void formations and reduced wetting. Suitable surface pretreatment increases the bond strength by altering the substrate surface in a number of ways including (a) increasing surface tension by producing a surface free from contaminants (i.e., surface contamination may cause insufficient wetting by the adhesive in the liquid state for the creating of a durable bond) or removal of the weak cohesion layer or of the pollution present at the surface, (b) increasing surface roughness on changing surface chemistry and producing of a macro/microscopically rough surface,

(c) production of a fresh stable oxide layer, and (d) introducing suitable chemical composition of the oxide, and (e) introduction of new or an increased number of chemical functions. All these parameters can contribute to an improvement of the wettability and/or of the adhesive properties of the surface. © 2004 Kluwer Academic Publishers

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## 1. Introduction

Polymeric materials that fall within the classifications of thermoplastics, thermosetting resins, elastomeric compounds, and natural adhesives (animal glue, casein, starch, and resin) may serve adhesive functions. Polymeric adhesives may be used to join a large variety of material combinations: metal-metal, metal-plastic, metal-composite, composite-composite, plastic-plastic, metal-ceramic, and so on. The primary drawback is the service temperature limitation. Organic polymers maintain their mechanical integrity only at relatively low temperatures, and strength decreases rapidly with increasing temperature. Even though the inherent strength of the adhesive may be much less than that of the adherend materials, nevertheless, a strong joint may be produced if the adhesive layer is thin and continuous. If a good joint is formed, the adherend material may fracture or rupture before the adhesive.

Polymers are attractive materials and usually offer the following advantages: (a) weight, (b) cost, (c) moisture and chemical resistance, (d) toughness, (e) abrasive resistance, (f) strength, (g) appearance, (h) insulation (both thermal and electrical), (i) formability, and (j) machinability. Polymeric materials, unlike metals, do not respond elastically to stress and undergo permanent deformation under sustained loading. The term viscoelastic describes the behavior of plastics when subject to stress. After the application of an initial load, the polymeric structure will move in response to the applied stress. The stress-strain curve for plastics change with time. When compared with metals, polymeric materials lack stiffness and their physical properties are temperature-dependent.

Service experience with adhesive bonded structures has been extremely varied, with some components providing excellent service and others failing or requiring extensive maintenance over a comparatively short service life time. The deficient adhesively bonded components have performed so badly when compared to conventionally fastened structures that they have been considered representative of the generic lack of reliability of bonded structures, leading to an overall poor acceptance of the technology.

Adhesively bonded joints offer essential advantages in comparison with other joining methods, such as higher joint stiffness and superior fatigue performance [1]. For this reason the number of adhesive bonding applications in various industries is steadily growing. Typical examples of beneficial applications of the adhesive bonding technology are in the construction of aircraft, rail vehicles and in the automobile industry. Since the nature of the bonding is dependent on the atomic arrangement and chemical properties of the molecular conformation, chemical constitution and diffusivity of elements in each constituent, it follows that the inter-

face between the different substrates has the specific properties.

As a result of theoretical considerations and extensive practical testing, the following recommendations [1] are made to achieve satisfactory joints: (a) *Suitable surface pretreatment*. Surface preparation is, perhaps, the most important process step governing the quality of an adhesive bond [2]; not only is a clean bond surface in the conventional sense required, but fresh cleaning to avoid adsorbed gases is often useful. Activated inert gases are sometimes used. (b) *Adhesive choice*. The adhesive should wet the adherend and solidify under production conditions of time, temperature, and pressure. Often the desired production conditions narrow the choice of adhesive. Some thermoplastic and thermosetting polymers are used as adhesives. Following forms of adhesives are available: liquids, pastes, and solids. (c) *Joint Design*. Adhesive joints are generally more resistant to shearing, compressive, and tensile stresses than they are to stress systems due to peeling. For example, it is easier to remove adhesive tape from a surface by peeling than by any other method of applying stress. (d) *Service condition*. Polymers as adhesives generally have higher thermal expansivities (i.e., the coefficient of expansion) than metals and ceramics. Furthermore, their expansion coefficients are not truly constants; that is, the polymers expand markedly in a nonlinear way with temperature. Epoxy resins have coefficient of linear expansion values between  $50 \times 10^{-6}$  and  $100 \times 10^{-6} \text{ K}^{-1}$  while polyester show values between  $100 \times 10^{-6}$  and  $200 \times 10^{-6} \text{ K}^{-1}$  [3]. Small compositional changes can have a marked influence on polymer expansion characteristics. If severe temperature changes are to be encountered, this effect and the required accommodations of the adhesive must be considered. Weathering and solvents that may be encountered in service are also important considerations.

### 1.1. Adhesives

Structurally, polymers are giant chainlike molecules (i.e., macromolecules) with covalently bonded carbon atoms forming the backbone of the chain. Polymers are structurally much more complex than metals or ceramic. Prolonged exposure to ultraviolet light and solvents can cause the degradation of the polymer properties. Due to predominantly covalent bonding, polymers are generally poor conductors of heat and electricity. Polymers, however, are generally more resistant to chemicals than are metals.

It is now useful to have an understanding of the basic molecular structure of polymers since the properties of the adhesives are much dependent on the molecular structure. The molecular structure of most polymers are based on hydrocarbons in which carbon

and hydrogen combine in the relationship  $C_nH_{2n+2}$ , known as paraffins [4]. Theoretically, these hydrocarbons can be linked together indefinitely to form very large molecules, the bonds between the atoms being single pairs of shared (covalent) electrons. Because there is no provision for additional atoms to be added to the chain, such molecules are said to be saturated. Bonding with the molecule is quite strong, but the attractive forces between adjacent molecules are much weaker.

Carbon and hydrogen can also form molecules in which the carbon atoms are held together by double or triple covalent bonds. Because such molecules do not have the maximum possible number of hydrogen atoms, they are said to be unsaturated and are important in polymerisation process, where small molecules join to form large ones with the same constituent atoms. In polymeric compounds, four electron pairs surround each carbon atom, and one electron pair is shared with each hydrogen atom. Other atoms or structures can be substituted for carbon and hydrogen, however. Chlorine or even a benzene ring can often take the place of hydrogen. Oxygen, sulfur, or nitrogen can substitute the place of carbon [4]. Thus, a wide range of polymeric compounds can be created.

The process of forming large molecules (macromolecules) from small ones (i.e., monomers) is called polymerization; polymerization is the process of joining many monomers, the basic building blocks, together to form polymers. In other words, the polymerization process is a reaction by which single molecules are linked to form large molecules. There are two important classes (mechanisms) of polymerization:

(a) *Addition polymerization (or Chain reaction polymerisation)*. Addition polymers can be considered as long chains of tightly bonded carbon atoms with strongly attached pendants of hydrogen, fluorine, or benzene rings. All bonds within the molecules are strong primary bonds. The attraction between neighboring molecules, however, is only by the much weaker van der Waals forces. In this process monomers join to form a polymer without producing any by-product. This process is generally carried out in the presence of catalysts. Depending upon the properties of each monomer, a range of characteristics may be obtained. For example, the copolymer of vinyl chloride and vinyl acetate to produce PVC is one of the important industrial thermoplastics. For these materials, the mechanical and physical properties are largely determined by the intermolecular forces. Because these secondary bonds are weakened by the elevated temperature, polymer of this type softens with increasing temperature and becomes harder and stronger when cooled. Activators, like  $H_2O_2 \rightarrow 2OH$ , initiate and terminate the chain. Thus, the amount of activator relative to the amount of monomer determines the average molecular weight or length of the chain. The average number of mers in the polymer is known as the degree of polymerisation and ranges from 75 to 750 in most commercial polymers.

(b) *Condensation (or Step reaction) polymerization*. In this process a stepwise reaction of molecules occurs and in each step a molecule of a simple compound, gen-

erally water, forms as a by-product. In contrast to polymerisation by addition, in which all of the component atoms appear in the product molecule, condensation polymerisation occurs as reactive molecules combine with one another in a stepwise fashion, while eliminating small by-product molecules, such as water. The structure of condensation polymers is often a three-dimensional framework in which all atoms are linked by strong primary bonds.

Copolymers are a special category of polymer in which two or more types of mers are combined into the same addition chain. This process (i.e., by addition mechanism), greatly expands the possibilities of creating new types of polymers with improved physical and mechanical properties. The small amounts of Plasticizers may be added to change the properties of the polymer, thus extending its application; the flexibility, ductility, and toughness of polymers may be improved with the aid of these additives. Their presence also produces reductions in hardness and stiffness. Plasticizers are commonly used in polymers that are intrinsically brittle at room temperature, such as polyvinyl chloride and some of the acetate copolymers. In effect, the plasticizers lowers the glass transition temperature, so that at ambient conditions the polymers may be used in applications requiring some degree of pliability and ductility. Plasticizers are usually liquids with high boiling points.

Based on their thermal characteristics, polymeric materials are usually divided into two main groups: (a) thermoplastic or (b) thermosetting, produced by either condensation or addition polymerization. The term thermosetting and thermoplastic refer to the material's response to elevated temperature. Thermosetting polymers are those with three-dimensional framework structure which all atoms are connected by strong covalent bonds. These materials generally result from condensation polymerisation, in which elevated temperature tends to promote an irreversible reaction, hence the term thermosetting. Once these materials are set, additional heatings do not produce softening. Instead, the materials maintain their mechanical properties up to the temperature at which they char or burn. Deformation requires the breaking of primary bonds, so that these polymers tend to be strong, but brittle. As a class, the thermosetting polymers are significantly stronger than the thermoplastics and have a lower ductility, a higher modulus of elasticity, and poorer impact properties. Thermosets undergo a curing reaction. Curing can be performed by the use of heat, radiation, or light (photoinitiation), moisture, activators, catalysts, multiple-component reactions, or combinations thereof [4]. The curing reaction of the thermoset polymers can be initiated by the following methods: (a) appropriate chemical agents (b) application of heat and pressure, or (c) by exposing the monomer to an electron beam. Thermosetting plastics are classified according to the resin used. The main classes of thermosetting polymers [5] are: (a) phenol formaldehyde, (b) urea formaldehyde, (c) melamine formaldehyde, (d) polyesters, (e) epoxies, and (f) silicones. In general, the most useful adhesive

materials for structural stressed applications are the thermosets and their alloys. Because the molecules of the thermosets are densely cross-linked, their resistance to heat and solvents is good and they show less elastic deformation under load than the thermoplastics. Thermoplastics are the polymeric materials that flow under the application of heat and pressure, i.e., they soften or become plastic on heating. Thermoplastic materials harden when cooled to room temperature. As a result of temperature change, their different behavior is due to the following factors: (a) molecular structure and shape, (b) molecular size, or mass, and (c) type of bond (covalent or van der Waals). Since they become increasingly softer with increase in temperature, certain members of the thermoplastic family are liable to permanent distortion under mechanical strain at relatively low temperature (i.e., 60°C). They may flow to an appreciable extent under load at room temperature. Thermoplastics have generally higher impact strength and pleasing appearance, and can be converted into a finished product at lower manufacturing cost.

There are five major areas of application for polymers: (a) plastics, (b) rubbers or elastomers, (c) fibers, (d) surface finishes and protective coatings, and (e) adhesives. Adhesives have been a technologically important application of polymers for many years. This class of materials possesses many interesting and useful properties that are completely different from those of the more traditional engineering materials, such as metals and ceramics, and that can not be explained or handled in design situations by the traditional approaches. The properties of these materials depend on the molecular structure of polymers. This molecular structure is the key to an understanding of the science and technology of polymers. An adhesive is defined as a polymeric substance with viscoelastic behavior, capable of holding adherends together by surface attachment to produce a joint with a high shear strength. Some thermoplastic and thermosetting polymers are used as adhesives. They are tough, strong, and reliable, and can be applied almost any combination of materials.

In thousands of years people have used natural adhesives (glues) made from animal sources. Many of the early natural adhesives are still used. These include starch and protein-based formulations such as hydrolyzed collagen from animal hides, hooves, and bones and casein from milk. However, with advances in polymers in recent years, synthetic adhesives with superior characteristics have appeared. As new adhesive formulations based on synthetic polymers (often the same polymers used in other applications) continue to be developed, the range of applications for adhesives has expanded dramatically (see for example [6–9]). One important aspect of this rapidly growing field is that thermosets, thermoplastics, and elastomers have all found applications as adhesives, and so-called alloys have been developed in which more than one type of polymer is used.

Adhesively bonded joints between various substrates have the following advantages [5, 10, 11]: (a) the capability of joining dissimilar materials without regard to galvanic corrosion, (b) bonding very thin sections

to heavy sections without distortion, (c) joining heat-sensitive alloys, (d) producing bonds with unbroken surfaces, (e) bonding small adherends. For example, it is hard to imagine welding abrasive grains to a paper backing to make sandpaper, or bolting the grains together to make a grinding wheel, (f) Adhesive bonds have lower stress concentrations than mechanical joints; in the adhesive joining of large adherends, resulting in low stresses, and holes (necessary for riveting or bolting), which invariably act as stress concentrators in the adherends, are eliminated, thus lowering the possibility of adherend failure. (g) In addition to joining, adhesives may also act as seals against the penetration of fluids. In the case of corrosive fluids, this, coupled with the absence of holes, where corrosion usually gains an initial foothold, can reduce corrosion problems. (h) Adhesive bonded joints weigh less than mechanically bonded joints; in terms of weight, it does not take much adhesive to join much larger adherends. As a result, it is not surprising that many of the newer high-performance adhesives were originally developed for aerospace applications. (i) Adhesive bonding has less sensitivity to cyclic loading. (j) Adhesive bonds permit smooth external surfaces at the joint. (k) Adhesive joining may offer economic advantages, often by reducing the hand labor necessary for other bonding techniques.

## 1.2. Surface pretreatments

Surface preparation is, perhaps, the most important process step governing the quality of an adhesive bond. Structural adhesive bonding of joints is achieved either by mechanical interlocking of the polymer with the adherend surface or chemical bonding of the polymer molecules with the metal oxide [2]. To improve bond strength and durable adhesive joint between different substrates, surface preparation is a necessary pretreatment prior to adhesive bonding. Certain bonding techniques provide adequate static strength, but have little durability when exposed to hot moisture environments, while others are susceptible to debonding in the presence of harsh environmental conditions, i.e., fuels, oils and cleaning solvents commonly encountered in industry such in aircraft application [2]. In addition, the nature of the surface treatment prior to bonding is found to be a major influence in the control of this effect [12]. Surface pretreatment increases the bond strength by altering the substrate surface in a number of ways including [2]: (a) increasing surface tension, (b) increasing surface roughness or (c) changing surface chemistry. By increasing surface roughness, an increase in surface area occurs which allows the adhesive to flow in and around the irregularities on the surface to form a mechanical bond [2]. Changing surface chemistry may result in the formation of a chemical bond e.g., between the polymer molecules in the polymer matrix composite and the metal oxide layer on the other adherend layer [2, 13–16].

As a result, the nature of the surface will also influence the stability of the joint. When exposed to hot/humid environmental conditions, a polymeric adhesive/polymer interface is much more stable than the

equivalent polymeric adhesive/metal interface. A well-chosen polymeric adhesive/polymer interface is unlikely to fail because of the environmental-induced stress due to the nature of the bond formed [2]. On the other hand, the durability of a polymeric adhesive/metal joint is not as stable. Early studies in the 1960s revealed that these joints did not perform well in hot/wet conditions with frequent occurrence of short-term interfacial bond failure.

Hart-Smith [17] has studied the interfaces in bonded, co-bonded, and co-cured composite structures using a peel-ply durability test coupon in order to assess durability of these materials. The composite structures fail during the service, even though they appeared to have been manufactured correctly, according to the short-term quality control coupons tested at the time of initial fabrication. The issue is not one of structural overloading. The interface between the adhesive and the composite surfaces simply disbonds without the trace of either material ever having adhered to the other. What appears to be a common element in many of these problems is contamination introduced by the use of a "released" peel ply without subsequent thorough abrasion of the bonding surfaces. Another common but unrelated contributor to premature interfacial failures is some form of pre-bond moisture. Moisture can be present in an undried laminate cured long before it was bonded, as condensation on the surface of adhesive film not stored or thawed out properly, or absorbed within adhesive film which had been left out too long in the lay-up room. Water absorbed by the nylon filaments before the original laminates are cured with the peel ply in place is also identified as a contributing problem. The cause of such weak bonds should be acknowledged as processing errors. This is that such weaknesses are invariably undetected by conventional non-destructive testing (NDT) techniques such as ultrasonic inspections, suggesting to some that the parts might not be defective after all. It took almost a decade to acknowledge the criticality of surface preparation for metal-bonded structures [17].

In present review, the following subjects have been studied: (a) first of all, the available adhesive materials including their recent advances are classified on the following basis; (i) organic chemistry, (ii) intended applications, and (iii) adhesives for high-temperature composites as adherends, (b) secondly, the thermodynamic factors affecting surface pretreatment methods including the adhesion theory, wettability, and surface energy of the substrates have been summarized, and (c) finally, available surface pretreatment methods as well as their recent progress for various substrates including polymers, polymer-matrix composites and metallic alloys have been presented.

## **2. Adhesive materials systems: available adhesives**

In adhesive bonding, a nonmetallic material (i.e., adhesive) is used to create a joint between two surfaces. The actual adhesives span a wide range of material types and forms, including (a) thermoplastic resins, (b) thermosetting resins, (c) artificial elastomers, and (d) even

some ceramics. They can be applied as drops, beads, pellets, tapes, or coatings (films) and are available in the form of liquids, pastes, gels, and solids.

In the present review, adhesive systems are classified on the following basis: (a) Organic chemistry, (b) Intended applications, and (c) high-temperature composites as adherends. With such a range of possibilities, the selection of the best adhesive for the task at hand can often be quite challenging.

Adhesive systems on the basis of organic chemistry are categorized into five different systems that accomplish the objectives [10]: (a) Solvent-based adhesives, (b) Latex adhesives, (c) Pressure-sensitive adhesives, (d) Hot-melt, and (e) Reactive adhesives. Whereas intended applications range [4] from (a) load-bearing (structural adhesives) to (b) light-duty holding (non-structural or fixturing adhesives, to (c) sealing (the forming of liquid or gas-tight joints). Commonly used structural (i.e., load-bearing) adhesives include [4] (a) epoxies, (b) cyanoacrylates, (c) anaerobics, (d) acrylics, (e) urethanes, (f) silicones, (g) high-temperature adhesives, and (h) hot melts. For these materials, the bond can be stressed to a high percentage of its maximum load, for extended periods of time, without failure.

Because of fatigue considerations, whenever possible, it is preferable to bond rather than mechanically fasten composite structures. For this reason, the increased usage of high-temperature resin-matrix systems for composite materials has necessitated the development of compatible and equally heat stable adhesive systems. Therefore, the adhesives used for bonding the composite materials can be classified as [18]: (a) high-temperature epoxy, (b) epoxy-phenolic, (c) condensation-reaction polyimide, (d) addition-reaction polyimide, and (e) bismaleimide adhesives [19, 20].

In the following sections, we will briefly summarize the above-mentioned adhesives in relation to the bonding of various substrates such as metallic alloys, polymers and composite materials.

### **2.1. Epoxy adhesives**

Epoxies are a broad family of polymer materials characterized by the presence of epoxy groups in their molecular structure. Although high-molecular-weight linear epoxies are often used as thermoplastics, they are most often used as thermosetting materials that cross-link to form a three-dimensional non-melting matrix. The thermosetting epoxies are the oldest, most common, and most diverse of the adhesive systems, and can be used to join most engineering materials, including metal, glass, composite, and ceramic. Just as epoxies are the most common matrix for advanced composites, epoxy adhesives are also the most common. Epoxy adhesives can be either one-stage (curing agent already mixed in) or two-stage where the user mixes in the curing agent just before use. The form of the one-stage material is most often a sheet, very much like a prepreg without the reinforcement, or in a paste. Both room temperature and elevated temperature curing systems are used, although many times the room temperature curing adhesives require postcuring to develop good mechanical properties at elevated temperatures. Cure times can

range from a few minutes for simple noncritical parts to more than 12 h for large, critical-performance parts [11]. All adhesives are sensitive to the surface conditions of the materials to be joined. However, epoxies are more sensitive than other adhesive materials in the case of metal. They have the following advantages: (a) strong, versatile adhesives that can be designed to offer high adhesion, (b) good tensile and shear strength, (c) high rigidity, (d) good chemical resistance, (e) excellent bonding, (f) good creep resistance, (g) easy curing with little shrinkage, and (h) good tolerance to elevated temperatures. Various epoxies can be used [4] over the temperature range  $-51$  to  $260^{\circ}\text{C}$ . After curing at room temperature, shear strengths can be [4] as high as 35 to 70 MPa.

The heat is used as the curing agent for single-component epoxies. Majority of the epoxies, however, are two-component blends involving (a) a resin and (b) a curing agent, plus (c) possible additives such as accelerators, plasticizers, and fillers that serve to enhance cure rate, flexibility, peel resistance, impact resistance, or other characteristics. Heat may again be used to drive or accelerate the cure.

Epoxy adhesives based on multifunctional resins [18] are available which exhibit excellent strength retention at temperatures up to about  $225^{\circ}\text{C}$ . Where long-term aging is required, epoxies are generally limited to applications requiring continuous service at temperatures no higher than  $175^{\circ}\text{C}$ . The adherends involved are most commonly aluminum alloys and epoxy-matrix composite structures.

However, these adhesives have the following disadvantages: (a) the relatively low peel strength, and flexibility, (b) the bond strength is sensitive to moisture and surface contamination, (c) often brittle at low temperatures, (d) the rate of curing is comparatively slow, (e) relatively high resin cost. Sufficient strength for structural applications is generally achieved in 8 to 10 h, with full strength often requiring 2 to 7 days [4].

The new epoxy adhesives developed for use on aerospace industry have excellent strength retention at temperatures up to  $215^{\circ}\text{C}$ . Strength then drops [18] rather sharply to 6.9 MPa at  $260^{\circ}\text{C}$ . After 3000 h aging at  $215^{\circ}\text{C}$ , the adhesive retains approximately 80% of its original lap shear strength [18].

### **2.1.1. $\text{FM}^{\text{®}}$ 300 epoxy based film adhesive and its modified version (i.e., $\text{FM}^{\text{®}}$ 300-2)**

For aerospace bonding applications,  $\text{FM}^{\text{®}}$  300 epoxy based film adhesive is widely used for bonding metal to composite structures (i.e., metal-to-composite substrate). Some of these applications range from bonding the wing-root assemblies (titanium to graphite epoxy), to composite sandwich structures on F-18 fighter aircraft, to bonding and surfacing applications on most commercial and military worldwide [21]. The  $177^{\circ}\text{C}$  curing adhesive is used in both co-cure and secondary bonding applications.

In the case of bonding metal to composite parts, the  $177^{\circ}\text{C}$  cure temperature for secondary bonding can lead

to significant thermal stresses due to the difference in coefficient of thermal expansion between metal and the composite. These induced stresses can result in the loss of dimensional stability, disbonds, or delamination in these parts. In order to overcome these problems the  $121^{\circ}\text{C}$  curing film adhesive (i.e.,  $\text{FM}^{\text{®}}$  300-2) was developed for providing the performance of  $177^{\circ}\text{C}$  curing film adhesives (i.e.  $\text{FM}^{\text{®}}$  300) in both metal and composite bonding applications [21]. This adhesive film designated  $\text{FM}^{\text{®}}$  300-2 is a  $121^{\circ}\text{C}$  cure version of  $177^{\circ}\text{C}$  curing  $\text{FM}^{\text{®}}$  300 adhesive film and provides similar stress-strain and mechanical performance to the  $\text{FM}^{\text{®}}$  300 system [22, 23]. This modified version of  $\text{FM}^{\text{®}}$  300 adhesive (i.e.,  $\text{FM}^{\text{®}}$  300-2) was developed for various bonding applications where higher performance is needed but the cure temperature can not be higher than  $121^{\circ}\text{C}$ .

The adhesive system, designated as  $\text{FM}^{\text{®}}$  300-2, is based on epoxy chemistry and is designed for bonding metallic and composite structures as well as structures fabricated from metallic, Nomex or fiberglass honeycomb. This adhesive system has been formulated to fully cure within 90 min at  $121^{\circ}\text{C}$  and has flow and handling properties similar to  $\text{FM}^{\text{®}}$  300 adhesive.

## **2.2. High-temperature adhesives**

High-temperature adhesives are specified [4] if their strengths keep constant at temperatures over  $290^{\circ}\text{C}$ . For example, epoxy phenolics, modified silicones, phenolics, polyamides, and some ceramics can be classified as high temperature adhesives. Epoxy-phenolics rival the polyamide adhesives in their ability to withstand short-time exposure to extremely high temperatures. For this reason, these adhesives are suited for use on missiles, and are generally preferred to polyimides because of their lower cost and ease of processing. Bond pressures of 0.28 MPa and cure temperatures of  $150^{\circ}\text{C}$  are usually adequate for most applications [18]. High-temperature adhesives are primarily used in the aerospace industry.

High-temperature adhesives based on condensation-reaction polyimide adhesives (precursors) have been marketed for over 15 years. Adhesives of this type are supplied in both liquid form and as solid films. In addition, they may be filled or unfilled. Aluminum-powder-filled adhesives are superior in strength to unfilled adhesives and are generally used for metal-bonding applications [18]. The disadvantages of these adhesives [4, 18] are (a) high cost, (b) long curing times, (c) high cure temperatures,  $260^{\circ}\text{C}$  or even higher, depending on the expected service temperature, (d) the high volatile content (about 12% for aluminum-filled adhesives and 30% for unfilled adhesives) of condensation-reaction polyimides.

$\text{FM}34^{\text{®}}$  was perhaps the first polyimide adhesive developed that gained any significant commercial acceptance. Its performance at temperatures up to  $540^{\circ}\text{C}$  showed that its strength retention up to  $540^{\circ}\text{C}$  did not significantly differ from that of the more easily processed epoxy-phenolic adhesive  $\text{HT}^{\text{®}}$  424 [18]. The thermal stability of this adhesive [18] was superior, showing no significant drop in strength over 40,000 h at  $260^{\circ}\text{C}$ .

### 2.3. Hot melts adhesives

Thermoplastic materials (which are solids at room temperature) are also used as adhesives for composites. These materials are called hot melt adhesives since they are melted to become fluid so they can be applied to the materials to be joined and then they reharden when cooled. Hot melts most often are used when speed in bonding is important. They should be avoided in applications where creep would be a problem. However, the thermoplastics generally have good peel and environmental resistance properties [11]. Although the hot-melt adhesives are not generally considered to be true structural adhesives, they are being used increasingly to transmit loads, especially in composite material assemblies. They are thermoplastic resins which are solid at room temperature but melt abruptly when heated into the range of 100 to 150°C [4]. The thermoplastics often form good adhesives simply by being melted to cause flow and then solidifying on cooling after contacting the surfaces under moderate pressure [10]. Many polymers can be used as hot-melt adhesives on certain adherends, including metals in some instances. Polyamides and poly(ethylene-co-vinyl acetate) are used frequently as hot-melt adhesives. Melted nylon is capable of wetting many substances and giving moderate adhesion; similarly the polyacetal “Delrin,” and a number of vinyl polymers and polycarbonates. The adhesion of all these can generally be improved by priming the surface of the adherend with a dilute solution of a phenolic resin-which almost classifies them as two-polymer adhesives. A method of application is to position the adhesive in the joint prior to operations such as the paint bake process in automobile manufacture. During the baking, the adhesive melts, flows into seams and crevices, and seals against the entry of corrosive moisture. The hot melts provide reasonable strength within minutes, but do soften and creep when exposed to elevated temperatures and become brittle when cold.

### 2.4. Acrylics (-based thermoplastic adhesives)

Acrylic adhesives permit the tailoring of the flexibility of the adhesive [11]. Two acrylic molecules (methyl methacrylate and acrylic acid) are copolymerized. Normally these materials are supplied as thin fluids. The acrylic-based thermoplastic adhesives have the following advantages: (a) one of the most attractive properties of acrylic polymers is their resistance to aging, which results from the ability of these polymers to absorb ultraviolet light in the solar spectrum and redissipate it as harmless energy in the infrared wavelength range [24], (b) good strength, toughness, and versatility, and (c) be able to bond a variety of materials, including plastics, metals, ceramics, and composites, even through oily or dirty surfaces [4]. Most involve application systems where a catalyst primer (curing agent) is applied to one of the surfaces to be joined and the adhesive is applied to the other. The surface pretreated parts can be stored separately for weeks without damage. The components react to produce a strong thermoset bond at room temperature when adhesively joined. The curing

can be accelerated by heat, and at least one variety cures with ultraviolet light. Comparing these with other adhesives, the acrylic-based thermoplastic adhesives offer strengths comparable to the epoxies, good resistance to water and humidity, and the added advantages of room temperature curing and a non-mix application system [4]. The disadvantages of these adhesives include (a) low high-temperature strength, (b) flammability, (c) an unpleasant odor when still uncured, and (d) comparatively expensive. These materials also have highest optical clarity, transmitting over 90% light.

### 2.5. Cyanoacrylates adhesives

These adhesives are liquid monomers that polymerize when spread into a thin film between two surfaces [4]. The cyanoacrylates are distinguished by their rapid setting properties at room temperature and by the very wide range of materials which they will bond; trace amounts of moisture on the surfaces promote curing at very high speeds, often as little as 2 seconds. Thus the cyanoacrylates offer a one-component adhesive system that cures at room temperature with no external impetus. Commonly known as superglues, this family of adhesives is now available in the form of liquids, gels, toughened versions designed to overcome brittleness, and even nonfrosting varieties. The cyanoacrylates have the following advantages [4]: (a) the excellent tensile strength, (b) fast curing, (c) good shelf life, and (d) adhere well to most commercial plastics. The disadvantages of these adhesives, however, are their (a) high cost, (b) poor peel strength, (c) brittleness, (d) poor bond properties at elevated temperatures.

### 2.6. Anaerobic acrylic adhesives

Anaerobic acrylic adhesives are monocomponent systems which are able to cure via a redox radical mechanism at room temperature and in the absence of air, hence their name [25]. Anaerobic adhesives belong to the large family of thermosetting acrylic polymers. These polyester acrylic adhesives remain liquid when exposed to air [4]. When confined to small spaces and shut off from oxygen, as in a joint to be bonded, the polymer becomes unstable. In the presence of iron or copper, it polymerizes into a bonding-type resin without the need for elevated temperature. Additives can reduce odor, flammability, and toxicity and speed the curing operation. Slow-curing anaerobics require 6 to 24 h to attain useful strength [4]. With selected additives and heat, however, curing can be reduced to as little as 5 min. These adhesives can bond almost anything, including oily surfaces. The joints resist vibrations and offer good sealing to moisture and other environmental influences. Unfortunately, they are rather brittle and are limited to service temperatures below 149°C.

Industrial use (mainly in the fields of automotive, aeronautics, electronics etc.) of anaerobics covers five applications [26]: (a) fitting (e.g., bearings into housings), (b) locking (e.g., nuts onto bolts), (c) sealing (e.g., liquid gaskets), (d) retaining (e.g., shafts into hubs), and (e) bonding (e.g., flanged couplings). As retaining and bonding media, they can either replace classical

systems based on shape (keys, splines, pins) or friction (interference fits, elastic rings, bolted joints) or, most profitably, can enhance the overall performance by combining with them. Typical benefits include elimination of backlash, reduction of fretting wear, improved corrosion resistance, airtight sealing action and remarkable increases of stiffness and strength. These adhesives have the following main advantages [26, 27]: (a) preliminary mixing not required, (b) handling time of approximately 15 min so that they are suited with rhythms imposed by assembly lines, and (c) final resistance obtained after 24 h, (d) elimination of backlash, (e) reduction of fretting wear, (f) improved corrosion resistance, (g) airtight sealing action, and finally (h) remarkable increases of stiffness and strength. However, as most adhesives, anaerobic adhesives require a decontamination of materials to be bonded and a surface treatment which can sometimes modify some characteristics of polymerization [28].

Following improvements have been made to ensure a higher level of performances for these adhesives [25]: (a) higher toughness by coupling polyurethane to acrylic monomers [29], (b) increased thermal resistance by use of polyamides with basic monomers [30], (c) greater resistance to impact and shearing stress by the incorporation of additives as elastomers [31].

## 2.7. Urethane adhesives

These adhesives are a large and diverse family of polymers that are generally applied at temperatures below 65°C and components that can undergo great elongation [4]. Urethanes are available as both one-part thermoplastic and two-part thermosetting systems. In general, they cure quickly to handling with 24 h to complete cure at room temperature. In comparing the other structural adhesives, the urethanes offer good low-temperature adhesion coupled with good flexibility and toughness. These adhesives are relatively moisture sensitive, deteriorate in many chemical environments, and can involve toxic components or curing products.

## 2.8. Silicone adhesives

Silicones are semiorganic spine molecules with alternating silicon and oxygen atoms. This family of synthetic polymers is partly organic and partly inorganic. Silicones are classified as fluids, elastomers, and resins. Thus, silicone polymers may be fluid, gel, elastomeric, or rigid in their form. Good physical properties are maintained from 232 to 260°C. The properties that make silicones attractive to engineers include: (a) low surface tension, (b) high lubricity with rubber and plastic surfaces, (c) excellent water repellency, (d) good electrical properties, (e) thermal stability, (f) chemical inertness, (h) resistance to oxidation, hot water and weather, and (i) retain their flexibility at low temperatures.

The silicone containing thermoset adhesives cure from the moisture in the air or adsorbed moisture from the surface being joined. They form low-strength structural joints and are usually selected when considerable expansion and contraction is expected in the joint, flex-

ibility is required (as in sheet metal parts), or good gasket or sealing properties are necessary. These adhesives can be used to join the metals, glass, paper, plastics, and rubbers. However, these adhesives have the following disadvantages: (a) relatively expensive, (b) curing is rather slow.

## 2.9. Pressure-sensitive adhesives

As the pressure-sensitive adhesives (PSAs) are viscous polymer melts at room temperature, these polymers must be used above their glass transition temperatures [10, 32]. They are caused to flow and contact the adherends by applied pressure, and when the pressure is released, the viscosity is high enough to withstand the stresses produced by the adherends, which obviously can not be very great. The key property for a polymer used in this application is tack, which basically is a viscosity low enough to permit good surface contact, yet high enough to resist separation under stress, something on the order of  $10^4$ – $10^6$  cP, although elasticity probably plays a role, also [10, 33]. Natural, SBR, and reclaimed rubbers are common in this application. The many varieties of pressure-sensitive tape are faced with this type of adhesive. Contact cements are a variation in which the rubbery polymer is applied to each adherend surface in the form of a solution, or increasingly, a latex. Evaporation of the solvent or water leaves a polymer film with the tack necessary to grab and hold the adherends when they are pressed together.

For good adhesive properties, the glass transition temperature for pressure-sensitive adhesives must be between 50 and 70°C below the temperature of use [32, 34, 35]. If the glass transition temperature  $T_g$  is too far below the temperature of use, the viscoelastic losses in the debonding process will be too low. On the other hand, if the  $T_g$  is too close to the temperature of use, the compliance will become too low, making it difficult to establish good contact with the adherend. Considering that most applications for PSAs are for room temperature or slightly above, the most useful polymers have  $T_g$ s between  $-50$  and  $-30^\circ\text{C}$ , with some exceptions [35]. One common solution for retaining the useful properties of a polymer while adjusting its  $T_g$  involves compounding with tackifying resins that allow the use of polymers with a lower  $T_g$ .

## 2.10. Addition-reaction to polyamide adhesives

These adhesives make it possible to obtain bondlines with extremely low void contents. Adhesives of this type are generally supplied as supported film containing sufficient alcohol to impart tack and drape to the adhesive. Unlike the condensation-reaction type, addition-reaction polyimides (PIs) remain thermoplastic after imidization and solvent removal have occurred. In contrast to the condensation-reaction PIs, which can be processed using the postcure concept, addition-reaction PIs must be held under pressure throughout the cure cycle. Therefore, relatively costly high-temperature presses or autoclaves are required to fabricate panels with addition PI adhesives. Composites made from addition-reaction



PIs are generally fabricated using 1.4 MPa pressure to ensure low void content in the laminate.

### 2.11. Latex adhesives

Natural rubber originates as a latex, i.e., an aqueous dispersion of minute rubber particles which are kept in suspension by an adsorbed layer of protein. These adhesives are based on polymer latexes made by emulsion polymerization; polymer particles are on the order of 0.05 to 0.15  $\mu\text{m}$  stabilized by the soap [10]. The total solid particles content of the latex as obtained from the tree is in the region of 30 percent. Similarly many synthetic rubbers and other flexible polymers are initially produced by a process known as emulsion polymerization in which the polymer is first produced as latex or emulsion similar in appearance to natural latex but stabilized by synthetic stabilizing and dispersing agents instead of proteins.

They flow easily while the continuous water phase is present and dry by evaporation of the water, leaving behind a layer of polymer. In order that the polymer particles coalesce to form a continuous joint and be able to flow to contact the adherend surfaces, the polymers used must be above their glass transition temperature at use temperature. These requirements are similar to those for latex paints, so it is not surprising that some of the same polymers are used in both applications, for example, styrene-butadiene copolymers and polyvinyl acetate. Nitrile and neoprene rubbers are used for increased polarity. A familiar example of a latex adhesive is "white glue," basically a plasticized polyvinyl acetate latex. Latex adhesives are displacing solvent-based adhesives in many applications because of their reduced pollution and fire hazards. They are used extensively for bonding pile to backing in carpets.

### 2.12. Reactive adhesives

These adhesives are either monomers or low molecular weight polymers which solidify by a polymerization and/or crosslinking reaction after application [10]. They can develop tremendous bond strengths and have good solvent resistance and high-temperature properties. The most familiar example of reactive adhesives are the epoxies generally cured by multifunctional amines. Polyurethanes also make excellent reactive adhesives.

The  $\alpha$ -alkyl cyanoacrylate "super glues" are now a familiar part of the consumer market. Originally, the monomers had extremely low viscosities, and so could crawl into narrow crevices and wet the adherend surfaces rapidly. On the other hand, they would not fill gaps, and were absorbed into porous adherends, giving poor bonds. Newer versions are available with higher viscosities to overcome these drawbacks. Unfortunately, being linear and polar, they have poor resistance to polar solvents (acetone is a good solvent), and they are subject to hydrolysis, and so have poor environmental stability.

Phenolic and other formaldehyde condensation polymers are also important reactive adhesives. Powdered phenolic resin is mixed with abrasive grains and

the mixture is compression molded to form grinding wheels. For example, A B-stage phenolic in a solvent is used to impregnate tissue paper. The solvent is evaporated, and the dry sheets are placed between layers of wood in a heated press, where the resin first melts and then cures, bonding the wood to form plywood. Similarly, sheets of paper impregnated with a B-stage melamine-formaldehyde resin are laminated and cured to form the familiar Formica<sup>®</sup> counter tops.

Unlike the previous examples of reactive adhesives, the phenolics and other formaldehyde condensation polymers evolve water as they cure. If trapped in the joint, this can result in serious weakness, which limits their adhesive applications. Note that all these examples of reactive adhesives are highly polar polymers. It is largely this polarity that accounts for their good bonding capabilities.

### 2.13. Bismaleimide (BMI) adhesives

A closely related reactive compound contained within additional polyimides (API) is the bismaleimide (BMI) family of materials [36–38]. The BMI resin system can vary from a crystalline diffusional compound to an oligometric amorphous material with difunctionality. In recent years many BMI resins and modifications have been developed primarily due to good drape and tack and "epoxy-like" cure conditions resulting in resins with higher temperature characteristics. BMIs possess thermal capabilities between 175–230°C (epoxies 120–175°C). BMI resins are very rigid system with a corresponding high degree of crosslinking, hence brittleness. This characteristic leads to microcracking and high shrinkage.

BMI adhesives fill a niche between high-temperature epoxy and PI adhesives. Unmodified BMI resins are hard, brittle solids. In order to impart drape to adhesive films based on these resins, they must be plasticized. However, unlike the PI resins, plasticization may be accomplished without resorting to the use of solvents. Volatile-free adhesive films having drape can be formulated through the use of reactive liquid monomers as plasticizers. Cure temperature requirements vary depending on the particular BMI resin employed and the specific monomeric plasticizers selected. In general, good results can be obtained using a cure of 2 h at 175°C under 0.28 MPa pressure followed by a 2- to 4-h postcure at 200 to 225°C [18].

BMI adhesives' strength retention is surprisingly good up to about 300°C. However, in applications where term exposure to high temperatures is involved, BMI adhesives are not expected to be durable beyond 200 to 225°C. In conclusion, almost limitless variations in formulation are possible with BMI adhesives.

### 2.14. Solvent-based adhesives

Here the adhesive polymer is made to flow by dissolving in an appropriate solvent to form a cement; solutions based on natural or synthetic rubbers are often called "cements". Good surface-wetting and other application properties can be obtained by dissolving solid adhesive constituents in organic solvents. The total solids content

may vary from 10 to 70 percent depending on the nature of the solid constituents, the type of solvent, and the viscosity and other rheological properties required. The adhesive hardens by evaporation of the solvent. The solvents used are mostly petroleum derivatives. Thus, the polymers used must be linear or branched to allow solution, and the joints formed will not be resistant to solvents of the type used initially to dissolve the polymer. To get a good bond, it helps if the solvent attacks the adherend also. In fact, solvent alone is often used to “solvent weld” polymers, dissolving some of the adherend to form an adhesive on application.

One of the drawbacks to solvent-based adhesives based on rigid polymers is the shrinkage that results when the solvent evaporates [10]. This can set up stresses that weakens the joint. An example of this type of adhesive is the familiar model airplane cement, basically a cellulose nitride solution, with perhaps some plasticizer. Rubber cements, of course, maintain their flexibility, but can not support as great a stress. Commercial rubber cements are based on natural, SBR (poly(butadiene-co-styrene)), nitrile (poly(butadiene-co-acrylonitrile)), chloroprene (poly(2-chlorobutadiene)), and reclaimed (devulcanized) rubbers [10]. Examples are household rubber cement and Pliobond<sup>®</sup>. Rubber cements may also incorporate a curing agent to crosslink the polymer after application and evaporation of the solvent. This greatly increases solvent resistance and strength.

### 2.15. Nonstructural adhesives

The adhesives classified as nonstructural have the limited load-bearing capabilities. The nonstructural adhesives are used in many different applications such as labeling and packaging. The hot-melt adhesives can be placed in this category. The followings are the some examples of the important nonstructural or special adhesives [4]: (a) Evaporative adhesives, (b) pressure-sensitive adhesives (PSAs), (c) Delayed-tack adhesives, (d) conductive adhesives, and (e) radiation-curing adhesives.

Evaporative adhesive use an organic solvent or water base, coupled with vinyls, acrylics, phenolics, polyurethanes, or various types of rubbers. Some commonly identified evaporative adhesives are rubber cements and floor waxes. Pressure-sensitive adhesives are usually based on various rubbers, compounded with various adhesives, and bond at room temperature with a brief applications of pressure. No cure is required, and the tacky adhesive-coated surfaces require no activation by water, solvents, or heat. This group of adhesives are used as peel-and-stick labels, cellophane tape, and Post-it notes. See Section 2.1.9 for more detail description of these adhesives.

Delayed-tack adhesives are similar to the pressure-sensitive systems, but are nontacky until activated by exposure to heat. They then remain tacky for several minutes to a few days to permit use or assembly.

Although most adhesives are electrical and thermal insulators, conductive adhesives are generally produced by incorporating selected fillers, such as silver, copper, or aluminum flakes or powder. Certain ceramic oxide

fillers can be used to provide thermal conductivity coupled with electrical insulation.

Radiation-curing adhesives are those designed to cure by exposure to radiation, such as visible, infrared, or ultraviolet light, microwaves, or electron beams. These adhesives offer rapid conversion from liquid to solid at room temperature and a curing mechanism that occurs throughout, rather than progressing from exposed surfaces. These adhesives are used for applications as a wide variety of dental amalgams that can fill cavities or seal surfaces while matching the color of the remaining tooth.

### 3. Adhesion, wetting and tack

In a simple system, bonding at an interface is due to adhesion between the adhesive and adherend. One talks of adhesion when a measurable amount of mechanical work is necessary to separate two surfaces of different chemical composition or shape [35]. In order to get good adhesion between adherend and adhesive, the first essential is to ensure good molecular contact. Although the maximum force necessary to break the bond may be defined as a measure of adhesion, the typical measure of the strength of an adhesive bond across an interface is the amount of energy necessary to break it, i.e., to separate two surfaces. Such a separation may involve the breakage of chemical or van der Waals bonds, as well as the plastic deformation of one or both of the bulk materials on either side of the interface. Typically, in all cases where good adhesion is obtained, the fraction of energy necessary to break the bonds at the interface is a very small fraction of the total energy necessary for the separation of the two surfaces; most of the mechanical work is used to deform, under stress, the material adjacent to the interface. Therefore, the measured energy of adhesion will be dependent on the ability of the interfacial bonds to sustain stress, as well as on the amount of plastic deformation caused locally by the above-mentioned stress [35, 39].

Tack refers to the adhesion of two surfaces of the same rubbery polymer. When two such surfaces are pressed together and subsequently pulled apart, the maximum force necessary to break the junction depends on the initial time of contact and the normal force applied, as well as the rate separation and the temperature and other variables [40–43]. From the dependence on temperature and polymer molecular weight, it can be inferred that the effectiveness of the bond depends partly on the interdiffusion of molecules across the interface and hence on molecular motions which are reflected in viscoelastic properties [42–44]. However, the effectiveness depends on the ultimate properties of the polymer itself.

If the two materials are the same material, the adhesion is called self-adhesion or autohesion. However, in the case of polymers, self-adhesion is usually dependent on the time of contact and, at infinite time, will eventually become the cohesive strength of the material rather than an adhesive property. In the more general case, where the two materials are dissimilar, adhesive bonds can be divided according to their strength (structural, permanent, and nonpermanent) and to the nature

of the adhesive/adherend pair [35]: (a) glassy polymer/glassy polymer, (b) glassy polymer/ non-polymer, (c) glassy polymer or non-polymer/elastomer or polymer melt, and (d) polymer melt/polymer melt.

The main applications of polymer/polymer adhesion in glassy polymers are in the development of alloys and blends made from immiscible polymers, and where the interfacial properties between the two phases are crucial to the performance of the material [35, 39, 45]. The ability of the interface to sustain stress is dependent on the number of well-entangled polymer chains that cross the interface [35].

Glassy polymer/non-polymer adhesion occurs in structural adhesives, where an adhesive strength equal or superior to the cohesive strength of the base material is required. Because interdigitation of the polymer chains is not possible, the surface of the solid material and not equilibrium thermodynamics determines the topology of the interface, so that surface roughness, the chemical interactions between polymer and solid play the role of stress transfer agents and the fracture energy is usually due to the resulting plastic deformation of the polymer [35].

Polymer melt/polymer melt adhesion is mostly relevant for the processing of elastomers prior to the crosslinking process, and is of particular importance to the tire industry. This type of adhesion is sometimes called tack or green strength [46].

Finally, polymer melt/solid adhesion is typical of non-permanent and relatively weak adhesion and is often called pressure-sensitive adhesion, because once a certain amount of pressure has been applied, a measurable adhesion between the two surfaces is observed. Interdigitation of the polymer chains is impossible, so chemical interactions, surface roughness, and the rheological properties of the adhesive are responsible for the measured energy of adhesion.

Although the detailed study of the adhesion is beyond the scope of the present work, some important generalization can be drawn. Adhesion can be attributed to five main mechanisms which can occur at the interface either in isolation or in combination to produce the bond (see Section 4 for more detail). Adhesion results [10, 47, 48] from (a) the mechanical bonding between the adhesive and adherend, and (b) chemical forces—either primary covalent bonds or polar secondary forces between the two. The latter are thought to be the more important, and this explains in part why inert, non-polar polymeric substrates such as polyethylene and polytetrafluoroethylene are very difficult to adhesive bond: They must first be chemically pretreated to introduce polar sites on the surface. To promote mechanical bonding, adherend surfaces are often roughened before joining, but this is sometimes counterproductive. It can trap air bubbles at the bottom of crevices which act as stress concentrators to promote failure in rigid adhesives.

With good bonding between adhesive and adherend, joint failure occurs cohesively (the adhesive itself or the substrate fails) [10]. Where the adhesive is weaker than the substrate, the properties of the adhesive polymer determine the properties of the adhesive joint; that is, the bond can be no stronger than the glue line. Brit-

tle polymers give brittle joints, polymers with high shear strengths give bonds of high shear strength, heat-resistant polymers produce bonds with good heat resistance, and so on.

To form a successful joint, the adhesive must intimately contact the adherend surface. This requires first that it wets the surface. The subject of wetting is considered in detail in treatises on surface chemistry [49, 50]. In general, wetting is promoted by polar secondary forces between adhesive and substrate [10], which is another reason why low-polarity polymeric adherends are difficult to bond with adhesives. To insure proper wetting and interfacial bonding, the following requirements are needed [10]: (a) it is generally necessary to pretreat the surface or “clean” the adherend surfaces carefully before joining [51], and (b) good contact also requires a viscosity low enough under conditions of application to allow the adhesive to flow over the surface and into its nooks and crannies. Once contact has been established, the adhesive must harden to provide the necessary joint strength.

It is commonly observed that roughening surfaces prior to bonding enhances the strength of adhesive joints, and many manufacturers specify the use of some form of abrasion as a surface treatment method. This recommendation is based on the perception that the abrasive process removes loose contaminated layers and the roughened surface provides some degree of mechanical interlocking or “keying” with the adhesive [52]. It is sometimes argued that the increased roughness also forms a larger effective surface area for the bond. While these mechanisms explain some of the general characteristics of adhesion to roughened surfaces, more detailed analyses suggest that the roughening process may introduce physico-chemical changes, which affect surface energy and wettability.

### 3.1. Interphase boundaries (or surfaces)

Surfaces are important to the study of microstructures, friction and wear, the joining of all materials by all means, the catalysis of chemical reactions, oxidation, corrosion, the mechanical behavior of small or thin bodies, the design of electronic devices, and a wide variety of other phenomena. The surfaces of phases always differ in behavior from the bulk of the phases themselves, because of the rapid structural changes which must occur at and near phase boundaries. If the forces on a molecule in the bulk are compared to the forces on a molecule at the surface, the forces on the bulk molecule cancel whereas the forces on the surface molecule are unbalanced. As a result of this unbalance force, equilibrium bonding arrangements are disrupted, leading to an excess energy (i.e., surface free energy,  $\gamma$ ), which is defined as the energy necessary to form a unit area of new surface or the energy necessary to move a molecule from the bulk to the surface.

The excess energy may be minimized by minimizing surface area. This tendency is called surface tension if the surfaces are liquid and a vapor,  $\gamma_{LV}$ . Surface energy may also be lowered by segregation of the various components to and from the surface; such behavior is called

adsorption [53]. The magnitude of  $\gamma$  may be estimated for metallic and covalent materials by considering the number and energy of the bonds which must be broken to form the surface. Similarly, calculations of work done against the Coulomb force lead to approximate values of  $\gamma$  for ionic materials. In both cases,  $\gamma$  depends on crystallographic orientation. Direct measurement of  $\gamma$  is possible by force equilibrium, if the phases are sufficiently mobile.

At the interface between two phases, the crystal structure, or the state of aggregation, or the composition must change in a fairly abrupt manner. The atoms in the vicinity of the surface are not in equilibrium states, since they are neither one phase nor the other. The excess energy due to the perturbed material at the interface is proportional to the surface area. Thus, a drop of liquid will tend to assume a spherical shape in order to minimize its surface area and, thereby, its surface free energy. In single-phase solids, similar surfaces exist. These are the grain boundaries, which exist between grains of different crystallographic orientations.

### 3.2. Wetting

When two electrically neutral surfaces are brought sufficiently close together there is a physical attraction which is best understood by considering the wetting of solid surfaces by liquids. Wetting can be expressed in terms of the thermodynamic work of adhesion  $W_a$  which represents a physical bonding resulting from highly localized intermolecular dispersion forces between different phases. The equation for the thermodynamic work of adhesion for the separation of a liquid from a solid (both in equilibrium with the vapor phase) states that [11, 53, 54]:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (1)$$

where  $\gamma_{SV}$ ,  $\gamma_{LV}$  and  $\gamma_{SL}$  are the specific surface energies, or surface tensions of the solid-vapor, liquid-vapor and solid-liquid interfaces, respectively. This equation can be related to the physical situation of a liquid drop on a solid surface, as shown in Fig. 1a, by using the Young equation (see Equation 4 below). More specifically, Fig. 1a defines the various phases for this equation (Equation 4) as well as contact angle,  $\theta$ , as simply the solid phase on which the liquid drop rests, and the vapor is above the both solid and liquid, while the contact angle is the angle between the liquid and the solid at the intersection. The surface tension of solids is difficult to measure whereas the surface tension of liquids can be determined relatively easily. It follows that glass and graphite with theoretically calculated [55] surface energies of 560 and 70 mJm<sup>-2</sup> respectively will be readily wetted by polyester and epoxy resins with surface energies of 35 and 43 mJm<sup>-2</sup>, respectively provided the viscosity of the resins is not too high. Zisman introduced the concept of critical surface tension of wetting  $\gamma_c$  such that only liquids with  $\gamma_{LV} < \gamma_c$  will spontaneously spread on the solid [54]. This is a useful parameter in considering the wetting adhesives by adherends. In contrast it will be difficult to wet polyethylene, which

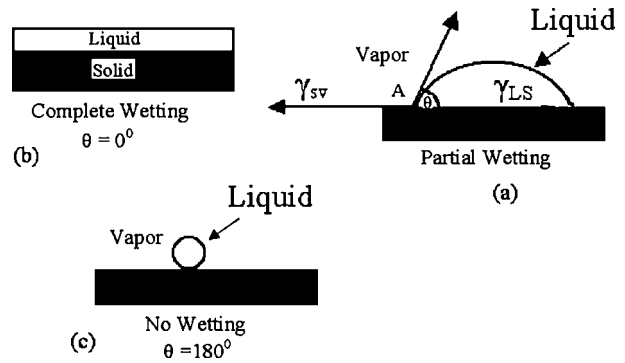


Figure 1 Contact angle  $\theta$  and surface tension ( $\gamma$ ) for a liquid drop on a solid surface: SV, SL and LV stand for solid- vapor, solid-liquid, and liquid vapor interfaces, respectively. Note that this figure indicates the interactions between solid, liquid and vapor materials. The terms  $\gamma_{SV}$ ,  $\gamma_{LS}$ , and  $\gamma_{LV}$  denote the surface energies of solid/vapor, liquid/solid, and liquid/vapor interfaces, respectively. Three different conditions of wetting (i.e., wetting of a substrate by a liquid) [3, 35] are: (a) Partial wetting:  $0^\circ < \theta < 180^\circ$ ;  $\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$ , (b) Complete wetting:  $\theta = 0$ ;  $\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$ , and (c) Non-wetting:  $\theta = 180^\circ$ ;  $\gamma_{SV} + \gamma_{LV} < \gamma_{SL}$ .

has a measured  $\gamma_c$  of 31 mJm<sup>-2</sup>, with these resins and some surface treatment will be required [54].

Various mechanisms can assist or impede adhesion. A key concept in this regard is that of wettability. Wettability tells us about the ability of a liquid to spread on a solid surface [3]. To know the wettability of a surface is useful to predict its adhesion potential. The contact angle  $\theta$  on a surface can characterize its wettability by the contacting liquid in a given environment.

Wettability of a solid by a liquid can be measured by considering the equilibrium of forces in a system of consisting of a drop of liquid resting on a plane solid surface in the appropriate atmosphere. A liquid spreads along a solid surface (i.e., wetting) rather than forming a spherical drop when [53]

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV} \quad (2)$$

that is, when the net free energy is lowered by replacing an S-V surface by an S-L and an L-V surface together. On the other hand, no wetting at all will occur if

$$\gamma_{SV} + \gamma_{LV} < \gamma_{SL} \quad (3)$$

(Complete) wetting and nonwetting are shown in Fig. 1b and c together with the case of partial wetting (Fig. 1a), which allows quantitative calculation of the surface energies. In the plane of the solid surface force equilibrium must exist between the three surface tensions because the liquid droplet is free to move until force equilibrium is established. Hence, when the forces at a point A are resolved in the horizontal direction, one can use the following expression [3, 53, 54], called Young's equation,

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (4)$$

where  $\theta$  is the contact angle which can be measured directly by a goniometer or calculated by using simple trigonometric relationships involving drop dimensions. A small  $\theta$  implies good wetting. The extreme cases

being  $\theta = 0^\circ$ , corresponding to perfect wetting, and  $\theta = 180^\circ$ , corresponding to no wetting. A low contact angle, meaning good wettability, is a necessary but not sufficient condition for strong bonding. One can have excellent wettability and a weak van der Waals-type low-energy bond [3]. In practice, it is rarely possible to obtain a unique equilibrium value of  $\theta$ . Therefore, a range of contact angles exist between the maximum or advancing angle,  $\theta_a$ , and the minimum or receding angle,  $\theta_r$ . This phenomenon is called the contact-angle hysteresis, which is generally observed in polymeric systems. This hysteresis can be due to the chemical attack, dissolution, inhomogeneity of chemical composition of solid surface, surface roughness, and local adsorption [3].

In principle the Young's equation applies only to one-dimensional spreading and becomes invalid if the substrate is not rigid and motion of the contact-line takes place in both horizontal and vertical directions. The force equilibrium ignores the vertical component of the surface tension which acts along the line of contact. As the capillary forces are not balanced, external forces must be applied to the solid to achieve equilibrium. These forces may produce even deformation in highly deformable solids, such as gels and rubber, destroying the co-planarity of interfacial tensions that is assumed in Young's equation and causing ridge formation at the interfacial region. With the use of Young's equation, it has to be stressed that only a "quasi-equilibrium" exists within the window of time when observations are made, provided that the solids deformation rate is small.

Using Young's equation (Equation 4) for the contact angle and then substituting in Equation 1 results in the following equations:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (5)$$

$$W_A = \gamma_{LV} + \gamma_{LV} \cos \theta \quad (6)$$

$$W_A = \gamma_{LV}(1 + \cos \theta) \quad (7)$$

Since the surface tension,  $\gamma_{LV}$ , and the contact angle,  $\theta$ , can be determined experimentally, the work of adhesion,  $W_A$ , can be found, as seen in Equation 7. However, the work of adhesion,  $W_A$ , should not be equated to the adhesive bond strength since the bond strength also contains the energy of dissipative process such as viscoelastic deformation, plastic deformation, local microcracking etc. [11]. But under certain conditions,  $W_A$  approximates the bond strength,  $W_{peel}$ . The conditions where this occurs are low temperatures or high peel rate [11].

The static contact angle data can be determined using a Video Contact Angle (VCA) Analyser [52]. The VCA can be used to register angles up to  $180^\circ$  on both sides of the drop without moving the substrate. The surface energy information is then calculated, in terms of dispersive and polar or non-dispersive components, using the geometric mean equation combined with Young's equation (i.e., Equation 4) [56].

$$\gamma_{LV}(1 + \cos \theta) = 2[(\gamma_{LV}^d \gamma_{SV}^d)^{1/2} + (\gamma_{LV}^p \gamma_{SV}^p)^{1/2}] \quad (8)$$

where  $\gamma_{LV}$  and  $\gamma_{SV}$  are the surface energies at the liquid/vapor and solid/vapor interfaces, respectively,  $\theta$  is the contact angle and the superscripts  $d$  and  $p$  represent the dispersive and polar components.

Wetting of the adherends by the adhesive is critical to the formation of secondary bonds in the adsorption theory [57]. It has been theoretically verified that for complete wetting (i.e., for a contact angle equal to zero), the surface energy of the adhesive must be lower than the surface energy of the adherend [58]. Therefore, the primary objective of a surface pretreatment is to increase the surface energy of the adherend as much as possible [59].

Wetting of liquid on solid surfaces is a topic of fundamental interest with widespread technological implications [60–63]. Examples include adhesive bonding, coating technology, thin film technology, and lubrication. Wetting of solid surfaces is extremely sensitive to surface geometrical/chemical (roughness/contaminants) disorder which manifests itself by the contact angle hysteresis phenomenon [60–62]. In earlier models of geometrical disorder [63], the case of periodic roughness  $h(x) = h_o \sin(2\pi x/h)$  was considered. An apparent contact angle,  $\theta_g \cong \theta - (dh/dx)$ , if  $h_o/\lambda < 1$  was defined with respect to the average solid surface in the case of a contact line parallel to the grooves (allowing local application of Young's equation). The maximum advancing or receding apparent contact angle was found to be  $\theta_g \cong \theta \pm (2\pi h_o/\lambda)$ . This model predicts a hysteresis of the contact angle when the contact line is parallel to the grooves [64]. Palasantzas and De Hosson [64] have also investigated the effects of surface roughness on the wettability of the substrate surfaces. In their study, surface roughness was described by an rms amplitude  $\Delta$ , an in-plane roughness correlation length  $\xi$  (average distance between consecutive hills or valleys on the surface), and a roughness exponent  $H(0 < H < 1)$ . It was shown that the apparent contact angle depends critically on the roughness exponent  $H$  and long wavelength ratio  $\Delta/\xi$ . For a contact angle  $\theta$  determined by Young's equation, smaller than certain transition angle  $\theta_{tr}$ , the apparent contact angle decreases with increasing roughness and vice versa for  $\theta > \theta_{tr}$ . The transition angle  $\theta_{tr}$  appears to be smaller than  $90^\circ$ , and decreases with increasing roughness exponent  $H$  (degree of surface irregularity at short length scales, i.e., for the range smaller than  $\xi$ ). Roughness of adherend surface has frequently been used as a design parameter for adhesive joints. A number of researchers have examined its effect on the strength and durability of adhesive joints using various adherends and adhesives [65, 66–70]. The relationship between roughness and adhesion is not very simple. Optimum surface profile varies from one adhesive to another, and depends upon the type of stress applied [71]. As mentioned earlier, one of possible positive effects of surface roughness [71, 72], increase in surface area results in increasing intermolecular bond and keying for mechanical adhesion. This in turn can divert the failure path away from the interface into the bulk of the adhesive [73]. However, the actual microscopic distribution of stress at the rough interface is complex.

### 3.3. Thermodynamics of adhesion

In the past many researchers have studied the molecular interactions between two surfaces. Prediction of bond strength between adhesive and adherend, or between the interphase and the adhesive, can be obtained by applying the general principles of surface chemistry [11]. Creton [35] has recently theoretically investigated the molecular interactions between two surfaces assuming that the contact between the adhesive and substrate is perfect, i.e., that there is no surface roughness and that the bond forms instantaneously upon contact. This assumption is clearly not true and has significant implications for the measurement of quick tack. However, it is easier to concentrate on the perfect contact case first, which is a reasonable assumption when interpreting peel test results.

In the simplest case of the contact of an adhesive A and a rigid substrate B, which do not react chemically nor have specific interactions, the process of forming A-B contact and then separating the surfaces involves the formation and then destruction of van der Waals bonds. The energy necessary to break these bonds per unit area of surface is given [35] by

$$W_{\text{adh}} = \gamma_a + \gamma_s - \gamma_{\text{as}} \quad (9)$$

where  $\gamma_a$  and  $\gamma_s$  are the specific surface energies of the adhesive and of the substrate, respectively, and  $\gamma_{\text{as}}$  is the interfacial free energy. If the forces are purely dispersive, the interfacial energy is approximately given by

$$\gamma_{\text{as}} = \gamma_a + \gamma_s - 2(\gamma_a\gamma_s)^{1/2} \quad (10)$$

so that the thermodynamic energy of adhesion is given by

$$W_{\text{adh}} = 2(\gamma_a\gamma_s)^{1/2} \quad (11)$$

On the other hand, the cohesive energy of the adhesive will be given by

$$W_{\text{cohA}} = 2\gamma_a \quad (12)$$

Two main observations should be made from these results: (a) first, the adhesion energy is predicted to increase with the surface energy of the substrate (see Equation 11) and, (b) second, such an approach would predict cohesive failure in the adhesive if the surface energy of the substrate is higher than that of the adhesive (i.e.,  $\gamma_s > \gamma_a$ ). None of these simple predictions have actually been quantitatively confirmed experimentally yet. Furthermore, it is well known that the measured adhesion energy  $W$  is usually several orders of magnitude higher than what is predicted by the thermodynamic equations.

### 3.4. Factors affecting the adhesion at the interface between the adhesive and substrate systems

Adhesion is the condition by which two surfaces are held together in one of the following ways [74]: (a) physically, that is, the components are held together by interlocking due to physical penetration; (b) chemically, that is, the components are bound together by valence forces of the same type which give rise to cohesion. To control the interface which can provide the material with improved mechanical performance and structural integrity, it is essential to understand the mechanisms of adhesion which are specific to each material system and the mechanics of load transfer at the interface.

The energy measured during the separation of the adhesive/substrate assembly is a complex function of the adhesion energy and also of the dissipative properties of both adhesive and substrate [75]. For example, when a stress is applied to a polymer, a part of the energy is dissipated by the movements of chains (viscous flow). These viscous losses are time (or speed or frequency) and temperature dependent. The effects of time and temperature are related by the well known time/temperature superposition principle. Dissipative phenomena occurring during an assembly separation are reflected through the dependence of the measured energy with the separation rate. The dependence of the adherence energy  $G$  with the separation speed  $V$  has been first determined by Gent and Shultz [76]:

$$G = W_a \phi(a_T V) \quad (13)$$

where  $W_a$  is the thermodynamic energy of adhesion,  $\phi$  is the dissipation function and  $a_T$  the William-Landel-Ferry shift factor for time-temperature equivalence.

A derived expression (Equation 14) which separates  $G$  into two terms, has been proposed by Maugis and Barquins [77]:

$$G - W = W \phi(a_T V) \quad (14)$$

This equation indicates that the adherence energy  $G$  is equal to the sum of the adhesion energy  $W$  plus the dissipation energy, which also depends on the adhesion energy  $W_a$ . As a consequence, a higher adhesion will induce more energy dissipation, even if the intrinsic dissipation ability of the polymer remains identical [76, 78, 79]. Different energy dissipation mechanisms have been proposed in the past [80–82]. Dissipation losses can be induced by chains pull-off, at a molecular scale, and can also affect a greater volume [83, 84] due to high entanglements density. Guillemin *et al.* [75] have investigated the adherence level of steel/polymer/steel assemblies (i.e., metal-to-metal joint) by using a wedge test, performed at different wedge introduction rates. The adherence energy  $G$  values measured for various wedge introduction speeds  $V$  are presented in Table I. The following expression

TABLE I Adherence energy value  $G$  as a function of the wedge introduction rate for steel/polymer/steel assemblies [75]

Speed (mm/min)	$G$ (J/m <sup>2</sup> )
0.8	30263
7.5	29408
1.5	30825
26.5	32524
37.5	35607
52.5	34991
75	36864

[75] has been used for the calculation of  $G$  [85, 86]:

$$G = \frac{3Eh^3\delta^2}{16L^4} \frac{1}{\left(1 + \frac{\lambda_o}{\lambda} 0.64 \frac{h}{L}\right)^4} \quad (15)$$

where  $E$  is Young's modulus of the steel substrate ( $2.1 \times 10^5$  MPa),  $h$  the substrate thickness (0.4 mm),  $\delta$  the wedge height (0.4 mm),  $L$  the crack length,  $E_a$  the modulus of the adhesive ( $3.03 \times 10^{10}$  MPa),  $h_a$  the thickness of the adhesive ( $4.5 \times 10^{-5}$  m) and  $b$  the width of the assembly,  $\lambda = (3k/Ebh)^{1/4}$  with  $k = bE_a/h_a$  and  $\lambda_o = (3k_o/Ebh^3)^{1/4} = 6^{1/4}/h$  with  $k_o = 2Eb/h$ . The adherence energy globally increases when the wedge introduction speed increases, and a transition was observed. A similar transition was detected on the curve of Young's modulus of the polymer versus tensile speed [75], attributed to the glass relaxation. The failure is pseudo-adhesive, i.e., partly cohesive, inside the adhesive layer, but very close to the steel/polymer interface. Strong interfacial bonds and great energy dissipation in the adhesive layer could explain the great adherence values.

Creton [35] has studied the effect of molecular weight on the adhesion properties (i.e., peel resistance, quick tack, and shear resistance) of the adhesives (i.e., polymer-to-polymer substrates). The molecular weight has an important effect on the adhesion properties through its influence on the intermediate and long relaxation times. A high molecular weight will favor adhesive separation, by slowing the process of chain disentanglement, which is responsible for fibril creep and eventually cohesive fracture [87]. However, the molecular weight can also influence the micromechanical deformation mechanisms within the adhesive layer which are eventually responsible for the measured energy of adhesion [35]. A high molecular weight  $M_n$  will negatively affect the formation of fibrils during the debonding process. Also, as shown in Fig. 2, the peel resistance ( $180^\circ$  peel fracture energy) decreases slowly with molecular weight for a series of polyisobutylenes [88a].

Gent and Petrich [89a] performed peel fracture tests against the reduced peel rate on an SBR polymer on Mylar before and after a milling operation (see Fig. 3). As shown in this figure, the measurements of  $W$  (peel fracture energy) versus the reduced peel rate showed two transitions for the milled sample, while only one transition was observed for the raw sample. The high peel rate transition was attributed to the onset of the

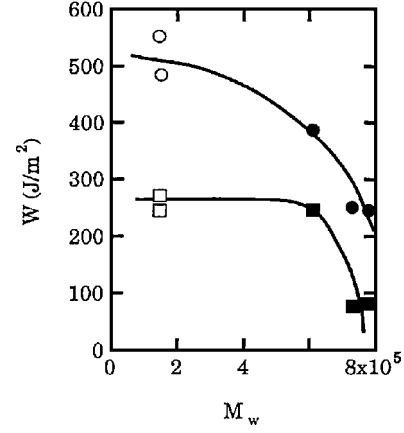


Figure 2 Effect [35] of the weight average molecular weight  $M_w$  on the  $180^\circ$  peel fracture Energy  $W$  at a peel rate of  $10^{-3}$  m/s (squares) and  $8.5 \times 10^{-3}$  m/s (circles) for polyisobutylene  $\square$ . Cohesive failure and  $\bullet$ : Adhesive failure. Note that these data were taken from the reference [88b].

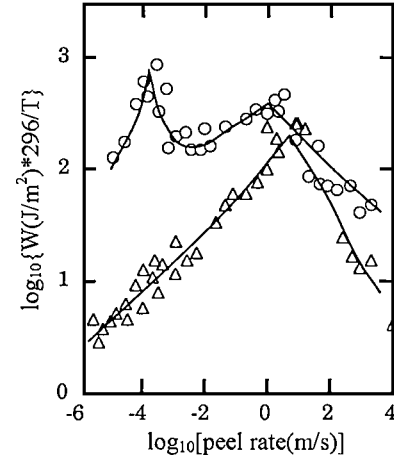


Figure 3 Peel fracture energy  $\{\log_{10}[W](J/m^2) * 296/T\}$ -peel rate  $\{\log_{10}[Ra_T](m/s)\}$  relation for SBR adhering to Mylar [35]. The raw material ( $\Delta$ ) has a high molecular weight which reduced by the milling operation ( $\circ$ ).

glass transition. The main difference between the two polymers is the terminal relaxation time which must be longer for the raw polymer. However, the transition in fracture energy observed for the milled sample at low rates could be due microscopically to the transition from high dissipation fibrillar fracture to low dissipation adhesive fracture.

Quick tack is more negatively affected by an increase in molecular weight because, in addition to the reason already mentioned for the adhesion properties, a high  $M$  will also increase the modulus at intermediate and long times, and can negatively affect the ability of the polymer to form a bond. Shear resistance, however, is positively affected by molecular weight [35]. The simplest approximation is to correlate creep resistance with viscosity, and it is now well established that the viscosity follows the empirical relation  $\eta \propto M^{3.4}$ . Therefore, a small change in molecular weight can greatly affect the shear resistance.

In conclusion, the general rule is that within the range of molecular weight that gives the adhesive separation,

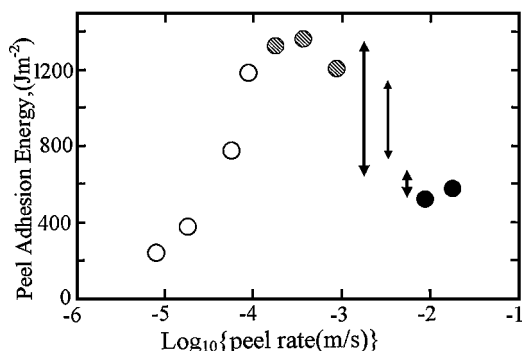


Figure 4 Effect of peel rate on the peel adhesion energy and mode of failure for: vinyl acetate-2-ethyl hexyl acrylate copolymer [35]. The adhesive films were on the polyester backing and peeled off clean glass at a 90° angle. ○: Cohesive fibrillar fracture, ⊗: Adhesive fibrillar fracture, and ●: Adhesive nonfibrillar fracture. The vertical arrows show the high and low values of the fracture energy in the domains of stick slip fracture where the force oscillates [Data taken from [89b]].

the tack and peel strengths decrease slowly with molecular weight while the creep resistance increases [35]. In practice, however, most polymers used industrially have a broad polydispersity, and an experimental study on polyisobutylenes showed that a wide molecular weight distributed can have a beneficial effect on all three properties [88].

Aubrey *et al.* [87] has studied the molecular effects of different polymer melts on adhesion using different approaches. The peel strength (the peel adhesion energy) of a polymer is shown in Fig. 4 against the reduced rate of peel. As shown in this figure three different microscopic deformation mechanisms exist [87]: (a) At low peel rate, the separation is fibrillar and cohesive for the polymer. (b) However, at higher rates, the vinyl acetate-2-ethylhexyl acrylate (VA-EA) copolymer shows a transition in fracture mechanism to fibrillar adhesive failure. It is important to emphasize that this transition is not associated with a discontinuity in the fracture energy versus peel rate. (c) When the peel rate is raised further, the polymer goes through a slip-stick regime, which is related to the mechanics of the peel test, and then undergo a transition to adhesive nonfibrillar fracture.

Schonhorn and co-workers [90–92] have studied the adhesion of polyethylene to various adherends. They found that the surface layer morphology strongly influences the adhesive joint strength. In a simple peeling test of bonded polyethylene-aluminum joints (i.e., polymer-metal substrate) [90], a relatively thick layer of polyethylene was found to adhere to the substrate surface. The observation by optical microscopy revealed that this layer consisted of transcrystalline material. The thickness of the transcrystalline layer increased with the bond-preparation time at the selected temperature. Later, Schonhorn and Ryan [92] studied the adhesion in epoxy adhesive-polyethylene film-epoxy adhesive pieces (i.e., polymer-polymer substrate). It was shown that the presence of a large transcrystalline surface layer in the polyethylene film considerably enhances the adhesive-joint strength. As Ishida and Bussi [93] concluded from these works, it appears that the major interest of a transcrystalline layer is that it preserves

the expected properties rather than brings any enhancement in itself. Therefore, when no transcrystalline zone is present, a weak boundary layer is formed, which decreases considerably the expected quality of adhesion [93]. Transcrystallinity prevents such a detrimental effect by extending the bulk properties of the matrix to the surface region. If the transcrystalline zone is damaged, this protective effect is lost. It was found [92] that a similar result can be achieved by crosslinking the surface layer through activated species. They used an analogy between the behavior of a transcrystalline layer and that of a crosslinked layer to explain the increased cohesive strength. Because of extensive surface nucleation, there is a strong competition between the chains at the surface.

Creton [35] has also studied the adhesion behavior at the adhesive-substrate interface. Although the bulk viscoelastic properties are of primary importance for an adhesive, a necessary condition for good adhesion is that the interaction at the interface is sufficiently strong to sustain the stress necessary to cause extensive plastic deformation in the bulk adhesive [35]. In order to understand the influence of the adherend on the peel energy and, in particular, the relation between the thermodynamic surface energy and the measured adhesion, some works were undertaken in the past [76, 94, 95]. In the absence of primary bonds at the interface, the measured peel strength is proportional to the thermodynamic energy of adhesion  $W_{adh}$  and the proportionality factor is dependent on the bulk viscoelastic properties of the adhesive [35]. These observations have been confirmed for crosslinked adhesive that did not show any fibrillar fracture. Toyama *et al.* [96] studied the probe tack and peel strength of a poly(*n*-butyl acrylate) on a variety of substrates and analyzed the dependence of their data on the surface energy of the adherends. They found a maximum in the peel strength when the surface tensions of the adhesive,  $\gamma_a$ , and of the adherends,  $\gamma_s$ , were closely matched and pointed out that in this situation the interfacial energy is minimum. Other workers have, however, found an increase in the peel strength at low surface energies of the adherend, followed by a plateau when  $\gamma_s > \gamma_a$  [34], or a monotonic increase in the tack with  $\gamma_s$  [97]. As mentioned by Creton [35], two general conclusions can be drawn from these results: (a) the surface energy of the adherend should not be below that of the adhesive, this being particularly true for tack. (b) If the surface energy of the adherend is comparable or higher than that of the adhesive, the influence of surface forces on the measured adhesion is relatively small compared to the effect of the viscoelastic losses in the adhesive layer.

As Creton pointed out [35] the effect of surface roughness is also important for the adhesion in the case of tack. Fuller and Tabor [98] showed that the measured adhesion of a crosslinked adhesive is dependent on its surface roughness down to fractions of a micrometer, and that a surface roughness of the order of a micrometer could decrease the measured adhesion by a factor of 10. The topology of the surface is never, however, considered in tack studies and may be responsible for



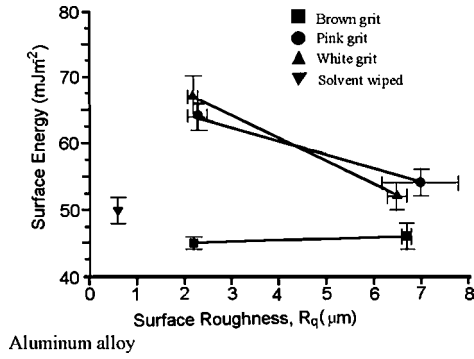


Figure 5 Effect of surface roughness on the surface energy of an aluminum alloy [52].

some quantitative discrepancies between experimental results [35].

Harris and Beevers [52] have investigated the effects of surface texture on surface energy, which might also be expected to affect adhesion using a mechanical surface pretreatment methods (i.e., grit blasting treatment). As shown in Fig. 5, in general, smoother grit-blasted surfaces display higher surface energy values for an aluminum alloy adherend. Hitchcock *et al.* [99] and Tamai and Aratanic [100] also observed that, within certain limits, roughening a substrate surface usually causes its wettability to decrease. Several workers have investigated this aspect of substrate surface behavior and a number of concepts have been proposed to explain the differences in wetting characteristics of rough and smooth surfaces. Harris and Beevers [52] have proposed a simple model that the peaks, ridges and asperities form barriers which restrict the spreading of the droplet. Huh and Mason [101] and Yost *et al.* [102] have pointed out that with acute contact angles the three-phase line is reluctant to flow over ridges and peaks. However, they also reported that the droplet “seek out” areas of the surface where it can spread more easily, particularly through roughs and valleys, perhaps as a result of capillary channelling. Bikerman [103] suggested that wetting was independent of roughness on grooved and ridged surfaces and implied that as a drop front moves over a ridge that the true contact angle (i.e., the angle related to the actual surface of the solid and not the mean plane) remains constant. Harris and Beevers [52] suggested that the changes in the surface energy might be attributable to changes in surface composition. Their proposal was supported by the data in Fig. 6, which indicate considerable shift in the polar component of surface energy between the different treatments. Also it was shown [52] that after grit blasting of the mild steel and aluminum alloy adherends, small amounts of Na and/or Mg appear on the treated surfaces and these correlate with the grit impurities.

Using a different approach, Wenzel [104] proposed that wetting and spreading properties are influenced more by the amount of effective surface area that can actually interact with the liquid, than the surface texture characteristics. He derived the ratio of the true surface area divided by the projected geometric area (Wenzel’s roughness factor,  $r$ ) and used this to provide a “correction” for the contact angle  $\theta$  from the expression

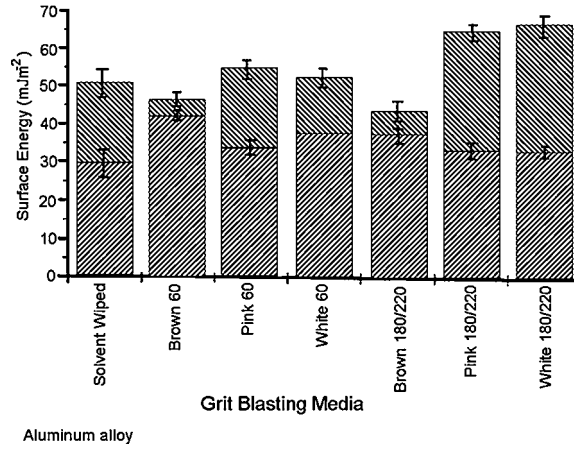


Figure 6 Effect of grit-blasting media on the surface energy of an aluminum alloy [52]. ▨ Dispersive energy and ▩ Polar energy.

$\cos \theta_{\text{rough}} = r \cos \theta_{\text{smooth}}$ . This correlation increased the contact angles and reduced the derived value of surface energy. Carre and Shultz [105] used a reverse concept to Wenzel’s analysis and proposed that a roughness factor could be determined from the contact angles measured on smooth and rough surfaces. Shuttleworth and Bailey [106] derived an alternative technique for correlation of the contact angles in which the adjustment was simply based on the mean slope of surface roughness obtained from two-dimensional profile measurements.

In recent years, many researchers in the adhesion field [107–114] have employed the JKR technique to analyze the fundamental forces of adhesion between two materials. An important advantage of the contact mechanics experiment is the very low cracks growth speeds which are accessible with this technique with higher sensitivity as compared with other adhesion tests such as the peel test [107–114]. Woerdeman *et al.* [112] have reviewed this JKR contact mechanics approach. The JKR theory, developed by Johnson *et al.* [115] is an extension of the Hertz analysis [116], which relies on a fracture mechanics-energy balance approach to describe the mechanics of interaction in the presence of adhesive forces. A most significant feature of the JKR contact mechanics approach is that it allows one to make a direct estimate of the work of adhesion,  $W$ , between the two solids of interest, unlike the conventional contact angle experiment, which requires the user to construct a calibration curve. Chaudury and Whitesides [113] led the renewed interest in the JKR contact mechanics technique, having developed an experiment based on the use of soft, hemispherical lenses on rigid, flat plates. In this technique, a material of low elastic modulus, in the shape of a hemispherical lens is brought into contact with a solid surface of interest, and the resultant contact area is monitored as a function of applied loading and lens penetrating depth. The contact area varies with applied loading according to the JKR equation (Equation 16), which describes the system behavior as a function of its geometry, material properties, and adhesive forces:

$$a^3 = \frac{R}{K} \{P + 3\pi WR + (6\pi WRP + (3\pi WR)^2)^{1/2}\} \quad (16)$$

where  $a$  is the contact radius,  $R$  is the effective radius of the system,  $K$  is the effective bulk modulus of the material,  $P$  is the contact load, and  $W$  is the work of adhesion.

The JKR predictions give rise to a second relationship, which describes the lens penetration depth,  $\delta$ , as a function of  $P$ ,  $a$ ,  $R$ , and  $K$

$$\delta = \frac{a^3}{3R} + \frac{2P}{3aK} \quad (17)$$

Researchers have previously demonstrated [110, 114, 117] that use of these two equations simultaneously provides an internal check of the validity of the small deformation approximation used in the JKR analysis. In particular, JKR theory assumes small deformations so that the depth of the strain field at the elastomer-rigid support interface is negligible compared with the depth of penetration [110]. Therefore, when the JKR contact mechanics technique is used to measure the work of adhesion between two solids in contact, it is now an adopted custom to analyze the plot of  $\delta$  versus  $a$  to assess whether or not the experimental data deviate from the JKR prediction at large contact areas [108, 110, 114, 117]. Deruelle *et al.* [110] have demonstrated that one can circumvent this problem by intercalating a thick ribbon of the same elastomer between the lens and its support. Alternatively, the experimentalist can make a special point of not over-compressing the elastomeric hemisphere during the loading experiment [108, 117], or in other words, can avoid deforming the hemisphere laterally, which has been known to occur when measurements are made at exceedingly large contact areas [117].

Fig. 7 shows the schematic description of the JKR experiment, whereas Fig. 8 indicates the sample data obtained during a JKR compression experiment [108]. In all cases, the symbols represent the data points and the solid lines trace the fits to the data for an epoxy lens against a  $\gamma$ -amino-propyl-triethoxysilane-modified silicon substrate. Fig. 8a depicts the contact radius cubed versus applied load ( $a^3$  versus  $P$ ), while Fig. 8b and c illustrate the relationships between  $\delta$  and  $a$ , and  $\delta$  and  $P$ , respectively. In this particular case, the suitability of the JKR model was good, which suggests that the experiment had been performed within the constraints of the theory.

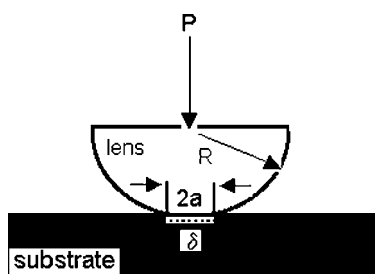


Figure 7 Schematic illustration of the JKR contact mechanics experiment, where  $P$  is the load,  $a$  is the lens contact radius,  $\delta$  is the penetration depth of the lens, and  $R$  is the radius of curvature of the lens.

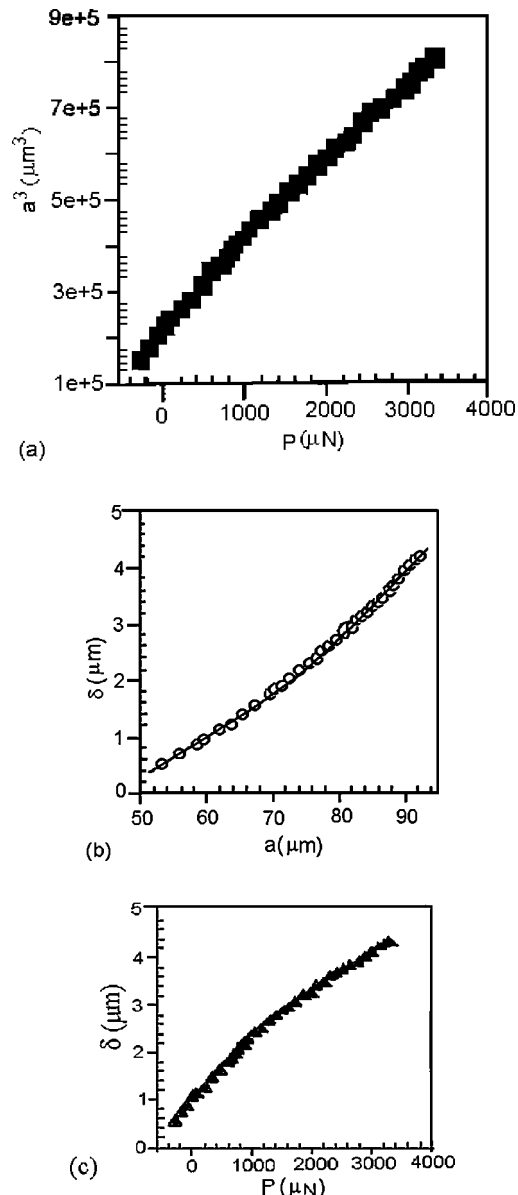


Figure 8 Typical curves obtained from a single JKR loading experiment [108]. In all cases, the symbols represent the data points and the solid lines trace the fits to the data for an epoxy lens against a  $\gamma$ -aminopropylane-modified silicon wafer: (a) Contact radius cubed versus applied load, (b) displacement versus contact radius, and (c) displacement versus applied load.

#### 4. Bonding mechanisms (or types) in adhesively bonded joints

It is important to control the interfaces between the adhesive and substrates. To do so, it is necessary to understand all the different possible bonding mechanisms, one or more of which may be acting at any given instant. Despite the wide use of adhesives, a good deal of controversy surrounds the nature of the bond. There are following bonding mechanisms or types existing in the literature, which are particularly useful in explaining certain phenomena associated with adhesive bonding [1, 3, 54, 118]: (a) physical bonding, (b) chemical bonding, (c) diffusion or interdiffusion theory, and (d) mechanical bonding or mechanical interlock theory. It is beneficial to summarize these bonding mechanisms because they indicate procedures commonly followed for optimal bonding.

## 4.1. Physical bonding

Physical bonding involves weak, secondary or van der Waals forces, dipolar interactions, hydrogen bonding and other low energy forces [3, 118]. The bond energy in such physical bonding is approximately 8–16 kJ/mol [3]. Physical bonding contains the following bonding types: (a) the absorption theory, and (b) the electrostatic attraction theory.

### 4.1.1. The absorption theory

This theory states that to be successful, an adhesive must wet the surface to be bonded (called the adherend). This theory has led to the development of materials with lower surface tension than that of the adherend [1]. Supporting this theory is the fact that epoxy wets steel and provides a good bond, whereas it does not wet the olefins PE, PP, and PTFE and does not bond them.

### 4.1.2. The electrostatic attraction theory

This theory postulates that as a result of the interaction of the adhesive and the adherend, an electrostatically charged double layer of ions develops at the interface. In another words, forces of attraction occur between two surfaces when one surface carries a net positive charge and the other surface a net negative charge as in the case of acid-base interactions and ionic bonding [54] (see Fig. 9a). The fact that electrical discharges are observed when an adhesive is peeled from a substrate is cited as evidence of these attractive forces [1]. A difference in electrostatic charge between constituents

at the interface may contribute to the force of attraction bonding. The strength of the interface will depend on the charge density [54]. This attraction is unlikely to make a major contribution to the final bond strength of the interface [118]. The bonding of this type will explain why silane finishes are especially effective for certain acidic or neutral reinforcements like glass, silica and alumina, but are less effective with alkaline surfaces like magnesium, asbestos and calcium carbonate [118].

## 4.2. Chemical bonding

A chemical bond is formed between a chemical group on the adhesive surface and a compatible chemical group in the adherend (Fig. 9b). The strength of the chemical bond depends on the number and type of bonds and interface failure must involve bond breakage. The processes of bond formation and breakage are in some form of thermally activated dynamic equilibrium [54, 118]. The chemical bonding theory is the oldest and best known of all bonding theories. The nature of the chemical bonding is the key to the physical and chemical behavior of matter. Atomic or molecular transport, by diffusional processes, is involved in chemical bonding. Solid solution and compound formation may occur at the interface, resulting a reaction zone with a certain thickness. This encompasses all types of covalent, ionic, and metallic bonding. Chemical bonding involves primary forces and the bond energy in the range of approximately 40–400 kJ/mol [3]. For example, a chemical reaction at the interface is of particular interest for polymer matrix composites because it offers the major explanation for the use of coupling agents on glass fibers and probably the surface oxidative treatments on carbon fibers for application with most thermoset and amorphous thermoplastic matrices.

Surface treatments often involve chemicals which produce surfaces with different chemical compositions and oxide stoichiometries. These morphological changes influence the nature of the chemical bonds. Subsequently, a relationship exists between chemical composition of the surface and the bond durability [57, 59, 119].

## 4.3. Diffusion or interdiffusion theory

This bonding mechanism is applicable to cases in which the adhesive contains a solvent for the adherend [1]. A type of bonding similar to diffusion bonding in metals develops, and molecules pass across the interface. This diffusion can obliterate the mechanical plane of the interface and its weakness. It is possible to form a bond between two polymer surfaces by the diffusion of the polymer molecules on one surface into the molecular network of the other surface, as illustrated schematically in Fig. 9c. The bond strength will depend on the amount of molecular entanglement and the number of molecules involved. The phenomena of interdiffusion has been called autohesion in relation to adhesives.

A bond between two surfaces may be formed by interdiffusion of atoms or molecules across the surface. As an example, the bond strength in polymer matrix

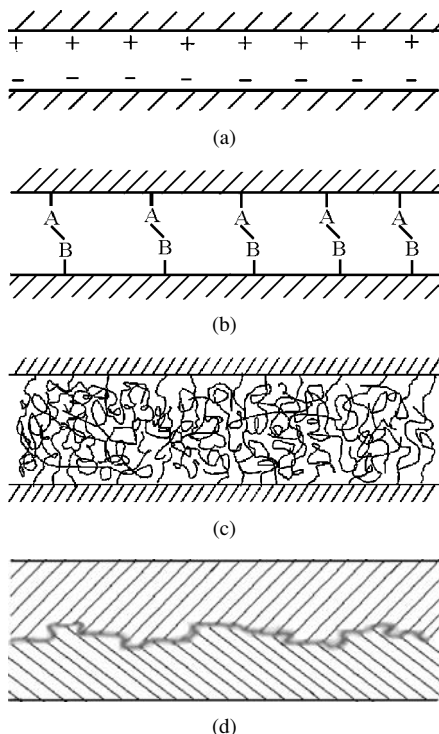


Figure 9 Types or mechanisms of bonding [54]: (a) Bond formed by electrostatic attraction, (b) Chemical bond formed between groups A on one surface and group B on the other surface, (c) bond formed by molecular entanglement following interdiffusion, and (d) mechanical bond formed when a liquid polymer wets a rough solid surface.

composites will depend on the amount of molecular entanglement, the number of molecules involved and the strength of the bonding between molecules [118]. Inter-diffusion may be promoted by the presence of solvents and the amount of diffusion will depend on the molecular conformation, constituents involved and the ease of molecular motion. For example, bonding between glass fibers and polymer resins through silane coupling agents by other than chemical bonding can be explained by inter-diffusion and interpenetrating network (IPN) formation at the interface region [60, 120–122]. The interface region thus formed has a substantial thickness, and its chemical, physical and mechanical properties are different from those of either the bulk fiber and matrix [123–126]. In metal matrix composites, inter-diffusion is also necessary for proper reaction between elements of each constituent to take place. However, interdiffusion here may not always be beneficial because undesirable compounds are often formed, particularly when the oxide films present on the fibers are completely disrupted under extremely high temperature and pressure in a solid state process [127]. To prevent or reduce the interaction it is necessary to apply an effective diffusion barrier in the form of a coating on the fiber. The selection of an appropriate diffusion barrier relies on a detailed knowledge of the nature of the interaction which is specific to each other.

It is generally agreed that the highest strength is achieved when, upon stressing, the fracture occurs in the body of the adherend or within the adhesive, not at the interface. The weak boundary layer theory holds that for an adhesive to perform satisfactorily, the weak boundary layer should be eliminated. For example, in case of metals with a scaly oxide layer, failure has a coherent oxide layer. Similarly, in the case of polyethylene, a weak, low-molecular-weight additive is present throughout the structure, and this leads to a weak interface. In both cases the potentially weak layers can be removed by surface treatments [1].

#### 4.4. Mechanical bonding or mechanical interlock theory

Some bonding may occur purely by the mechanical interlocking of two surfaces as illustrated in Fig. 9d. This theory points out that surfaces on a micro scale are very rough [1]. Therefore, when a liquid adhesive is placed between two surfaces, it penetrates the crevices and pores and then solidifies. Thus a cement interlocks with the surface layers on both sides and provides a mechanical bond. The fact that fresh, roughened surfaces provide the best bond support this theory. Simple mechanical keying or interlocking effects between two surfaces can lead to a considerable degree of bonding. In general, mechanical bonding is a low-energy bond vis a vis a chemical bond, i.e., the strength of a mechanical bonding is lower than that of a chemical bond [3]. Pure mechanical bonding alone is not enough in most cases. However, mechanical interlock bonding could add, in the presence of reaction bonding, to the overall bonding.

Mechanical bonds involve solely mechanical interlocking at the surface. The strength of this interface is

unlikely to be very high in transverse tension, but the strength in shear may be significant dependent on the degree of roughness [118]. However, mechanical bonding is efficient in load transfer when the applied force is parallel to the interface [3]. In addition to the simple geometrical aspects of mechanical bonding, there are many internal or residual stresses in composite materials which develop during fabrication process due to matrix shrinkage and differential thermal expansion between fiber and matrix. Among these stresses, the residual clamping stress on the fiber provides a major bonding at the interface of many ceramic matrix composites which plays a decisive role in controlling the fracture resistance of these materials.

Roughness or an increase in the surface are results in increased mechanical interlocking of the adhesive to the adherend. It has been shown that as a result of the high stability of the fresh oxide layer to moisture degradation, good durable bonds can be achieved [38].

#### 5. Surface pretreatments for polymers, polymer composites, and metallic materials substrates

Good surface pretreatment is achieved by one or a combination of the following [58]: (a) the production of a surface free from contaminants, (b) the production of a macro/microscopically rough surface, (c) the production of a fresh stable oxide layer, and the chemical composition of the oxide.

Surface treatments enable the nature of the chemical groups present at the surface to be modified and they may be used to modify the topography. Depending on the treatment used, the modification may be carried out without changing the bulk properties of the polymer. The alterations to the polymer may come under many different forms, as stated by Lennon *et al.* [128]: (a) removal of the weak cohesion layer, or of the pollution present at the surface, (b) introduction of new or an increased number of chemical functions, and (c) increase the roughness of the surface. All these parameters can contribute to an improvement of the wettability and/or of the adhesive properties of the surface. However, the efficiency of a surface treatment depends on the nature of the substrate and on the depth of treatment. There is often a compromise between the functionalisation and the degradation of the surface.

There are many methods available to pretreat polymers and metallic alloys substrates. These include both physical and chemical surface pretreatments. With the former, material with low cohesive strength is removed and the topography may be changed. With chemical methods a number of changes may occur [129], namely, (a) removal of weak material, (b) roughening, and (c) the introduction of functional groups into the polymer. The methods used to pretreat a polymer or metallic material surface are highly varied. More specifically, they can be [128, 129]: (a) chemical or electrochemical, (b) mechanical, (c) thermal, (d) photochemical, or (e) plasma. Over the last 25 years, the possibility of using electrochemical methods to pretreat polymers has been examined in particular by Brewis, Dahm and co-workers (see for example [129]). Many chemical

TABLE II Examples of surface pretreatments for plastics or elastomers substrates [129]

Plastics	Elastomers
Abrasion	Abrasion
Solvent cleaning	Solvent cleaning
Corona <sup>a</sup>	Conc. sulphuric acid <sup>a</sup>
Flame <sup>a</sup>	Trichloroisocyanuric acid <sup>a</sup>
Plasma <sup>a</sup>	Halogen gases <sup>a</sup>
Active gases <sup>a</sup>	
Specific reagents <sup>a</sup>	

<sup>a</sup>Expected to cause chemical modifications to substrate surfaces.

treatments involve oxidative methods but reagents usually used with fully fluorinated polymers e.g., sodium in liquid ammonia, are powerful reducing agents. It is possible to provide both powerful reducing or oxidising conditions using electrochemical methods.

In their review article, Brewis and Dahm [129] discussed the pretreatments of polymers. In general, the methods that have been shown to be effective with plastics are considerably different from those that are effective with elastomers (Table II). Typical composite surface treatments include traditional abrasion/solvent cleaning techniques for thermoset composites, while thermoplastic composites require surface chemistry and surface topographical changes to ensure strong and durable bond strengths. However, To increase strength and durability a more intimate bond is necessary; to achieve this the following conditions should be met [129]: (a) increasing surface tension, (b) increasing surface roughness, and (c) changing the surface chemistry.

Clearly, not all the methods listed for plastics, or elastomers, are effective with all plastics or all elastomers. For example, physical methods such as abrasion are not effective with polyethylene (PE). It is normally necessary to chemically modify PE to achieve good adhesion, for example with a corona discharge. A key difference between plastics and elastomers is that the

latter generally contain large quantities of cohesively weak additives. These are often present, in substantial quantities, on the surface and if they can not be absorbed by the adhesive used, poor bond strengths will result. For those elastomers which contain a substantial quantity of functional groups, e.g., nitrile rubber, a physical method which removes any weak layers may be sufficient to provide good adhesion. However, with elastomers which possess few functional groups, it may be necessary to remove any weak layers and chemically modify the elastomers. It may not be necessary to remove the weak layer if this is chemically modified to make it compatible with the adhesive used so that the layer can be absorbed. Selection of surface pretreatments for polymers depends on several factors [129] including (a) cost, (b) safety, (c) environmental impact, (d) effectiveness, and (e) stability of the treated surface in service. In some cases it will be necessary to pretreat 3-dimensional objects while in other cases it may be required that one side of a sheet is treated.

A variety of surface pretreatments have been used with various degrees of success to increase surface tension, increase surface roughness, change surface chemistry, and thereby increase bond strength and durability of polymer composite adhesive joints and are shown [2] in Table III. Wetting of the adherends by the adhesive is critical for the formation of secondary bonds in the absorption theory [57]. It has been theoretically verified that for complete wetting (i.e., for a contact angle  $\theta$  equal to zero) the surface energy of the adhesive must be lower than the surface energy of the adherend [58]. For thermoplastic composites the primary aim of the surface treatment is to increase the surface energy of the adherend as much as possible. Surface treatments [2] (a) decrease water contact angle, (b) increase surface tension, and (c) as a result increase bond strength.

The researchers [65, 139–146] have used many different titanium alloys as substrates in the past, however Ti-6V-4Al is the most widely used one in the aerospace

TABLE III Showing the effects of various surface pretreatments methods on the surface tension, surface roughness, surface chemistry, bond strength and durability of the polymer composites [2]

Treatment type	Material	Nature of treatment	Surface tension	Surface roughness	Surface chemistry	Bond strength	Durability	Sources
(1) Abrasion and solvent wipe	Thermoset and thermoplastic	Remove mold release		Y		Increased found for thermosets	Good for thermosets	[130, 131]
(2) Grit blasting	Thermoset and thermoplastic	Remove mold release		Y		Increased found for thermosets	Good for thermosets	[131–133]
(3) Acid etch	Thermoset and thermoplastic	Etch <sup>a</sup>	Y		Y	Slight increase	Poor	[131, 134, 135]
(4) Peel-ply	Thermoset	Remove mold release		Y		Increase	Good	[131]
(5) Tear-ply	Thermoset	Remove mold release				Increase	Good	[136]
(6) Corona discharge	Thermoplastic	Oxidising	Y		Y	Double	Good (90 days)	[133]
(7) Plasma treatment	Thermoplastic	Ablation and/or oxidation <sup>a</sup>	Y	Y	Y	Increase	Good (90 days)	[130, 135–137]
(8) Flame treatment	Thermoplastic	Oxidising <sup>a</sup>	Y			Increase		[131, 138]
(9) Laser treatment	Thermoset and thermoplastic	Ablation and or oxidation		Y	Y	Increase	More research is necessary	[131]

<sup>a</sup>Depends on polymer matrix material.

industry [2]. Durability studies of T-6Al-4V reveal that surface preparations that produce no roughness (macro or micro) yield the poorest bond durability. Those that produce significant macro-roughness but little micro-roughness yield moderate to good durability. Finally those that produce significant microroughness yield the best durability (Table IVA). Table IVB gives the six surface pretreatment procedures and their effects for titanium alloys.

The surface pretreatments used for polymeric and metallic materials are highly varied (see for example Tables III and IV), and can be conveniently classified (see for example [2, 52, 59, 128, 129, 151–153]) into: (a) Mechanical, (b) chemical, (c) electrochemical, (d) thermal, (e) photochemical, and (f) plasma. The followings are surface pretreatment methods used for polymeric materials: (a) Abrasion/solvent cleaning, (b) grit blasting, (c) peel-ply (or tear films), (d) tear-ply, (e) acid etching, (f) corona discharge treatment, (g) plasma treatment, (h) flame treatment, (i) laser treatment, and (j) silver electrolytic pretreatment process. Whereas for metallic materials such as titanium alloys the following methods are used to surface pretreat them: (i) Abrasion and grit blasting, (ii) VAST (Vought Abrasive Surface Treatment), (iii) Acid etchants, (iv) Alkaline peroxide etch, (v) Phosphate fluoride process, (vi) Modified phosphate fluoride process, (vii) TURCO 5578, (viii) DAPCOtreat, (ix) Pasajell 107 Treatment, (x) Electrochemical reactions, (xi) Chromic acid anodization, (xii) Sodium hydroxide anodisation, (xiii) Cathodically deposited aluminum oxide, (xiv) Plasma Treatment, (xv) Sol/Gel Methods, (xvi) Primers, (xvii)  $\gamma$ -APS, (xviii) Laser.

The various surface pretreatment methods used for polymeric materials and titanium alloys, and the qualitative descriptions of their effects on the surface tension, surface roughness, bonding strengths and durability of these materials are presented [2] in Tables III and IV. Both thermoset and thermoplastic composite materials have been bonded to titanium with varying degrees of success [154]. However, it is noted that thermoplastic materials are inherently more difficult to bond [155]. Carbon-fiber-reinforced polymer composite material has been widely used as the adherend in the past [156]. Although glass-fiber-reinforced composite material has a much lower modulus than carbon fiber, bond integrity tends to be dominated by the characteristics of the matrix, rather than the fiber and for this reason the research conducted on fiber composite is also relevant to studies involving glass-fiber [2].

Thermoset polyester or epoxy composites can have a resin-rich surface layer, which can cause particular problems in bonding [2]. The reason for this is that most of them contains a gel coat at the surface, or if the latter has not been deliberately created the surface layer usually contains a higher proportion of resin as opposed to the interior. Both the gel coat and the resin-rich surface layer are very brittle and can subsequently fail catastrophically when overload. Highly compliant adhesives are a particularly good choice, as they spread the applied load over a large area and hence reduce the stress borne by the surface of the composite.

These surface pretreatment methods mentioned above are summarized in the following sections (see for example recent works by Molitor *et al.* [2, 59] and Green *et al.* [153]).

TABLE IVA Showing the effects of various surface pretreatment methods on the surface roughness, oxide layer, bond strength, and durability of titanium alloys [2]

Treatment type	Alloy	Nature of treatment	Surface roughness	Oxide layer (nm)	Bond strength	Durability	Sources
Abrasion and solvent wipe	Ti-6Al-4V	Remove mold release	Macro		Poor	Poor	[145]
Grit blasting	Ti-6Al-4V	Remove mold release	Macro		Increase	Adequate	[131, 145]
VAST	Ti-6Al-4V	Remove mold release	Macro		Good	Poor	[131, 145]
Acid etch	Ti-6Al-4V	Etch	Micro		Adequate poor	Poor	[145, 147]
Alkaline etch	Ti-6Al-4V	Etch	Micro	60–200	Good	Good	[145, 147, 148]
Phosphate-fluoride	T-6Al-4V	Etch	None	20	Adequate	Poor	[145, 147]
Modified phosphate-fluoride	Ti-6Al-4V	Etchant and oxidation	None	8	Adequate	Better than phosphate-fluoride	[145, 147]
TURCO	Ti-6Al-4V	Oxidising	Macro	17.5	Adequate	Adequate	[145, 147]
DAPCOtreat	Ti-6Al-4V		Macro	6	Increase	Good	[147]
Pasajell	Ti-6Al-4V	Oxidising	Macro	10–20	Adequate	Adequate	[145, 147]
Chromic acid anodisation	Ti-6Al-4V	Oxidising	Micro	40–140	High	Excellent	[147]
NaOH anodisation	Ti-6Al-4V	Oxidising	Micro	80–90	High	Excellent	[147]
Cathodically deposited Al <sub>2</sub> O <sub>3</sub>		Oxidising			Adequate	Adequate	[145, 147]
Plasma spray	Ti-6Al-4V	Ablation and oxidation	Micro	130	High	Excellent	[145, 147]
Sol gel	Ti-6Al-4V	Coupling and oxidation			High	Good	[140]
Laser treatment	Ti-6Al-4V	Ablation and oxidation	Macro		High	Poor	[146]

TABLE IVB Showing the procedures applied and their surface modification effects of selected surface pretreatment methods for titanium alloys substrates [59]

Surface treatment	Procedure	Surface effect
Surface modification by excimer laser	Produced using a wavelength of 308 nm with XeCl. The focal length was 100 mm and the fluence produced was 77 J/cm <sup>2</sup> .	Riblets or wavelike structures were produced on the surface which were approximately 40 μm deep with 100 μm period
Surface cleaning by excimer laser	Produced using a wavelength of 308 nm with XeCl. The focal length was 150 mm and the fluence produced was 2.8 J/cm <sup>2</sup> .	A homogenised area of ~4 mm <sup>2</sup> was produced. Each irradiated zone was overlapped in both x and y directions.
Plasma spray	The titanium specimens were heated to 100°C in an oven to remove moisture, grit blasted with 180/220 Al <sub>2</sub> O <sub>3</sub> grit, rinsed with a cleaner and subsequently dried. Plasma spraying was applied by spraying Hamdry 6506. TiO <sub>2</sub> powder.	A TiO <sub>2</sub> coating of thickness 50 μm was produced.
Pasa Jell 107	Pasa Jell 107 was applied to grit blasted samples. It was applied for 12–15 min. After which it was rinsed with deionised water at room temperature. The specimens were subsequently dried and sprayed with a thin layer of the primer Redux 101 using a De Vilbiss suction feed cup spray gun, type JGA.	Etched the existing oxide film
Sodium hydroxide anodisation	Performed as described by Ingram and Ramani [149]. The samples were degreased in methylthylketone (MEK) for 10 min, pickled by in 15% volume of 70% nitric acid, 3% by volume of 50% hydrofluoric acid at room temperature for 30 s. They were subsequently rinsed in 2 baths of agitated deionised water for 5 min. Anodisation was performed in a 5 M NaOH electrolyte at 10 V for 20–30 min. Upon removal from the solution, the samples were rinsed for 5 min in running water. The samples were allowed to dry and sprayed with a thin layer of the primer Redux 101 using a spray gun.	Cleaned and created a fresh oxide film
Chromic acid anodisation	Performed as described by Arnold <i>et al.</i> [150]. The samples were degreased in MEK for 10 min, pickled in 15% by volume of 70% nitric acid, 3% by volume of 50% hydrofluoric acid at RT for 30 s. They were subsequently rinsed in 2 baths of agitated deionised water for 5 min. Anodisation was performed in an electrolyte containing 5% CrO <sub>3</sub> and 0.1% NH <sub>4</sub> HF <sub>2</sub> at RT. The voltage was applied after the specimens were immersed in the solution and increased from 2 to 10 V at a rate of 2 V/min. The voltage held constant for 20 min. Upon removal from the solution, the samples were rinsed in the agitated deionised water and subsequently rinsed for 5 min in running water. The samples were allowed to dry and sprayed with a thin layer of the primer Redux 101 using a spray gun.	Cleaned and created a fresh oxide

## 5.1. Mechanical surface pretreatments

### 5.1.1. Abrasion, grit blasting and solvent cleaning

A mechanical treatment is used primarily to produce a clean macroscopically rough surface and to remove some of the existing oxide layer [2] (see Tables III and IV). The combination of a clean adherend surface with significant macro-roughness improves the initial dry strength [145]. However, abrasion and grit blasting techniques are not adequate methods of surface treatment, but when combined with chemical or electrochemical treatment, durable bond strengths can be obtained [157].

Abrasion/solvent cleaning may be employed to degrease the surface and remove mold release agents from the adherend [133, 135, 136]. For example, the composite sheets can be lightly abraded using 180/220-mesh alumina, then wiped clean with a solvent such as methylethylketone (MEK) and allowed to dry. Previous researchers have found a significant increase in surface roughness and bond strength for thermosets [2]. However, the same treatment for thermoplastic polymer composites did not reveal any significant increase in bond strength or durability, due to the fact that some of

these composites have very smooth low surface energy surfaces [133, 135, 137].

Solvent degreasing must be performed in a controlled atmosphere to prevent surface re-contamination [132]. Surface contamination should be removed as the first step in surface preparation as degreasing after abrasion or chemical treatment will result in a layer of partially solvent dissolved contamination remaining on the prepared surface which may inhibit adhesion [139].

The type of solvent is also important. Care is required to ensure that the solvent does not degrade the structure being degreased. For example, many chlorinated hydrocarbon solvents can cause stress corrosion cracking [58]. Solvents with a rapid evaporation rate are best for hand degreasing, because any residual pools of solvent will spread partially dissolved contamination as the material evaporates; the faster the solvent evaporates, the less surface is contaminated. Degreasing must be performed using a solvent rather than a detergent. Detergents function by wetting the surface better than the contamination, thus displacing it from the surface. This means that the detergent will become a contaminant unless it can be removed from the surface

[132]. Note that water solubility of a detergent is not a guarantee of removal.

As important as selection of an appropriate solvent is the selection of an appropriate wipe cloth which will not contaminate the surface. Shop rags, cheesecloth and even some proprietary wipe cloths may contain contaminants. Others contain lanolin (which is a food release agent) to reduce skin abrasion on the hands of the user. These must be avoided.

Alternatively, an alumina grit blast (of particle size 45  $\mu\text{m}$ ) with three passes at a distance of 15–20 cm may be employed, followed by solvent rinse and dried in nitrogen [2]. MEK may not be compatible with local government regulations for industrial applications and as a result may have to be phased out and be replaced by a less hazardous solvent. The DLR (German Aerospace Research Establishment) has investigated three different types of cleaning agents to be used with mechanical methods of surface treatment [132]. These included acetone, frigen and ethylacetate. Of these, the latter gave the highest lap shear values. Again, as with the abrasion and solvent wipe, grit blasting gave strong and durable bond strength for thermosets but revealed very little degree of success with thermoplastic materials [2].

In summary, grit blasting is far more effective in production of an active surface, mainly because it is a non-contact process with a clear visible measure of effectiveness [152]. One requirement for grit blasting is that the abrasive must cut the surface, not punch the surface. Thus abrasives such as glass beads, walnut husks, sand and steel shot are not suited. Aluminum oxide powder and even zirconia have been found to be effective [158]. It is important that the abrasive powder is not recycled, to prevent re-contamination of exposed surfaces.

The grit should be delivered in a dry inert gas stream. Compressed air is not suited, due to oil and water content. Current practice in defence applications is to use dry nitrogen gas which readily available at service bases because of its use for inflation of tyres and shock struts. Grit particulates must be contained within the worksite, and extracted using a vacuum system which must exhaust away from the aircraft. Particles may break into fine needles, pass through fuel filters and cause fuel system malfunctions. Failure to extract fine dust from fuel tanks has led to in-flight engine failures.

One factor which influences the adhesive void content is the level of abrasion by grit blasting. Excessive

abrasion by either high pressures or slow pass rates will cause folding of the surface [159] leading to trapped moisture which evaporates during heat cure of the adhesive causing voiding in the adhesive layer. The grit blast should be light enough to avoid folding, but sufficiently heavy to remove the surface oxides. This can be easily controlled by abrading until the surface sheet is removed, but not so hard that the surface of aluminum alloys turn a dull, dark grey. With limited training, most operators easily master the appropriate level of abrasion.

*5.1.1.1. Effect of grit blasting on surface properties for adhesion.* Harris and Beevers [52] have investigated the surface energy and adhesion characteristics of a mild steel and an aluminum alloy using the grit blasting with different alumina grits. The coarser grit produced rougher surfaces and in general the rougher surfaces exhibited lower surface energies. Harris and Beevers have explained this observation using the effects of geometric features of the surfaces on the spreading of the droplet and the measurement of the contact angle. However, it was also observed that the grit-blasting process introduces chemical changes on the surface of the substrate and these in turn affect the surface energy [52].

The surface energy and adhesion characteristics of a surface are dependent on a complex interaction between surface texture and chemical components [52]. The following factors can also influence these interactions: (a) the substrate material, (b) the grit-blasting media purity and contamination, and (c) the grit-blasting media particle size. Although it is difficult to derive a generalised hypothesis for the relationship between surface texture and surface energy and the resulting adhesion characteristics, an interpretation of these complex interactions may be drawn from the summary of changes resulting from the surface pretreatment of surfaces using different sized grit-blasting media as depicted [52] in Table V. It should be emphasized that this table does not show actual properties for a particular treatment but indicates changes which occur with increasing grit size and the associated greater surface roughness. From this table it may be concluded that initial strengths were relatively insensitive to grit type or size. However, durability characteristics were found to give different responses and thus Table V attempts to correlate these changes with other effects.

TABLE V Summary of responses of surface properties to changes (including the surface energy, surface chemistry and durability) for mild steel and aluminum alloy substrates in grit size from 180/220 to 60 grit [52]

Substrate material	Grit type	Response of surface properties to increase in grit size		
		Surface energy	Surface chemistry	Durability
Mild steel	Brown	No change	Mg ↓ Al ↓	Lap no change Butt ↓
	Pink	Polar ↓	Na ↓ Al ↓	
Aluminum alloy	White	Polar ↓	Na ↓ Al ↓	Lap ↓ Butt ↓
	Brown	No change	No change	
	Pink	Polar ↓	Na ↓	
	White	Polar ↓	Na ↓	



### 5.1.2. VAST (*vought abrasive surface treatment*)

Using this pretreatment (Table IVA), the titanium is blasted with a slurry of fine abrasive alumina (220 mesh) containing 2% fluorosilic acid under high pressure [2]. A post treatment rinse in 5% nitric acid is required for Ti-6Al-4V titanium alloys to remove grey smut after blasting. An oxide film is produced which is crystalline in nature. This results in joint durability, which is reported to be slightly lower than TURCO 5578 and slightly higher than the phosphate fluoride process [65, 145]. Most chemical treatments alter the titanium substrate by etching the existing oxide film. If the solvents are reducing agents, then a fresh thin oxide film is produced after the metal is removed from the solution, while in an oxidising solvent a thicker oxide film is produced [145].

### 5.1.3. Peel-ply (*or tear films*)

Peel-ply (also known as tear films) (Table III), an impregnated ply is removed immediately prior to bonding [2]. Previous research has shown that successful joints were obtained by increasing surface roughness, degreasing and removing of mold release agents [157]. The peel-ply is released from the surface because of the non-stick nature of the substrate within which it is impregnated. These are frequently fluorine silicon or fluorine compounds, which contaminate the laminate surface. Consequently, this implies that further treatment of the surface, e.g., by abrasion, is required if the strength of the subsequent bond is not to be seriously impaired [148]. If the ply contains release agent, the adherend must be subsequently cleaned with a solvent and dried in a stream of nitrogen.

Typically, three forms of tear films are used: (a) The first type are a thin fiber-glass layer which is difficult to remove, and will cause delamination damage in thin laminates. There is a real danger of removing the first few layers of laminate with the tear film; (b) The second type are usually a nylon product. Unfortunately, nylon forms good chemical bonds with epoxy resins so some form of release agent is applied to the fibers to enable the operator to remove the tear film without causing excessive damage to the laminate. Tests [160] have shown that this release agent is transferred to the bonding surface and reduces the effectiveness of any adhesive bond formed with that now contaminated surface. Most reputable manufacturers clearly state that all coated fabrics have the potential to transfer release agent to the surface exposed by removal of the tear film; (c) The third form of tear film uses heat setting or corona discharge treatment to glaze the surface of the fibers. This is the usual process for polyester tear films. The glazed surface is so slick that it releases from the resin when required. Unfortunately, it leaves a replicate of that glazed surface on the laminate surface again resulting in a reduced bond effectiveness on that surface. While the surface remaining is clean, it is not chemically active, apart from a few locations where the weave bundles cross over each other and the resin is fractured [160].

For thermosetting plastic matrix composite surfaces, practice is to use tear films, a sacrificial layer placed on the surface during the laminating process. The tear film remains in place until the adhesive is to be applied. It is then removed, taking surface contaminants with it. The concept is flawed and is based again on the “clean surface” theory.

### 5.1.4. Tear-ply

Tear-ply is mainly used for thermoset composites (Table III) as thermosets are reactive upon heating and hence do not require a chemical surface treatment [2]. It is fundamentally different from peel-ply and consists of a fabric, which is completely impregnated by the laminate matrix resin, and as the name implies subsequently peeled off the molding. Superficially, the surfaces of the laminates treated with either peel-ply or tear-ply appear very similar as both exhibit the pattern of the ply fabric. Tear-ply exploits a laminate property, which is generally regarded as being a serious disadvantage: the lack of strength in the  $z$  direction (normal to the surface). Immediately prior to a bonding operation, a corner of the fabric is raised with a knife and the tear-ply is then torn off the molding, thus fracturing the resin interface between the tear-ply and the bulk molding.

The tear-ply must be carefully selected to enable it to be removed without any difficulty following the molding process. Polyester resin has fracture characteristics, which permit this, and have little adhesion to the nylon fibers in the fabric. However, as pointed out by Molitor *et al.* [2], some resins are not compatible with this technique and hence peel-ply must be employed despite the difficulties arising from contamination.

## 5.2. Etching

For any adhesive bonding process, a fresh chemically active surface is essential [152]. This may be generated chemically by etching, but may also be produced by abrasion. Production facilities usually use tank etching methods for metallic surfaces, and field level facilities usually rely on abrasion of the surface. The function of abrasion is often misunderstood to be enable the adhesive to key into the surface. Removal of sanding debris is difficult, leading many specifications to require solvent cleaning after abrasion. Because bonding relies on the chemical activity of the surface and the absence of contamination, solvent cleaning after abrasion only succeeds in partially dissolving contaminants and spreading them over the surface, reducing the effectiveness of the active surface. Sanding debris is best removed using a dry wipe process until all debris is removed.

### 5.2.1. Acid etching

Acid etching has produced similar results to abrasion and grit blasting, in that an increase in bond strength is recorded for thermoset polymer composites, whereas little or no effect was recorded for thermoplastics [130, 136, 148].

A number of acid mixtures have been used to treat the surface of titanium, including nitric-hydrofluoric acid,

hot sulphuric acid, and sodium dichromate-chromic acid [2]. Most of these treatments give adequate dry strengths but durability is reported to be very poor [161]. Both stressed and unstressed peel and lap shear joints have shown to perform equal to or better than phosphate fluoride or modified phosphate fluoride processes [65]. An additional problem associated with these treatments is hydrogen pick up. However, this problem can be avoided with the use of alkaline solutions as opposed to acid etchants.

### 5.2.2. Alkaline peroxide etching

As shown in Table IVA, Molitor *et al.* [2] have used the alkaline peroxide etching initially at room temperature for the Ti-6Al-4V alloy, but this process, which lasted up to 36 h, was too lengthy for industrial applications. The immersion time can be reduced to 20 min by increasing the temperature to 50–70°C [145]. Depending upon the concentration of sodium hydroxide and hydrogen peroxide, the metal is either etched or oxidised. Those concentrations, which produce grey oxides, have been found to produce adhesive wettable surfaces. An oxide layer up to 2  $\mu\text{m}$  thick, which is stable up to 200°C and capable of forming high bond strengths at elevated temperatures and high-humidity environments were produced using a sodium hydrogen peroxide etch [148]. Alkaline peroxide etch is reported to be satisfactory but has long heat up times and has high hydrogen peroxide consumption. Oxide formation is related to the rate of hydrogen peroxide decomposition. The rate of decomposition is increased by adding 5–10% heavy metal ions to the hydrogen peroxide solution.

### 5.2.3. Phosphate fluoride process

This process has been used to pretreat the titanium alloys (see Table IVA), which is based on combinations of trisodium phosphate, disodium tetraborate, potassium fluoride and hydrofluoric acid [162]. A process of pre-etching in 3% hydrofluoric acid and 15% nitric acid followed by a 2 min dip in the 5% trisodium phosphate, 2% potassium fluoride and 2.6% hydrofluoric acid mixture has become known as the phosphate fluoride process (US Patent 2 864 732). The rinsing procedure after this treatment is critical to remove excess chemicals and a 15 min soak in di-ionised water at 60°C has been recommended [145].

Modified phosphate fluoride process has also been applied to treat the surface of titanium alloys (Table IVA), which has been shown that on exposure to warm moist environments, the anatase oxide layer produced by the phosphate, fluoride process slowly reverts to rutile [2, 145]. As a result, there is a decrease in volume of about 8%, which results in the development of stresses at the adhesive/oxide layer interface. By stabilising the anatase structure the joint durability is enhanced. This is achieved by adding 0.75% anhydrous sodium sulphate into the etch solution [65, 145]. However, both of these treatments have been out-performed by treatments such as TURCO 5578, sodium hydroxide anodisation and chromic acid anodisation [145].

### 5.2.4. TURCO 5578

TURCO 5578 is an alkaline-based etchant, which contains caustic soda, sodium metasilicate and pyrophosphate [2]. This pretreatment process produces a large amount of macroroughness with little or no microroughness, which can be used to treat the surface of titanium alloys (Table IVA). The oxide film produced is  $\approx 17.5$  nm thick with a macroroughness of 3.4  $\mu\text{m}$  peak to valley [163]. The durability of this treatment is much better than that of the phosphate fluoride treatments. In durability trials, TURCO 5578 is only out-performed by chromic acid anodisation [65]. However, the added advantage of the TURCO 5578 treatment is that there is no hydrogen embrittlement as observed in the acid etching process.

Another surface pretreatment, DAPCOtreat, which is similar to TURCO 5578, is also applied to titanium alloys, in that it results in an increase in macroroughness with little or no microroughness [2]. DAPCOtreat produces a thin 6 nm oxide layer on the titanium substrate [65].

### 5.2.5. Pasajell 107 treatment

This pretreatment is recommended (Table IVA) as a pre-bond treatment for titanium [65, 144, 145, 164, 165]. The chemical composition of pasajell 107 is 40% nitric acid, 10% combined fluorides, 10% chromic acid, 1% couplers and the balance is water. It is available as a thixotropic paste for brush applications or as an immersion solution for tank treatment. A recommended treatment time is 10–15 min. Pasajell 107 is applied in combination with a pre-treatment of MEK wipe, blast with 320 grit non-silicone sand, followed by non-chlorinated solvent wipe [136]. After applying the pasajell for 10–15 min, the coated area is rinsed with deionised water. This process produces [2] an amorphous looking oxide, which has anatase structure, which is stable up to 175°C and converts to rutile at 350°C. Comparing this treatment to the alkaline peroxide etch, the bond durability of the pasajell treatment is reported to greatly exceed that of the alkaline peroxide etch at elevated temperatures and humid environments [144].

## 5.3. Corona discharge treatment

Corona discharge, namely exposing the substrate surface to excited atoms, ions and free radicals at atmospheric pressure has been widely used to pretreat polymeric materials surfaces (Table III) for adhesive bonding [135, 166, 167]. The success of corona discharge in treating carbon-fiber-epoxide, carbon-fiber-PEEK and glass-fiber-polypropylene composites for bonding is reported, as is its use for treating polyolefin films to make them receptive to printing inks. Results [133] reveal that corona treatment increases surface tension and in some cases alters the surface chemistry by oxidizing the polymer matrix, which results in the increase in bond strengths.

Corona discharge pretreatment method and technique was described in detail by Tohra Vehara [168] and Sutherland *et al.* [169] using a modified continuous

treatment type machine allowing small number of samples on a flat electrode plate to be treated, with the arc struck between it and the moving bar electrode above it. Optimization of the treatment of the maximum surface energy, using standard wettability inks and was found to be  $58 \text{ dyn} \cdot \text{cm}^{-1}$ . For example, the process parameters for homopolymer polypropylene, HF 133 M were as follows [153]: number of passes = 1, treatment width = 0.18 m, speed =  $15 \text{ m min}^{-1}$ , electrode-sample gap = 1 mm and power = 33 W (power density =  $120 \text{ Wm}^{-2} \text{ min}^{-1}$ ).

#### 5.4. Plasma treatment

As presented in Table III, the use of plasma treatment to pretreat polymers has been known for more than 20 years [2]. The plasma treatment involves a low-pressure plasma gas, which is electrically conductive and consists of excited atoms, ions and free radicals [170]. This allows polymer surfaces to be cleaned, etched or chemically modified [136, 170]. The plasma particles react not only with each other but also with the surfaces, which are exposed to the gas, giving rise to the following effects [136]: (a) surface cleaning, (b) degradation of the polymer chains, (c) removal of material from the surface, (d) formation of radicals on the surface, and (e) change of tacticity of the polymer chains.

The combined effect of these processes results in an improvement of the adhesion properties of the surface [2]. Plasma treatments involving various gases have been found to enhance the surface tension, oxide the polymer matrix and increase the bond strength of PEEK composite [137]. Results obtained by Blackman [130] and Barron [155, 171] echo the results obtained by corona treatment [135], in that plasma treating the PEEK composite produced an increase in surface roughness, surface tension and bond strength.

Both glow discharges and plasma sprays have been examined as methods of surface treatment for titanium alloys [2]. Aronsson *et al.* [172] investigated the use of glow discharge. Results obtained revealed that this method of plasma treatment produced clean surfaces and reproducible results, depending upon the degree of treatment. Furthermore, oxidation in pure oxygen resulted in uniform and stoichiometric  $\text{TiO}_2$  surface oxide layers with reproducible composition and thickness.

Plasma spraying involves rapidly heating either,  $\text{TiO}_2$ ,  $\text{TiSi}_2$ ,  $\text{MgO}$  or  $\text{SiO}_2$  powder to a molten or semi-molten state and then spraying it onto the substrate at high velocity. This is another method of surface treatment employed for adhesive bonding that involves no hazardous chemicals or pollutants [2]. Other advantages of plasma spraying over chemical treatments include [143]: (a) flexibility to design coatings for specific applications, (b) insensitivity to surface contamination, (c) indefinite shelf life prior to bonding, and (d) low processing costs.

Successful plasma treatments of titanium have been reported, whereby bond strengths equivalent to the best chemical treatments were obtained [143]. At high temperature, the plasma-sprayed titanium joints produced superior results. Ramani *et al.* [147] employed a simi-

lar technique to plasma spray called silicon sputtering, where a  $200 \text{ \AA}$  thick silicon layer was sputtered onto titanium. An increase in bond strength and durability was recorded and attributed to an increase in surface tension and surface roughness, which allowed the molten polymer adhesive to flow in and around the increased surface area and interact with the silicon and oxides.

Use of microwave plasma in post discharge has the advantage of a less severe effect on the surface properties than treatments where the polymer is placed directly within discharge [173]. In post-discharge, the polymer substrate is not exposed to high-energy entities such as electrons or high-energy ions which can have a highly destructive impact. The principal effects of a microwave post-discharge treatment are known to be the cleaning of the surface (removing pollution or weak boundary layer), the crosslinking of the surface and the chemical modification by introducing of functional groups [128]. The modification of the roughness of the surface is generally less marked for this type of treatment but has been shown to occur in certain cases especially for drastic treatment conditions (high power and long treatment times) [174].

The use of nitrogen/oxygen mixtures for the plasma treatment of polymers is well-known and has been studied [175–178]. They are used to incorporate oxygen functions at the polymer surface, and leading to an increase in wettability. Several studies [179, 180] indicate that the use of a mixture of the two gases is more efficient than the use of oxygen alone as they lead to a higher concentration of atomic oxygen, the main active species in the oxygen plasma.

Low-pressure O/N vacuum plasma pre-treatment can be used for the Polyolefins components, using a large-scale evacuation chamber. The processing and equipment of large-scale low-pressure plasma chambers was properly described by Wertheimer [168] and covers the equipment and processing technique used. For example, the process parameters for homopolymer polypropylene, HF 133 M were as follows [153]: pressure =  $2.6 \times 10^{-2} \text{ mbar}$ , voltage = 2500 V, current = 2.3 A, pump-down time = 5 min, plasma reaction time = 35 s, hold time following plasma = 60 s and repressurisation time = 10 min.

Agrodyn<sup>TM</sup> atmospheric plasma pre-treatment or “air” plasma allows the pre-treatment of complex-shaped articles under atmospheric conditions without the need for batch processing using vacuum chambers required by other forms of plasmas. This treatment can be carried out using a process described by US-Patent 5837958 [181]. Air plasma relies on the use of a plasma jet being formed from the nozzle of a rotating sparking nozzle, which are set up as pairs of nozzles. The sample is then placed below the nozzles within the plasma cone and pre-treated in a processing method similar to that used for flame. The process parameters are set to create the greatest surface energy by the use of wettability inks, which was identified as being in excess of  $120 \text{ dyne cm}^{-1}$ . For example, the process parameters for homopolymer polypropylene, HF 133 M were as follows [153]: gas = air at atmospheric pressure, input pressure = 2 bar, output jet pressure = 13.9 mbar,

rotation speed of nozzle = 1500 rpm and speed = 10 mm min<sup>-1</sup>.

### 5.5. Flame treatment

This treatment is widely used in the surface modification of thermoplastics such as polyolefins (see Table III), to improve printability and paintability, by introducing oxygen containing functional groups to the surface [166, 182–185]. An oxidising flame is very similar to a gas plasma in that it contains excited species such as atoms, ions and free radicals, which oxidise the surface of the specimens. The distance from the surface to be treated, the air/gas ratio and the dwell time are all critical parameters in producing a successful treatment. By oxidising the surface prior to bonding an increase in hydrophylicity and hence bond strength can occur.

In the flame surface pretreatment a row of propane burners is passed repeatedly over the substrates in a continuous and uniform manner as demonstrated by Sutherland *et al.* [186]. However, the gas ratio and pass speed are kept constant throughout and optimized for maximum surface energy, which was found to be 56 dyn cm<sup>-1</sup>. For example, the process parameters for homopolymer polypropylene, HF 133 M were as follows [153]: number of passes = 8, speed = 25 m min<sup>-1</sup>, propane flow = 3.751 min<sup>-1</sup>, air flow = 881 min<sup>-1</sup>, cone height = 4 mm, burner gap = 13 mm, power density = 207.5 mJmm<sup>-1</sup> and burner length = 265 mm.

### 5.6. Laser treatment

A novel method of surface treatment, namely, the laser treatment [131, 187, 188] has been employed to increase the bond strength of adhesive joints to polymers and metallic substrates (Tables III and IV). Initial results are promising with respect to durability but more research is necessary. Park *et al.* [161, 189] has recently shown that laser treating polymer composite surfaces prior to bonding can produce high-strength adhesive bonds. Laser treatment results in increase in surface roughness due to the ablation of the polymer matrix.

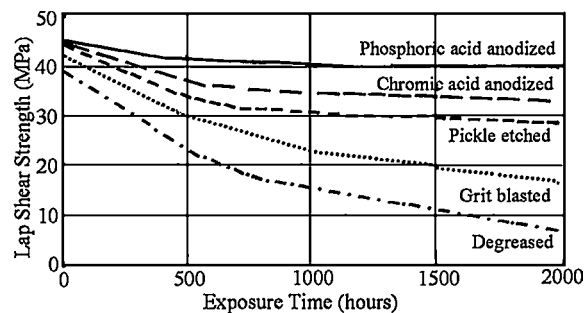
In the past surface treatment of titanium substrates has been based on either chemical or electrochemical processes. Although these treatments have been very successful, many contain hazardous chemicals such as chromates. As a result, new methods have been developed which are environmentally friendly. Recent studies have shown that Excimer laser treatments result in an increase in surface roughness and the formation of a thin oxide layer [146]. The parameters that affect the degree of surface treatment include wavelength, polarisation and intensity. For Excimer laser treatment, the parameters governing the quality of treatment are the wavelength, polarisation, power density, beam diameter, speed and pulse length [151, 190]. In particular, the pulse length or dwell time strongly influences the material depth that will be affected. Surface cleaning by Excimer laser also yielded high peel strengths. Surface cleaning by this method ablate the natural oxide layer on the surface and do not produce macroroughness as produced by surface modification by Excimer laser.

Results obtained [146] reveal no significant difference in single lap shear strength results obtained using Laser treatment compared to chromic acid anodisation which augers well for an environmentally friendly surface treatment. Broad *et al.* [151] have revealed good durability results using the patented CLP (CIBA Laser Pretreatment) laser treatment, whereby laser treated adhesive joints to an aluminum alloy substrate have not failed after 1400 days.

Another laser treatment called, the IR (infrared) laser surface pretreatment is carried out using carbon black doped on a substrate (for example on the homopolymer polypropylene, i.e., HF 135 M samples). The carbon black is added as an IR absorber (i.e., 2% by weight of the total mass). Although the Excimer laser techniques is described by a number of authors for different substrates such as PEEK, the use and technique of the IR laser has not to date been published [153], but the technique is similar to that used by Frerichs *et al.* [191] for the surface pre-treating of PEEK using an Excimer laser. The parameters can be optimized by the use of wettability inks to maximize measured surface energy. For example, the process parameters for homopolymer polypropylene, HF 133 M were as follows [153]: (a) a diode IR laser was used to give a square beam profile at 940 nm, (b) the samples were pre-treated within an oxygen atmosphere at an output of 100 W over a treatment area of 675 mm<sup>2</sup>, and (c) the laser sample gap was set at 139 mm whilst the samples were passed underneath the laser upon a translating track at a speed of 2.5 m min<sup>-1</sup>.

#### 5.6.1. Comparison of laser surface preparation with wet pretreatments

Certain metals and their alloys require a surface pretreatment in order to achieve highly durable adhesively bonded joints. This is the case when aluminum and its alloys are adhesively bonded and is clearly demonstrated [151, 192] in Fig. 10. For durable adhesively bonded aluminum joints a simple degreasing or grit blasting is not sufficient. With regard to joint properties a variety of surface pretreatments for aluminum substrates, such as (a) phosphoric acid anodizing, (b)



Epoxy adhesive  
Exposed to water at 50°C

Figure 10 Effects of various wet pretreatments (i.e., phosphoric acid anodized, chromic acid anodized, pickle etched), grit blasted, and degreased methods on the adhesively bonded lap shear strengths of aluminum alloy substrates [151, 192].

chromic acid anodizing or (c) pickle-etching, are well known in the aerospace industry [151]. These surface pretreatments can be classified as “wet pretreatments”. Joints with long-term durability can be achieved by applying such pretreatments. Irrespective of their excellent performance regarding the joint properties, wet pretreatments suffer from certain major disadvantages [151]: (a) ecological disadvantages (disposal of chemicals and waste water), (b) long pretreatment times, (c) compatibility problems with short cycle times (e.g., in the automotive industry), (d) limited surface stability, (e) pretreatment of the whole submerged surface, and (f) high pretreatment costs. One main disadvantage of wet pretreatments is one of an ecological nature as they require disposal of high quantities of chemicals and contaminated rinsing water [151]. Furthermore, due to their relatively long process times wet pretreatments approach their limit with regard to economically acceptable effort when larger parts have to be pretreated with short cycle times. A typical example could be in the automotive industry where the pretreatment of large body parts with short cycle times would require very large acid and rinsing baths. This would result in high investments and running costs. The limited stability of the wet pretreated surfaces often requires increased logistical effort and additional processing steps to protect the surfaces with a conservation primer. Additionally, the wet surface pretreatments generally do not allow for selective treatment of the area to be bonded. The whole surface of the part which is submerged, has to be pretreated even when only a small area of it requires bonding. This clearly increases costs of such processes.

Another surface treatment process called Ciba Laser pretreatment (CLP) was developed and patented. As Broad *et al.* [151] claimed this newly developed and patented Ciba laser pretreatment avoids the above-mentioned disadvantages of wet surface pretreatments and at the same time facilitates the achievement of good joint properties for substrates such as aluminum, aluminum alloys, and stainless steels. The CLP process consists of the following process steps only: (a) primer application (including evaporation of solvent), and (b) laser treatment. A suitable laser and optimum parameters should be chosen according to the substrate and the production requirements. Laser technology from small mobile lasers to high-performance stationary laser units allows for a wide range of CLP-applications, from repair to high-volume series production. Pretreatment speeds depend on the power of the laser being used; for example, for CLP with a high-performance laser it is easily possible to pretreat a width of 4 cm at a speed of 8 m/min. Therefore, by the choice of suitable lasers, compatibility of CLP with short cycle times can be achieved. The primer applicator and the laser can be adopted to industrial robots and in this way CLP can be integrated as an in-line pretreatment into the overall production process.

The recent progress in Laser pretreatment applications on the adhesive bonding of aluminum, stainless steels and titanium alloys substrates will be reviewed in Section 6.

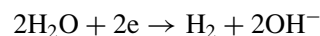
## 5.7. Electrochemical reactions

Electrochemical reactions have been used for various pretreatment purposes including cleaning, etching and oxidising metal surfaces, where the metal acts as an anode or cathode. Anodisation creates an oxide surface that is dependent upon the electrolyte, anodisation voltage, times and temperature [164]. For example, there are various anodisation techniques employed for titanium alloy surface treatment (see Table IVB) including (a) chromic acid anodisation, (b) sodium hydroxide anodisation, (c) cathodically deposited Aluminum oxide.

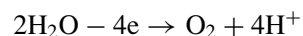
Methods of electrochemically generating oxidising and reducing conditions are also used to pretreat a range of polymers. The methods include reversible anodic and cathodic generation of soluble redox couples as mediators capable of reacting with polymer surfaces, and directly contacting polymers with polarised electrodes. Environmental conditions play an important role in the choice of pretreatment methods. This leads to the use of flame, plasma and corona discharge treatments all of which have a low environmental impact [129]. These methods are however of limited use for the treatment of complex shapes which often require wet methods. Electrochemical pretreatments offer some advantages over purely chemical methods in that the need for the storage of aggressive and toxic reagents is reduced or eliminated and by continuously regenerating the spent solutions further savings may be made by reducing waste disposal costs [129].

### 5.7.1. Basic principles

Brewis and Dahm [129] have recently reviewed the basic principles of the electrochemical process. Electrochemical reactions take place at the interphase of an electronic conductor, the electrode and an ionic conductor i.e., the electrolyte. The anode has been made the working electrode (WE) and only oxidation processes are considered. We can also use the same argument to study reduction (electronation) reactions by making the cathode the WE. The cathode is made electron-rich by pumping electrons into it and when the potential of the cathode is sufficiently high these electrons may cross the interphase and reduce i.e., electronate a substrate situated in the vicinity of the cathode. The electrolyte itself may be electronated or deelectronated more readily than the substrate itself. In the case of an aqueous electrolyte water may exchange electrons with the electrode according to



[Reduction (electronation) of water] (18)



[Oxidation (deelectronation) of water] (19)

It is therefore frequently necessary to use a non-aqueous electrolyte if really powerful oxidizing or reducing conditions are to be obtained.

We can use of these principles for the treatment of polymers in two ways: (a) The electrode may be brought

into direct contact with the polymer surface, the so called direct electrochemical process or, alternatively, (b) an indirect approach may be used where a soluble species is converted into a powerful oxidizing or reducing agent by electronation or deelectronation at an electrode. The redox reagent thus generated then transfers electrons to or from the polymer regenerating the original species which merely acts as an electron carrier or mediator transferring electrons between the electrode and the polymer. Both approaches have been used to treat the surface of polymers with the aim of improving their bondability.

### 5.7.2. Chromic acid anodisation

This technique produces a surface with significant microroughness and an oxide thickness of 40 and 80 nm for the 5 and 10 V treatments, respectively [65]. In addition, chromic acid anodisation oxides are reported to exhibit remarkable bond durability and provide the target bond strengths and durability for all other treatments.

### 5.7.3. Sodium hydroxide anodisation

Previous researchers investigated the use of sodium hydroxide-hydrogen peroxide anodisation and peroxide free sodium hydroxide anodisation as methods of surface treating titanium for adhesive bonding [142]. It was found that specimens prepared by these methods produced high-strength adhesive bonds and exhibited good durability when exposed to conditions of heat, moisture and stress. The presence of hydrogen peroxide was found to be neither necessary nor beneficial and in some cases resulted in a decrease in bond strength [2]. In addition, the sodium hydroxide anodising solution could be reused and was considered to present very low operational and environmental hazards.

### 5.7.4. Cathodically deposited aluminum oxide

Cathodic depositions of metal oxides from alcohol solutions containing inorganic nitrides have shown good wettability and environmental resistance in hot and humid conditions [2]. A recommended solution is based on 10 g of hydrated aluminum nitride dissolved in 11 g of isopropyl alcohol [145]. By making titanium, the cathode of an electrolytic cell at 30 V the oxide is deposited on the surface. Results have shown joint strengths and durability to be better than the VAST and TURCO 5578 processes [145].

### 5.7.5. Polymer surface pretreatments based on anodic oxidation reactions

The surface pretreatment of polymers usually involve oxidation resulting in the introduction of various functional groups onto the polymer backbone [129]. The following techniques are used to achieve this: (a) exposure to plasma, (b) UV light, reactive gasses, or (c) conventional aqueous oxidising agents such as acid dichromate or potassium permanganate [193].

However, in principle it should be possible to bring about surface oxidation by exposing the polymer to an

anodically polarised electrode or to some soluble reactive, anodically generated oxidising agent. But there are certain difficulties associated with this approach: (a) firstly, the oxidation potentials of saturated polymers are very high so that the electrolytes used tend to be oxidised instead of the polymer. Electrolytes resistant to oxidation at these very high anodic potentials tend to be expensive and extremely unpleasant typically consisting of mixtures of fluorosulphonic acid with anhydrous antimony pentafluoride, the so called super acids [194]. (b) Secondly, it is unlikely that the treated polymer surface is an electronic conductor so that an anodic oxidative process proceeding from a single point contact anode can be ruled out. A number of water soluble reversible redox couples were considered for the role of mediator including [129, 195]  $\text{Ce(IV)/Ce(III)} E^\circ = 1.72 \text{ V}$ ;  $\text{Co(III)/Co(II)} E^\circ = 1.83\text{--}1.92 \text{ V}$  and  $\text{Ag(II)/Ag(I)} E^\circ = 1.98 \text{ V}$ .

### 5.7.6. Cathodic pretreatments of polymers

Brewis and Dahm [129] have reviewed the possibility of cathodic pretreatments of polymers. A number of fluoro polymers have been shown to react with various electron donors. The cathodic reduction of a solution of poly(chlorotrifluoroethylene) (PCTFE) in  $\gamma$ -butyrolactone containing lithium tetrafluoroborate has been reported [196, 197], but the use of the cathodic technique as a surface pretreatment for this particular polymer does not appear to have been investigated. On the other hand, large increases in failure loads have been observed with ethylene-chlorotrifluoroethylene copolymer (ECTFE), and with poly(vinyl) fluoride (PVF) upon treatment with sodium naphthalenide [129]. Considerably longer reaction times are required than is the case for the treatment of PTFE. It is possible that the naphthalenide ion assumes the role of a base rather than an electron donor resulting in the polymer surface [129].

In summary, it appears that electrochemical carbonisation of perhalogenated polymers may be achieved by directly contacting the polymer surface with the cathode or by using a mediator whereas partially halogenated materials may be treated using bases including those generated electrochemically [129]. There are two types of electrochemical attack on solid polymers, which depend on the nature of the polymer.

Polymers containing groups capable of forming rather stable radical anions or dianions are said to undergo accumulative reductive electrochemical attack. One example of such system is the cathodic reduction of PET in aprotic solvents containing tetralkylammonium salts as support electrolyte where initial two electron transfer to the aromatic moieties is particularly facile.

Polymer containing good leaving groups such as halogen are said to undergo dissociative electrochemical attack where electron transfer and elimination of halide ion are concerted without the formation of stable charged intermediates. The electrochemical reduction of PTFE by lithium amalgam is quoted as an example of such a process as well as the catalytic electrochemical reduction of poly(chlorotrifluoroethylene) (PCFET) at graphite and carbon black using solutions

of lithium and sodium salts in aprotic solvents such as  $\gamma$ -butyrolactone.

### 5.7.7. The direct electrochemical oxidation of polymers

The recent observation has shown [198] that it is possible to pretreat the surfaces of PP and HDPE by oxidising the polymer. This can be done by bringing the polymer into close contact with the exposed edge of a platinum electrode held at approximately 2 V versus the saturated calomel electrode (SCE) in dilute nitric acid in the absence of silver ion [129]. Direct electron transfer under these relatively mild conditions is extremely unlikely. Nitric acid is oxidised [199] at a platinum anode in the region of 2 V to yield highly reactive, short-lived nitride radicals capable of initiating the oxidation of low molecular weight alkanes and hence by implication of polyofins by way of hydrogen atom abstraction. It was suggested [198] that such a process is likely to be strictly less demanding than the concerted mechanism suggested for oxidation by the  $\text{AgNO}_3^+$  ion. In addition, attack at the more reactive tertiary hydrogen atoms of PP is likely to be favored which would account for the higher failure loads achieved for PP when compared with HDPE [129].

### 5.7.8. Silver electrolytic surface pretreatment process

Silver electrolytic surface pretreatment method can be carried out following a surface pre-treatment described by Brewis *et al.* [200]. This process is based upon mediated electrochemical oxidation by the use of Ag(II) to oxidise organic material at ambient temperatures. The process involves the reaction of  $\text{AgNO}_3^+$  with water to produce hydroxyl radicals, which are able to oxidise the surface of an organic material using a “H” cell. Owing to the recombination nature of the cell, no silver is consumed, since it is only used as mediator. For example, the process parameters for homopolymer polypropylene, HF 133 M were as follows [153]: dip time = 60 s, anodic composition = 50 ml of 5.5 M nitric acid containing 3 mM silver nitrate, electrode = large area platinum mesh, current = 1.1 A and voltage = 9 V. It was noted that following pre-treatment the anode solution had become dark brown suggesting transfer of the  $\text{Ag}^+$  ion.

## 5.8. Sol/gel pretreatment methods

The term “sol/gel” may be broadly used to describe two processes, one starting from a particulate (colloidal) inorganic sol (often aqueous) and another using organometallic precursors, chiefly metal alkoxides, usually in solution with alcohol and water. Since many treatments have hazardous pollutants and/or working environments, alternative methods of surface treatment have been developed such as the sol/gel method for titanium alloys substrates (Table IVA); the sol/gel process was initially used for making pure oxide glasses and ceramics. The sol/gel formation is water based; hence contains no hazardous pollutants. This recently

developed system is based on the principle of a hybrid organic/inorganic coating providing a gradient between titanium substrate and the adhesive [139]. This system has covalent bonding through the gradient coating, thereby reducing dependence of Lewis acid base and hydrogen bonding interactions for adhesive bonding, which in turn increases bond durability in hot wet environments. Researchers have used an acid catalysed sol consisting of zirconium alkoxide and glycidtrimethoxysilane coupling agent in water [140]. In addition, a pre-bond treatment of solvent wipe and/or grit blasting prior to the sol/gel treatment was used. Drench and spray techniques as well as immersion are employed for the application of the sol/gel. Results obtained compared very favorably with chromic acid anodisation results after 2000 h of hot/wet exposure [140].

## 5.9. Primers

Primers may be applied to titanium substrate surfaces for one or more of the following reasons [2]: (a) to protect the substrate surface until bonding is carried out, (b) to increase surface wettability, (c) to block pores of porous surface thereby preventing adhesive escaping, (d) as a vehicle for corrosion inhibition, and (e) as a coupling agent capable of forming chemical bonds with the adherend and adhesive.

Coupling agents are believed to form covalent bonds between the adhesive and adherend, thereby producing strong and durable joints. Silanes are widely used coupling agents. Silane coupling agents have the following structure  $R - \text{Si}(\text{OR}')_3$  where  $R$  is the functional group that chemically reacts with the adhesive.  $R'$  is usually an ethyl or methyl group. The main advantage of silane coupling agents is to improve durability of adhesive bonds in the presence of water or water vapor.

$\gamma$ -APS (aminopropyltriethoxysilane) is a common primer used on titanium and titanium alloys [65, 141]. The  $\gamma$ -APS primer is applied by immersing the titanium substrate in 1%  $\gamma$ -APS for 15 min followed by blowing the excess off in a stream of nitrogen [201]. The reported increase in the wet strength between Ti-6Al-4V and epoxy was 50% [202]. The  $\gamma$ -APS and  $\gamma$ -GPS (glycidoxypropylmethoxysilane) have been shown to improve the level of durability of grit-blasted specimens to that of sodium hydroxide and catalytic hydrogen peroxide etch [65]. In addition a primer called BR-127 is recommended by CYTEC the manufacturers of the adhesive FM-300, while BR-127, EC-3960 and EA-9223 are suitable primers for bonding titanium to composites [144]. However, the problem with BR-127 is that it contains hazardous chromates. Alternative primers recommended include the non-chromated CYTEC XBR 6757.

## 6. Recent progress in surface pretreatment methods

### 6.1. Effects of mechanical surface pretreatments on the bonding of composite-composite and metal-metal adherend systems

Kohli [21] has recently studied the effects of surface preparation of thermoplastics and thermoset composite

substrates (composite-composite system) bonding with the FM<sup>®</sup> 300-2 adhesive film. In this work, effects of humidity, laminate layup, and as using the various mechanical tests including the lap shear and hinged double cantilever beam testings, well as surface pretreatments on the durability of the bonded structure were also studied. For thermosetting composites of secondary bonding, eight epoxy/graphite or epoxy/glass prepreg systems with cure temperatures ranging from 121°C to 177°C were selected. Whereas for secondary bonding of thermoplastic laminates APC-2 (PEEK) or KIII, laminates were used. For the Ciba 6376/3 K 70P prepreg system, the composite surface preparation studied included (a) dry Nylon peel ply, (b) Peel ply/hand sand, and (c) Peel ply/grit blast. The surface preparation for the Hercules 3501-6 carbon/epoxy prepreg, on the other hand, included (a) peel ply and (b) peel ply/hand sand. For all metal or secondary bonding of composite substrates, the following cure cycle was utilized: Heat-up rate 1.7°C/min to 121°C, 0.28 MPa, hold 90 min at 121°C. Ciba 6376/3 K 70P (an epoxy/graphite prepreg system, Hercules 3501-6/3 K 70P (an epoxy/graphite fabric prepreg system), and Hercules 8551-7/AS-4 (an epoxy/graphite fiber tape system) were cured for the following conditions: 177°C for 120 min, 0.35 MPa, heat-up rate: 1.7°C/min, laminate thickness: 3.1 mm (except that the first substrate were heated-up at the rate of 1.7°C/min). Hercules 8551-7/AS-4 and Hercules 8551-7/glass substrates consist of 1.27 mm laminate thickness and ( $\pm 45, \pm 90, 0$ )<sub>2</sub> laminate lay-up.

The effects of various surface pretreatments, and hot/wet conditions on the lap shear strength of the secondary bonding of Ciba 6376 Prepreg with FM<sup>®</sup> 300-2 M are shown in Table VIA. These data show that peel

TABLE VIA Secondary bonding of Ciba 6376 Prepreg with FM<sup>®</sup> 300-2 M. Effect of substrate surface pretreatment on carbon-carbon lap shear strength [21]

Composite surface preparation	Composite surface conditioning	Test results (MPa)			
		-55°C	23°C	82°C	82°C/Wet <sup>a</sup>
Peel ply	Dry 1 h @ 82°C	18.5	20.7	22.9	27.9
Peel ply/hand sand	Dry 1 h @ 82°C	17.4	20.1	29.9	29.1
Peel ply/grit blast	Dry 1 h @ 82°C	25.7	30.6	31.5	31.5

<sup>a</sup>Wet conditioning: 30 days at 71°C/100% RH.

TABLE VIB Secondary bonding of Ciba 6376 precured substrates with FM<sup>®</sup> 300-2 adhesive film. Effect of composite surface pretreatment on double cantilever beam testing [21]

Test	Composite surface preparation	Test results		
		-55°C	23°C	82°C/Wet
Hinged double cantilever test (MPa)	Peel ply	45.0	35.0	44.0
Crack energy (kg)	Peel ply/hand sand	45.5	39.0	47.9
Substrate dried 1 h @ 180 (MPa)	Peel ply/grit blast	73.6	49.0	80.4

Note: Wet conditioning: 30 days @ 71°C/100% RH.

ply followed by the grit blasting offers the best overall mechanical performance and the dry peel ply is the worst. The effect of the surface on the hinged double cantilever beam test for the Ciba 6376 prepreg is shown in Table VIB. These test results also show that grit blast in addition to peel ply provides the most durable bond. In the case of the Hercules 3501-6, there was no significant difference between the peel ply versus the peel ply/hand sand surface preparation. Either of these two surface preparations provided good performance under both the dry and the hot/wet conditions. The failure modes for most of the lap shear tests ranged from cohesive in the case of grit blast prepared substrates to mostly interfacial between the adhesive and the laminate for the peel plied surface preparation [21].

In the case of Hercules 8551-7 epoxy/glass and 8551-7 epoxy/graphite laminates the surface preparations included (a) solvent wipe only, (b) hand sanding/solvent wiping, and (c) sandblast/solvent wipe. No peel ply was used. Laminate layup was ( $\pm 45, \pm 90, 0$ )<sub>2</sub> for both the glass and the graphite substrates. Humidity exposures were carried out by exposing individual lap shear specimens to 30 days at 71°C/100% RH. Test results are shown in Table VII. The data on the secondary bonding of Hercules 8551-7/graphite laminates show that sand blast followed by solvent wiping provided the best overall strength in the bonded structure. Lap shear values from the hand sanded specimens were on an average 10–20% lower than the sand blasted specimens. The solvent wipe only was found to be the least effective method for surface preparation of Hercules 8551-7/graphite laminates. The failure modes for both solvent wipe as well as hand sanded surface preparations were predominantly adhesive to laminate, whereas for the sand blast prepared specimens, the failure mode was mostly laminate failure. The laminate failure was mostly in the top plies of the  $\pm 45^\circ$  layup.

However, in the case of Hercules 8551-7/glass precured laminates, it was more difficult to evaluate the effect of surface preparation on the lap shear strength. Due to the laminate lay-up, laminate failure was predominant failure mode for both sanded and sand blasted specimens. Both solvent wipe only and hand sanded specimens provided higher overall shear values as compared to the sand blasted specimens.

In conclusion, results from this study show that peel ply followed by grit blast provided the best overall durability of the bonded structure. Where it is not practical to grit blast, light hand sanding should be considered in addition to peel ply.

Harris and Beevers [52] have recently investigated the process of dry grit blasting to generate different levels of texture, simply by using different particle sizes of nominally similar alumina abrasive media. It was intended [52] that this should minimize variability, which might otherwise arise from the different surface treatment processes such as chemical effects during etching. Main aims of this investigation were to find reliable and reproducible methods of grit blasting and surface measurements. They used mild steel CR1 and aluminum alloy 5251 (i.e., metal-metal bonding). Three types of alumina oxide blasting media were used with



TABLE VII Effect of surface preparation on the LSS of FM 300-2 K, 390 gm/m<sup>2</sup> adhesive bonded precured Hercules 8551-7 laminates lap shear strength (MPa) [21]

Test temp.	Hercules 8551-7/ graphite	Failure modes	Hercules 8551-7/ glass	Failure modes	Surface preparation
-55°C	13	AL	0.8	AL	Solvent wipe only
24°C	19.6	AL	16.3	AL	
82°C	21.6	AL	19.0	AL	
82°C/Wet	15.1	AL	11.6	90% A, 10% C	
-55°C	18.2	AL	14.8	LF	Hand sand (320 grit sandpaper/solvent wipe
24°C	23.7	AL	17.9	LF	
82°C	25.6	AL	18.6	AL	Sand blast/solvent wipe
82°C/Wet	17.8	50% A, 50% C	12.8	90% A, 10% C	
-55°C	22.6	LF	12.7	LF	
24°C	27.5	LF	14.8	LF	
82°C	27.5	LF	14.7	LF	Sand blast/solvent wipe
82°C/Wet	19.9	50% A, 50% C	11.0	40% A, 60% C	

Note: Laminate: Hercules 8551-7 Uni-laminate ( $\pm 45$ ,  $\pm 90$ , 0)<sub>2</sub>.

Cure cycle: 1.7°C/min to 120°C, 60 min at 120°C, /28 MPa.

Failure modes: AL = Adhesive to laminate; C = Cohesive; LF = Laminate failure; A = Adhesive.

slightly different composition and shape. The two grit sizes used to vary the level of surface texture were sieve mesh numbers 180/220 and 60, having opening sizes of 71–92 and 250  $\mu\text{m}$ , respectively. Prior to grit blasting, the substrates were solvent wiped with MEK and after blasting, a jet of clean dry air was blown across the surface to remove loose grit particles and dust. Surface texture was measured using a non-contacting laser profilometer with a spot size of 1  $\mu\text{m}$  and a stand-off of 2 mm.

To measure the adhesion properties the single lap shear and tensile butt strength tests were used. The adhesive used to manufacture these joints was a two-part room temperature curing epoxy (Araldite 2011), which was cured in ambient conditions for 24 h and then subjected to a post curing process of 1 h at 60°C. The static contact angle data was generated using a Video Contact Angle (VCA) Analyser. The surface energy information was then calculated, in terms of dispersive and polar or non-dispersive components (see Equation 8), using the geometric mean equation combined with Young's equation (see Equation 4) [56].

Surface energy values for the polar and dispersive components for the liquids used in the calculations are given in Table VIII. Note that the contact angle measurements were made with di-ionised water and diiodomethane taking an average of twenty 20  $\mu\text{m}$  drops with each type of liquid.

The most intermediate effects of grit blasting are seen as changes in surface texture. The results of surface roughness analysis for different grits, based on 3D profilometry measurements, are shown in Table IX. This

TABLE VIII Surface energy components (i.e., dispersive and polar; according to Equation 8) of wetting liquids [52]

Liquid type	Surface energy (mJ/m <sup>2</sup> )		
	$\gamma_{LV}^d$	$\gamma_{LV}^p$	$\gamma_{LV}$
De-ionised water	21.8	51	72.8
Diiodomethane	49.5	1.3	50.8

table displays the average departure of the profile from the mean plane ( $R_a$ ), the root mean square of the average departure from the mean plane ( $R_q$ ) and Wenzel's roughness factor ( $r$ ), which is a ratio between the actual surface area and the geometric area. The observations confirm the expected relationships that the finer grit particles produced smoother surfaces and the aluminum alloy surfaces displayed higher levels of roughness than the mild steel when treated with the same size of grit.

The effect of the grit-blasting media on surface energy as calculated from static contact angle measurements is shown in Table X, along with the measured contact angle data. It can be seen that the Pink and White grits produced similar surface energy characteristics, but the Brown has a lower total surface energy with higher dispersive and lower polar components than the other grit types (see Fig. 6). The polar component also shows greater variation between the different surfaces than the dispersive. The effect of the surface roughness on surface energy for aluminum alloy is shown in Fig. 5, with the Pink and White grits the smoother surfaces exhibited higher surface energy readings than the 60 treated surfaces but with the Brown grit, surface energy values appear to be independent of roughness. Harris and Beevers [52] concluded that the mild steel treated substrates produced higher surface energies than the aluminum alloy, although these values of surface energy are significantly lower than values sometimes quoted for metals [203].

The analyses of the elemental composition of the surface before and after treatment for the mild steel and aluminum alloy substrates were also performed using the XPS (X-ray photoelectron spectroscopy) method in this work [52]. This analysis has shown that sodium (Na) is present on the White and Pink treated surfaces with both the mild steel and aluminum alloy substrates. On the mild steel, the Brown grit seems to have also introduced magnesium (Mg), in addition to aluminum (Al) from the alumina grit residues. The elemental concentrations of these residue contaminants appear to be dependent on the abrasive particle size, with the coarse grits generally resulting in lower concentrations. It can

TABLE IX Surface roughness results of the surface pretreated mild steel and aluminum alloys substrates using various grit blasting and solvent wiping [52]

Surface treatment	Surface roughness ( $\mu\text{m}$ )					
	Mild steel			Aluminum alloys		
	$R_a$	$R_q$	$r$	$R_a$	$R_q$	$R$
Solvent wiped	$1.2 \pm 0.1$	$1.4 \pm 0.0$	1.02	$0.4 \pm 0.0$	$0.6 \pm 0.0$	1.01
Brown 180/220	$1.3 \pm 0.1$	$1.7 \pm 0.1$	1.05	$1.7 \pm 0.0$	$2.2 \pm 0.0$	1.07
Brown 60	$3.4 \pm 0.3$	$4.5 \pm 0.4$	1.12	$5.1 \pm 0.1$	$6.7 \pm 0.1$	1.17
Pink 180/220	$1.3 \pm 0.1$	$1.7 \pm 0.2$	1.05	$1.8 \pm 0.1$	$2.3 \pm 0.2$	1.08
Pink 60	$3.2 \pm 0.2$	$4.3 \pm 0.3$	1.13	$5.1 \pm 0.5$	$7.0 \pm 0.8$	1.21
White 180/220	$1.3 \pm 0.0$	$1.7 \pm 0.1$	1.05	$1.7 \pm 0.1$	$2.2 \pm 0.1$	1.07
White 60	$3.0 \pm 0.1$	$4.0 \pm 0.2$	1.11	$4.9 \pm 0.2$	$6.5 \pm 0.2$	1.18

TABLE X Contact angle ( $\theta$ ) and surface energy data [dispersive ( $\gamma^d$ ), polar ( $\gamma^p$ ) components and total ( $\gamma^{\text{total}}$ )] for grit-blasted and solvent wiped surfaces for mild steel and aluminum alloy substrates [52]

Surface material	Surface treatment	Contact angle ( $^\circ$ )		Surface energy ( $\text{mJ/m}^2$ )		
		De-ionised water	Diiodomethane	$\gamma^d$	$\gamma^p$	$\gamma^{\text{total}}$
Mild steel	Solvent wiped	$68 \pm 5$	$37 \pm 7$	$36 \pm 4$	$10 \pm 3$	$46 \pm 3$
	Brown 180/220	$52 \pm 7$	$18 \pm 4$	$41 \pm 2$	$16 \pm 4$	$57 \pm 3$
	Brown 60	$61 \pm 4$	$21 \pm 4$	$41 \pm 2$	$11 \pm 2$	$52 \pm 2$
	Pink 180/220	$8 \pm 3$	$27 \pm 3$	$34 \pm 1$	$40 \pm 1$	$74 \pm 1$
	Pink 60	$28 \pm 4$	$30 \pm 3$	$34 \pm 1$	$34 \pm 1$	$68 \pm 2$
	White 180/220	$6 \pm 2$	$26 \pm 4$	$33 \pm 1$	$41 \pm 1$	$74 \pm 1$
	White 60	$34 \pm 10$	$25 \pm 3$	$36 \pm 2$	$29 \pm 6$	$65 \pm 5$
Aluminum alloy	Solvent wiped	$54 \pm 3$	$45 \pm 5$	$29 \pm 3$	$21 \pm 3$	$50 \pm 2$
	Brown 180/220	$76 \pm 4$	$33 \pm 3$	$39 \pm 2$	$5 \pm 2$	$44 \pm 1$
	Brown 60	$75 \pm 5$	$30 \pm 4$	$41 \pm 2$	$5 \pm 2$	$46 \pm 2$
	Pink 180/220	$34 \pm 3$	$31 \pm 3$	$34 \pm 1$	$30 \pm 2$	$64 \pm 2$
	Pink 60	$51 \pm 3$	$35 \pm 5$	$34 \pm 2$	$20 \pm 2$	$54 \pm 2$
	White 180/220	$28 \pm 6$	$30 \pm 3$	$34 \pm 1$	$34 \pm 3$	$68 \pm 3$
	White 60	$59 \pm 3$	$28 \pm 4$	$38 \pm 2$	$14 \pm 2$	$52 \pm 2$

also be noted that the appearance of Na and Mg on the surfaces after grit blasting correlates with the presence of these elements in the composition of the grit.

Harris and Beevers [52] determined the initial joint strengths of the bonded Pink treated surfaces for the lap shear and tensile butt configurations. They showed that the initial joint strengths were relatively independent of grit type (although the joints with grit-blasted surfaces were typically 50% higher than the solvent wiped surfaces). They therefore carried out joint durability tests in order to measure adhesion characteristics produced by different sizes of pink grit. Bonded lap and butt joints were immersed in de-ionised water at  $60^\circ\text{C}$  and tested at intervals up to 12 weeks. The results in Fig. 11 show that with mild steel substrates, the lap shear joints displayed no difference between the two surface textures. However, with the tensile butt joints the rougher surfaces showed a higher level of durability. As observed by Harris and Beevers [52], with the aluminum alloy, both the lap shear and butt joint configurations displayed the same characteristics with the smoother surfaces producing the higher level of strength retention. The failure modes of the lap shear joints were consistently 100% apparent adhesion failure by non-magnified visual inspection for both substrate materials. With the tensile butt joints, however, the failure increased from 30% apparent adhesion failure to 70% exposure for both the mild steel and aluminum alloy substrates.

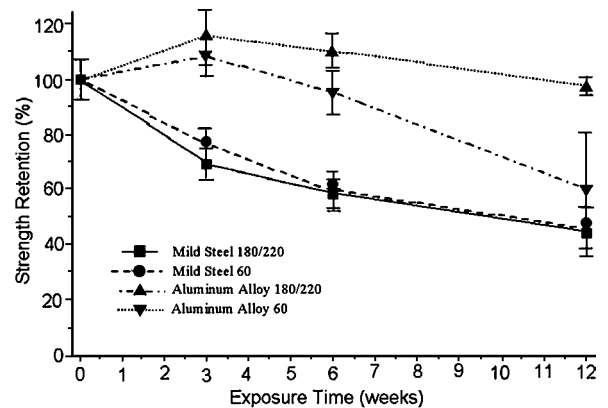


Figure 11 Effects of grit-blasting media on the strength retention characteristics of the lap shear joint durability for a mild steel and an aluminum alloy [52].

## 6.2. Effects of non-mechanical pretreatments on the bonding of metal-composite, metal-metal and polymer-polymer substrate systems

Molitor and Young [59] have recently investigated alternative techniques for bonding of a glass fiber reinforced composite structure to a titanium alloy (grade Ti-15-3) sheet metal component (i.e., metal-composite system bonding). This was an aerospace application where the bond would be subjected to cyclic loading in a hot moist

environment and furthermore exposed to de-icing fluids and cleaning agents. This work was conducted in two stages. Firstly, selected surface pretreatments for the titanium adherend were evaluated by 90° peel tests. For these tests, thin strips of flexible aluminum alloy (Al-2024-T3) were bonded to rigid strips of the titanium alloy using a phenolic-based film adhesive. The adhesive, recommended for metal/metal bonding, was only used for these screenings tests and was not used in the metal/composite bonding. The two best performing titanium surface treatments were then evaluated following exposure to a hot/humid environment.

Whereas in those tests, which investigated the environmental durability of the titanium/composite bonding, a number of parameters were varied as part of the study: (a) two types of glass fiber material were evaluated—a thermoset epoxy material and a thermoplastic material; (b) two film adhesives (approved for use in the aerospace industry) were used. The test specimens were manufactured in accordance with the standard BS EN 2243; Part 2: 1991 (Test methods for structural adhesives). The rigid adherend material was the titanium alloy Ti-15-3 [204]. In addition to Ti, the alloy also contains V (14–16%), Cr (2.5–3.5%), Al (2.5–3.5%), Sn (2.5–3.5%) as well as smaller percentages of O, N, C, H, and Fe. The flexible or “peeling” adherend was a thin strip of the aluminum alloy Al-2024-T3. The adherends were bonded with the phenolic-based film adhesive Redux 775 [2] at 150°C for 60 min in an autoclave at a pressure of 350 kPa. For these tests, a tensile loading rate of 70 mm/min was applied to the load cell and the peeling force recorded.

As a pretreatment the titanium alloy was degreased in methylthylketone (MEK) for 10 min and rinsed in distilled water. Table IVB gives the procedures for the six selected titanium surface treatments and their effects. Prior to adhesive bonding, the aluminum alloy was degreased with MEK, rinsed with distilled water and pickled in a chromic acid solution at 60–65°C for 30 min [59]. Following pickling, the material was rinsed in running water and dried. The peel force was recorded over a stripping length of 150 mm on the titanium surface. The average peel force was then determined over five intervals of 25 mm along this length and was expressed as N/25 mm. These results are given in Table XI. Based on the mean peel strengths given in Table XI, the best performing titanium surface treatments were: surface modification by Excimer laser (97N/25 mm), surface cleaning by Excimer laser (96 N/25 mm) and sodium hydroxide anodisation (SHA) (84 N/25 mm). Failure

TABLE XI 90° Peel test results for the surface pretreated titanium alloy using various surface preparation methods [59]

Surface treatment	Peel strength (N/25 mm)
Untreated	20
Surface modified by Excimer laser	97
Surface cleaned by Excimer laser	96
Plasma sprayed	60
Pasa Jell 1078	64
Sodium hydroxide anodization	84
Chromic acid anodization	54

in each case was mostly cohesive, thus indicating adequate titanium surface treatment. Surface modification by Excimer laser did yield peel strengths as high as 138 N/25 mm and as low as 78 N/25 mm. The difference between the two techniques was that surface modification was achieved at a fluence of 77 J/cm<sup>2</sup>. For this reason, surface cleaning of titanium by Excimer laser does offer an attractive industrial option if comparable peel strengths can be achieved at a significantly lower fluence than surface modification by the same laser.

In conclusion, while these surface treatments did produce good peel strengths, it was pointed out [59] that the same treatments might not produce durable bonds when exposed to a high/humid environment. In particular, the durability of Excimer laser treatments has not been well documented, and this technique may be outperformed by the traditionally durable chromic acid anodisation [65].

Lennon *et al.* [128] have investigated the effects of microwave plasma surface treatments of polyamides (PA) film, polyamide 12 (Orgasol® 2002D: PA 12) and polyamide 11 (Rilsen BD30: PA11 as substrates (i.e., polymer-polymer system), using the two surface pretreatment processes: the ammonia and nitrogen mixtures by changing the O/N mixtures and NH gases. Two epoxy adhesives were used in this study; an epoxy-anhydride system and an epoxy-amine system. In both cases, the epoxy prepolymer is a diglycidyl ether of bisphenol-A (DGEBA) of low molecular weight (DER 332). The anhydride hardener used is methyltetrahydrophthalic anhydride (MTHPA) with a polymerisation catalyst methylimidazole. These two adhesive systems were chosen [128] because they differ in their polymerisation mode, the functional groups present in the reactive systems and the ductibility of the networks (the MTHPA based network was more brittle than the Jeffamine based network at room temperature).

Lennon *et al.* [128] used two treatments (i.e., ammonia and nitrogen/oxygen mixtures) in the microwave plasma in order to investigate the wettability of polyamide films. They evaluated the effects of nitrogen, power and treatment time on the surface energy. As seen in Fig. 12 the improvement of the wettability

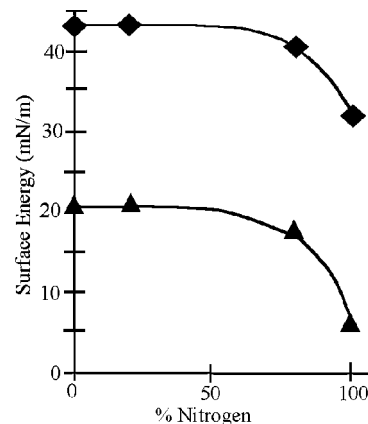


Figure 12 Effect of nitrogen % in the O/N plasma on the surface energy of the Polyamide 11 (i.e., PA 11) substrate film [128]: (a) polar component (▲) and (b) dispersive component (◆); Microwave plasma surface treatment conditions: power = 800 W, gas flow = 100 cm min, treatment time = 120 s.

depends not essentially on the quantity of oxygen in the mixture but simply on its presence. The surface energy (i.e., polar and dispersive components) does not change by treatment with nitrogen alone. Once oxygen is added, the wettability increases significantly with a reduction of the water contact angle on the PA11 from 75° to approximately 45°. However, there was not any difference between the wettability or the O/C ratios of the films treated in pure oxygen and those treated with the gas mixture. From the investigation of the plasma power and the treatment time on the surface energies of the polyamides 11 and 12 Lennon *et al.* [128] concluded that an improved level of wettability can be obtained for a 200 W treatment and raising the power does not amplify the effects, whereas the the surface energies show a rapid increase with treatment and the energies continue to rise between 100 and 360 s plasma exposure times. Whatever the power and the treatment time the two kinds of PA have similar behavior. The surface energy obtained after 360 s of treatment is over 60 mN/m compared to the value of 40 mN/m of the untreated films [128]. Optimal treatment conditions with respect to the wettability and the chemical composition of the surface can therefore be determined as 100 cm min, 200 W, 360 s, which can be used to evaluate the adhesion of the substrate [128].

They used also three mechanical tests for the adhesion measurements between the epoxy networks and the PA film covering a steel substrate; (a) pull-off, (b) three-point bending, and (c) lap-shear tests. For the pull-off test, an aluminum stud was adhesively bonded to the PA film substrate and a 4.9 N compression load applied to each stud. The three-point failure test was carried out according to the standard NFT 30010. The epoxy adhesive was used as a stiffener on the PA coated substrates (10 × 50 × 0.8 mm) with a contact surface of 5 × 25 mm. The ultimate load ( $F$ ), the ultimate displacement  $\Delta l$  and the subtended energy ( $W$ ) were used. The lap-shear test was carried out according to the standard NFT 76107. In all these three tests, after curing, the samples were left in an air-conditioned room (22°C, 50% RH) for 24 h before testing. The results using pull-off test on assembly constituted with O/N plasma treated PA and epoxy/anhydride reactive system are presented in Fig. 13. It can be seen that the O/N plasma treatment increases strongly the toughness of the PA/adhesive interface. The increase of rupture energy (by a factor of 5.4 for a treatment of 6 min and by a factor of 4 for a treatment of 4 min) is a much important as the O/C ratio increases [128]. This behavior is in agreement with other studies for PA [193, 197] and other polymers [205, 206].

The comparison with the NH plasma treatment was made with the optimum conditions, with the same exposure time (6 min) using the lap-shear test and the anhydride based system as adhesive. The results are presented in Fig. 14. Both plasma treatments principally lead to an increase of the non-dispersive component of the surface energy related for O/N treatments to the increase of the O/C ratio and for NH treatments to the introduction at the surface of nitrogen species.

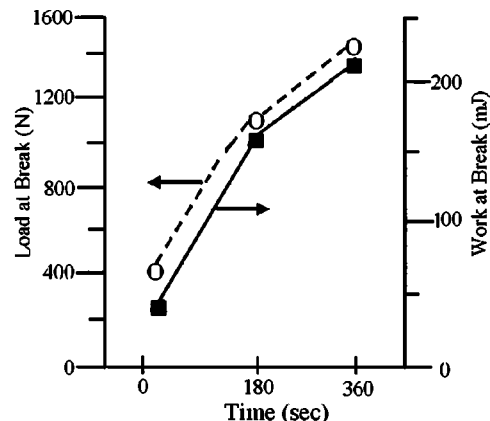


Figure 13 Effect [128] of surface pretreatment time on the pull-off test on the assembly constituted by O/N microwave plasma treated Orgasol 2002D and DGEB/MTHPA/MIA (O: load at break and ■: work at break).

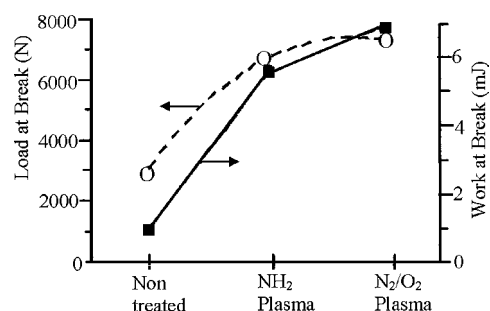


Figure 14 Influence of the nature of microwave plasma surface pretreatment on the adhesive properties of Orgasol 2002D/DGEB/MTHPA by lap shear test [128] (O: load at break; ■: work at break).

(b) gas flow, and (c) composition of the gas mixture in the case of O/N treatment has lead to determine optimal treatment conditions with respect to the wettability: for O/N, a composition 20–80%, a power of 200 W with a gas flow of 100 cm min during 180 s were chosen whereas for ammonia treatment the optimal conditions were 200 cm min—600 W—180 s.

In conclusion, after plasma treatment and whatever the gas used, a great increase of the adhesion properties was noticed whatever the epoxy reactive system. The propagation zone was located near the interface PA/primary adhesive showing clearly that the plasma treatment reinforces the PA/epoxy interface. As regards, the adhesion of the NH-plasma-treated films shows an important increase compared to the untreated samples that can be attributed to the introduction at the surface of nitrogen species (N/C goes from 0.09 to 0.15 after 6 min of treatment). These results are in good agreement with those of Wertheimer *et al.* [207], who show that load for crack propagation during peel test is slightly higher for N/O plasma treatment than with NH one in the case of aromatic polyamides. With the untreated Orgasol<sup>®</sup> 2002D, studied in three-point bending, both the initiation and propagation zone are located at the polyamide-epoxy interface. When the polyamide is plasma treated (both with NH or N/O) the crack initiation is again located at the interface PA/epoxy but, undoubtedly, the crack enters the polyamide film, near the interface PA/primary adhesive, showing clearly

that the plasma treatment reinforces the PA/epoxy interface.

Green *et al.* [153] have studied the effects of various surface pre-treatments on the polypropylene (PP) (monomer:  $\text{CH}_2 = \text{CH}-\text{CH}_3$ ) substrates (i.e., polymer-polymer substrate). Among the pre-treatment methods studied were corona discharge, flame, fluorination, low pressure vacuum plasma and atmospheric plasma were the most effective ones. It was found that all these five surface pretreatment methods showed the highest surface chemical modification of the pretreatments studied. It was identified that the surface chemistry, concentration depth and topography varied widely across the five pretreatments. However, all have been shown to have similar bond strength with polyurethane adhesives, indicating that a number of significant factors were responsible for bond strength. It is surmised that the depth of the functional group concentration is the determinant joint strength parameter and the O/C ratio or surface roughness.

Among the pretreatment methods studied, corona discharge, flame, fluorination, vacuum plasma and air plasma were found to increase surface oxygen content through the incorporation of oxygen groups into the near-surface region, whilst all other pretreatments were found to have incorporated no additional oxygen into the surface layer (see Table XII). Corona was found to incorporate the least amount of oxygen (6.69 at%) into the surface of the 5 pre-treatments, whilst vacuum plasma induced the most (12.99 at%), following the trend from left to right of decreasing oxygen content has been observed:

Vacuum plasma > air plasma > fluorination > flame  
> corona discharge.

It was found that pre-treatments, which physically modified the surface leading to an initial contact angle of less than  $60^\circ$ , gave an increased O/C ratio. It was noted that within the high-resolution carbon spectra, significant peak broadening occurred for substrates with a contact angle less than  $60^\circ$ . This significant peak broadening is due to multiple types of functional groups being present on the surface. Corona discharge and flame surface pre-

TABLE XII Effects of various surface pretreatment methods on the surface chemistry modifications (i.e., changes of C, N, O, Si, F, and O:C ratio) of homopolymer polypropylene, HF 135 M [153]

Pre-treatment	C (at.%)	N (at.%)	O (at.%)	Si (at.%)	F (at.%)	O:C
None	99	0	0.5	0.5	0	0.005
Corona	93.16	0	6.69	0.15	0	0.072
Flame	91.75	0	7.58	0.51	0	0.083
Fluorination	79.1	0	10.3	0	10.24	0.130
Vacuum plasma	84.549	2.46	12.99	0	0	0.154
Air plasma	87	0.84	12.16	0	0	0.140
0.025% MA	100	0	0	0	0	0.000
0.05% MA	100	0	0	0	0	0.000
Proprietary coating	99.1	0	0.9	0	0	0.009
IR laser	98.1	0	1.9	0	0	0.019
Ag(II)	97.2	0	2.7	0	0	0.028

TABLE XIII Roughness values for corona discharge, flame, fluorination, vacuum plasma and air plasma pretreatments for homopolymer polypropylene, HF 135 M [153]

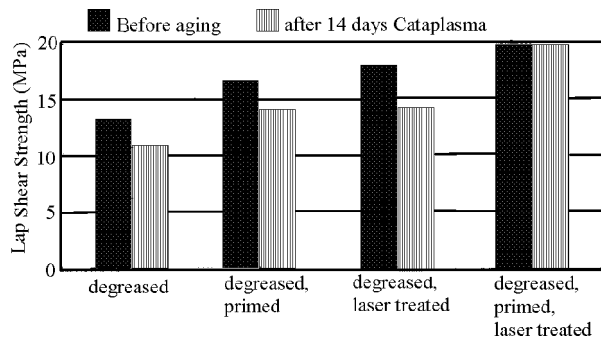
Pretreatment	$R_A$ (nm)
Corona discharge	1.325
Flame fluorination	1.173
Vacuum plasma	0.616
Air plasma	1.201

treatments have been found to incorporate oxygen functional groups into the surface. Vacuum plasma and air plasma have been found to include both oxygen and nitrogen functional groups. Similarly, the fluorination-treated PP spectra were found to contain both oxygen and fluorine functional groups.

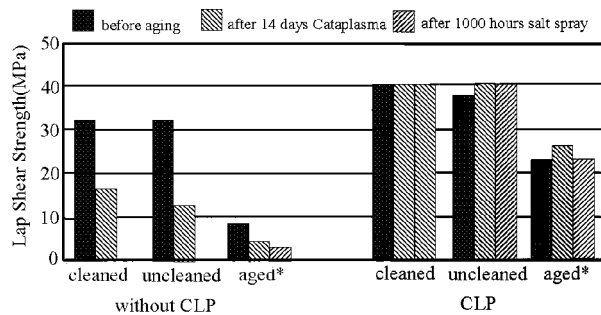
Using the AFM (atomic force microscopy) microscopy the characteristics of surface topography of the substrate was studied following the pre-treatment. The roughness values of pre-treated surfaces for various methods are presented in Table XIII. All the pretreatment methods (i.e., corona, flame, vacuum plasma and air plasma all involved most oxidised surfaces) examined were found to increase roughness above that of the original “atomically smooth surface” moulded up cleaved mica. The roughness was described by the  $R_A$  value, which is the ratio of the actual surface length to the surface length of a smooth surface. The  $R_A$  value is an arithmetic mean of the absolute value of the departures of the profile from the mean line and is often quoted as an engineering measurement of surface roughness. Corona discharge was found to produce a very microrough surface with features and nodules around 100 nm in diameter. Flame treatment was found to create a “macrorough” surface. Fluorination was found to only roughen the surface in a very microrough manner with large domed nodules creating a dimpled surface. Vacuum plasma was found to create an extremely heterogeneous surface with a very high surface density of equally sized and spaced microfine nodules. Air plasma was found to induce a “micro-rough” surface with features of  $\sim 80$  nm diameter.

To evaluate the effects of various surface pretreatments mentioned in (Table XII) the maximum lap shear strength of the treated substrates bonded using polyurethane adhesive was measured. Of all the surface pretreatments examined it was found that corona discharge, flame, fluorination, O and N vacuum plasma and Agrodyn<sup>TM</sup> atmospheric (air) plasma were the most effective at chemically modifying surface. It was noted that the silver electrolysis pretreatment caused little surface pretreatment effect, which is contrary to findings of Brewis *et al.* [200]. Green *et al.* [153] concluded that the bond strength increases can be correlated to the successful increase in O:C ratio of the surface chemistry.

Broad *et al.* [151] have investigated the effects of the Ciba laser pretreatment (CLP) process on the joint performance of the aluminum and titanium alloys, and stainless steel (i.e., metal-metal substrate). Fig. 15a shows that using CLP pretreatment process, better joint strengths with fully cohesive failure modes were achieved before and after aging for the aluminum alloy



(a)



(b)

Figure 15 Comparison [151] of the Ciba laser pretreatment (CLP) method with other surface preparation techniques using the lap shear strength of various substrates joints: (a) an aluminum alloy substrates joint with with 2-component epoxy adhesive before aging and after 14 days Cataplasma and (b) an aluminum alloy substrate (contaminated surface).

substrate. The “degreased only” specimens break at considerably lower strength levels and with adhesion failure. By applying primer alone or treating solely with a laser, the joining characteristics have improved; however, the joints still fail by adhesion failure after ageing. Only the combination of primer application and laser treatment leads to such a strengthening of the adhesion forces between the aluminum surface and the adhesive to give high joint strengths with cohesive failure modes before and after ageing. As shown in Fig. 15b, the CLP did not necessarily require cleaned surfaces prior to surface pretreatment. The better durable adhesively bonded joints can also be achieved for other metallic alloys (i.e., stainless steel and titanium alloy) using the CLP process [151]. Whereas without application of CLP the majority of specimens showed the failure modes even for the uncleaned and artificially aged surfaces of the alloys mentioned above, in all cases to cohesive failure [151]. It was claimed [151] that the CLP is applicable in combination with various adhesive types, i.e., one- or two-component epoxy adhesives as well as polyurethane adhesives and sealants.

Broad *et al.* [151] have also performed the Stress-humidity testing on the adhesive bonding using the CLP process. In this test, small lap shear specimens were subjected to cyclic elevated temperatures at 100% relative humidity and a mechanical load of 5 MPa. The demands on the adhesive were increased by the three holes drilled into the overlap area, thereby drastically reducing to a minimum the distance for diffusion of moisture into all areas of the joint; note that this test specimen is made of aluminum bonded by the one-

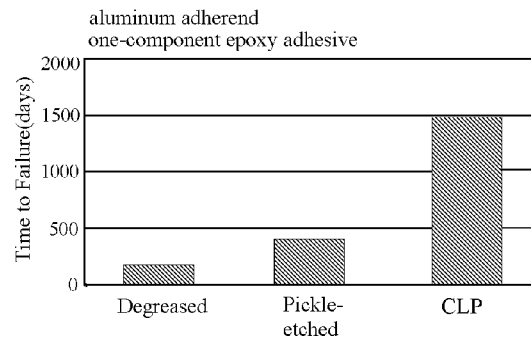


Figure 16 Test results [151] showing comparison of the time to failure (at the creep conditions of 5 MPa and between the test temperatures of 42–48°C under the 100% relative humidity) of the CLP method with the degreased and pickle-etched surface preparation processes, indicating that the joints produced with the CLP method differ greatly from those simply degreased or pickle-etched.

component epoxy adhesive. The test criterion was the duration until breaking of the specimens. Even under these demanding test conditions the joints produced with CLP differ greatly from those simply degreased or even pickle-etched (see Fig. 16). Despite using a structural adhesive, the joints on aluminum surfaces that have been degreased alone failed after only 90 days. A higher durability of 350 days was achieved with a wet process (i.e., pickle-etching). This suggests an evidence for the effectiveness of CLP to achieve adhesively bonded joints with good durability [151].

## 7. Factors affecting the durability of adhesively bonded joints

As pointed out by Davis and Bond [152], the formation of a suitable surface chemistry is the most important step in the surface preparation process because the integrity of this surface directly influences the durability of the adhesive bond. To study the ability of surface pretreatments to promote adhesion and to protect the surface against corrosion, it is usually necessary to run accelerated aging test to differentiate the surface treatment quality. Aging tests run under normal conditions of temperature and humidity after the curing of the adhesive may not provide results allowing a clear ranking of different surface pretreatments adhesion promoter, and anti-corrosion protector abilities. To do so, adhesively bonded samples have to be exposed to severe conditions of temperature and humidity. As pointed out by Lapique and Redford [208], when aging tests are run to evaluate the quality of surface pretreatments, changes in the mechanical properties of the adhesive should also be taken into account. They may affect the stress transfer from the adhesive layer to the interface and modify the results of the mechanical testing. In order to analyze correctly such experiments, the behavior of the adhesive should be studied under aging test conditions. Lapique and Redford [208] have recently studied such an aging test (40°C in water vapor) on the Araldite 2014 epoxy adhesive samples and the adhesive properties recorded over a period of 36 days. Araldite 2014 is an adhesive paste that can be cured at room temperature. This can be important in commercial applications where the substrates to be joint

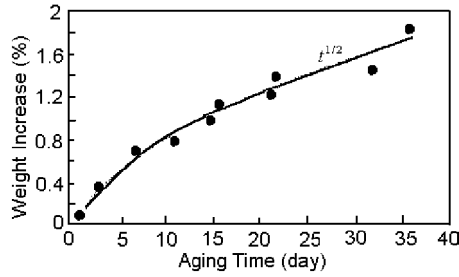


Figure 17 Weight increase versus aging time during aging test for samples with a thickness of 1.5 mm. The weight increase follows a  $t^{1/2}$  law [208].

do not tolerate high temperature. As seen in Fig. 17, the measurement of the weight of the samples shows a weight increase due to an increasing water content in the epoxy with the exposure time. The weight increases with the square root of time in agreement with the standard Fickian diffusion. According to Fig. 17 the water diffusion continues even after 36 days and no equilibrium state is reached during that period of time. Water works usually as plasticizer leading to a softening of the material. This is also the case for the epoxy adhesive Araldite 2014. Fig. 18 shows how the mechanical properties (stress at break, E-modulus) and deformation at break) are affected by the exposure time and thus by water content. As Lapique and Redford [208] concluded, the E-modulus and the stress at break are lowered while the deformation at break and the plastic contribution to the total deformation are increased with increasing aging time.

Some form of substrate pretreatment is always necessary to achieve a satisfactory level of bond strength. In order to obtain a strong and stable bond between a substrate (such as a metal) and the adhesive, the naturally formed surface oxide on metal has to be removed and replaced with a new, continuous, solid and corrosion resistant oxide layer during such a surface pretreatment process. Almost all treatment methods do bring some degree of change in surface roughness but grit-blasting is usually considered as one of the most effective methods to control the desired level of surface roughness and joint strength [73]. Grit-blasting does not only remove weak boundary layers but can also alter the chemical characteristics of the adherends [52, 70].

Shahid and Hashim [73] have studied the effects of surface roughness on the cleavage strength of a mild

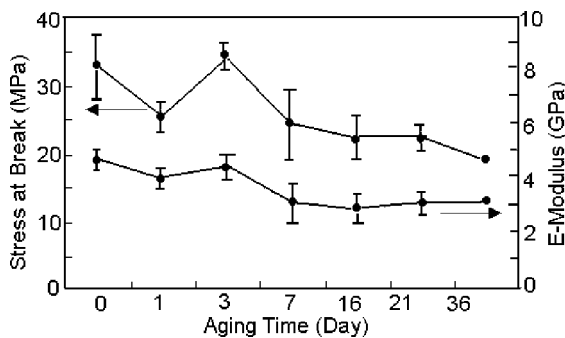


Figure 18 Mechanical properties (i.e., stress at break, E-modulus) during aging test measured in tension. Each point is the average of measurements performed on five samples [208].

TABLE XIV Surface roughness for a mild steel (i.e., BS4360 grade 43A) using various grit-blasting grades, and polished surface [73]

Surface finish	Average roughness ( $\mu\text{m}$ )	Average profile length ( $\mu\text{m}$ )	Average root mean square slope ( $^\circ$ )
	$R_a$	$R_{lo}$	$R_{dq}$
Grit-blasted surface			
120/180	$0.98 \pm 0.05$	$13.44 \pm 0.01$	$12.52 \pm 0.59$
40/60	$2.97 \pm 0.18$	$13.69 \pm 0.04$	$22.70 \pm 0.56$
30/40	$4.23 \pm 0.25$	$13.84 \pm 0.04$	$24.24 \pm 0.89$
24/30	$6.31 \pm 0.28$	$13.95 \pm 0.07$	$25.96 \pm 0.82$
Polished surface	$0.04 \pm 0.02$	$12.79 \pm 0.01$	$0.13 \pm 0.02$

steel specimens using the diamond polishing and grit-blasting with four different sizes (i.e., 120/180, 40/60, 30/40 and 34/30 mesh) of alumina grit. The material used in this study were mild steel to British Standard BS4360 grade 43A as substrate and structural epoxy adhesive, Araldite 420A/B (Redux 420A/B). After pretreatment, the surface roughness of adherends, measured as average roughness  $R_a$ , linear profile length  $R_{lo}$ , and root mean square slope ( $^\circ$ )  $R_{dq}$  values are presented [73] in Table XIV. Note that  $R_{lo}$ , and  $R_{dq}$  parameters were defined according to the standards ISO 4287 (1984) and ISO 4287 (1997), respectively. Fig. 19 shows the relationship between the average cleavage strength and the  $R_a$  values of the adherend surfaces. It can be seen that the cleavage strength appears to increase linearly with the  $R_a$  value. As suggested by Shahid and Hashim [73], the increase in cleavage strength may be attributed to an increase in surface area by forming of mini scarf joints on adherend surfaces at micro level. This finding is consistent with that of Sargent [209]. However, Harris and Beevers [52], They *et al.* [210] and Critlow and Brewis [65] found no appreciable change in joint strength with increasing adherend surface roughness by mechanical treatment. These contrasting findings may be due to the fact that each researcher used different set of adherend, adhesive and joint geometry [73]. Moreover, the overall effect of grit blasting is not limited to the removal of contamination or to an increase in surface area. This also relates to changes in the surface chemistry of adherends [52, 70] and to inherent drawbacks of surface roughness, such as void formations and reduced wetting [211].  $R_{lo}^2$  was considered as a measure of the effective surface area available for bonding. These values were then compared with cleavage strengths as shown in Fig. 20. It

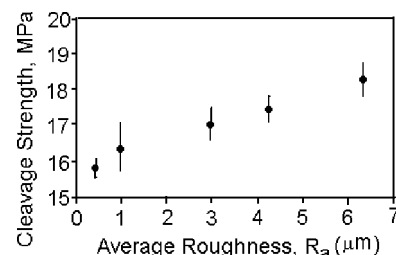


Figure 19 Graph showing variation of cleavage strength with average roughness,  $R_a$  [73].

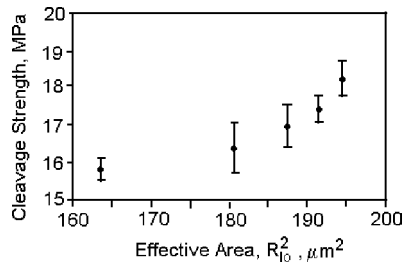


Figure 20 Variation of cleavage strength with effective area of bonding (experimental results) [73].

can be seen that the cleavage strength increases as the effective surface area increases. It is, however, realistic to believe that this increase in strength combined with an increase in surface area shall be limited by bulk adhesive strength, i.e., until failure becomes cohesive within the adhesive [73]. Shahid and Hashim [73] have also observed that the specimen prepared by grit-blasting steel adherends with coarser grit have shown significantly higher crazing (stress whitening zones due to micro-cracking) in the initial area of the joint compared to those prepared with the finer grit. In both cases, however, failure was near the interface region and apparently in a mixed adhesion/cohesion mode.

Bockenheimer *et al.* [212] have studied the effects of blasting with alumina grit or with glass beads on the topography of an aluminum alloy +3% Mg substrate. These two pretreatment methods has changed the topography and chemical state of the aluminum surface. Unexpectedly, after surface pretreatment the oxide was not in all cases  $\text{Al}_2\text{O}_3$ .  $\text{Al}_2\text{O}_3$  was only found for the etched surface, whereas  $\text{Al}_2\text{O}_{2.87}$  and  $\text{Al}_2\text{O}_{1.3}$  were found 1 day after blasting with glass beads and alumina grit, respectively. Hence, not all Al atoms possess their maximum degree of oxidation (+3) in the blasted surfaces. These aluminum atoms are expected to be very reactive due to their deficit of electron density. Therefore, it was concluded [212] that the effect of mechanical treatment for aluminum bonding is very complex and comprises topological changes and changes in the chemical surface state of the adherends. Also, the pretreated surface not only influenced the formation the

network structure in the near-interphase region but also far from the substrate.

The pretreatment of the aluminum substrate is essential in order to prevent or hinder the deterioration of the mechanical performance of the joints as a result of exposure to a wet and corrosive environment [136, 213]. Degradation of adhesive joints is associated with diffusion of water to the adhesive/substrate interface causing hydration of the oxide conversion coating and loss of adhesive strength. A moderate temperature increase, which in the absence of water does not have an adverse effect on a structural joint, leads to a much more pronounced loss in strength. Presence of chloride ions is further expected to accelerate the loss of adhesion, e.g., by propagation of localized corrosion of the metal beneath the adhesive [228].

Lunder *et al.* [214] have recently investigated the effects of various surface pretreatment methods on the surface characteristics and durability of adhesive bonded AA6060-T6 aluminum alloy joints (see Table XV for various surface pretreatment methods applied in this study). Aging of the lap joints was performed by exposure for 50 days in climate chamber at 82% RH and 40°C, corresponding to standard conditions employed in filiform corrosion testing (DIN EN 3665). Table XV also gives the oxide film thickness occurred as a results of these pretreatments. As expected, these films are considerably thinner than the AC anodized films, particularly the ones given a final acid etch. Fig. 21 shows the tensile test results (i.e., in terms of maximum load) of the lap joints. The results show hardly any degradation of hot AC anodized (pretreatments 1 and 2) and FPL etched (pretreatment 7) specimens as a result of the climate chamber exposure. A significant reduction in joint strength was observed for the alkaline etched specimens (pretreatment 3), and the relative strength loss was further increased when specimens were desmuted after alkaline etching (pretreatments 4 and 5). Application of the phosphate-permanganate conversion coating (pretreatment 6) after alkaline etching results in still poorer results, both in terms of initial strength and degree of degradation. The analysis of specimen surfaces has shown that the alkaline etched surface exhibits a mixture of Al and

TABLE XV Various surface pretreatment applied on the AA6060-T6 aluminum alloy. This table also shows the metal removal by these pretreatment methods and approximate thickness conversion oxide films based on gravimetric measurements [214]

Pretreatment	Metal removal ( $\mu\text{m}$ )	Oxide thickness ( $\mu\text{m}$ )
1. AC Anodizing of the as-received extrusion in hot (80°C) 15% sulphuric acid at a current density of 10 A/dm <sup>2</sup> (rms) for 4 s, rinsing under tap then distilled water, and draying in hot air.	0.08	0.10
2. As pretreatment 1, but with anodizing time of 12 s.	0.24	0.22
3. Degreasing in acetone, then etching in 10 wt% NaOH solution for 50 s at 60°C, rinsing under tap then distilled water, and air drying.	5	0.01
4. As pretreatment 3, but with a 15 s de-smutting in concentrated nitric acid following alkaline etch.	5	0.002
5. As pretreatment 3, but with a 15 s de-smutting in 15% sulphuric acid + 2 vol% nitric acid following the alkaline etch.	5	0.002
6. Pretreatment 3 followed by conversion coating in phosphatepermanganate solution (100 g/l $\text{NaH}_2\text{PO}_4$ , 30 g/l $\text{KMnO}_4$ and 0.5 g/l NaF adjusted to PH2 with sulphuric) for air drying.	5	0.02
7. FPL etch pretreatment; degreasing in acetone, hot water rinse, immersion in FPL etch solution (16.3 vol% $\text{H}_2\text{SO}_4$ , 6 wt% $\text{Na}_2\text{Cr}_2\text{O}_7$ ) for 20 min at 60°C, 20 min rinse under tap water, drying with hot air stream.	1	0.004



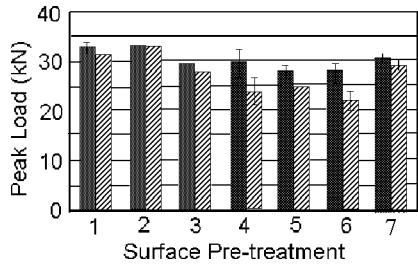


Figure 21 Tensile test results obtained for adhesive bonded AA6060-T6 single lap joints before and after exposure in climate chamber (82% RH, 40°C, 50 days). Error bars indicate standard deviation for three replicate specimens [214]. ■: Reference specimens and ▨: After corrosion testing.

Mg, which are removed by desmutting. It was suggested [136, 215–217] that a high MgO concentration in the oxide layer is unfavorable for the bond durability. Whether Mg is present as an oxide or a hydroxide is probably of significance. As pointed out by Lunder *et al.* [214], the Mg enriched oxide formed as a result of heat treatment may be more susceptible to hydration and subsequent delamination than the Mg rich hydroxide formed as a result of alkaline etching. However, presence of Mg oxide in the aluminum oxide film is expected to improve the stability in alkaline environment due to the fact that Mg oxides are thermodynamically passive at high pH [214]. Fig. 22 shows a correlation between the joint strength after corrosion testing and the extent of cohesive failure. As might be expected, these results indicate a higher degree of adhesive failure for the inferior pretreatments. Furthermore, the degree of adhesive failure is generally increased on all variants as a result of environmental exposure, also on the AC anodized joints (pretreatment 2) where a negligible strength loss was observed.

In summary, pretreatment of the AA6060 material by alkaline etching in hot NaOH solution resulted in the formation of a scalloped surface with a Mg enriched hydroxide film. A significant reduction in joint strength of about 7% was observed for the specimens as a result of corrosion testing. Desmutting in nitric or sulphuric acid to remove the Mg enriched hydroxide film resulted in still higher losses in strength. Application of a phosphate-permanganate conversion coating to the alkaline etched substrate also had no beneficial effect. However, all pretreatments employed are superior to acetone degreasing alone.

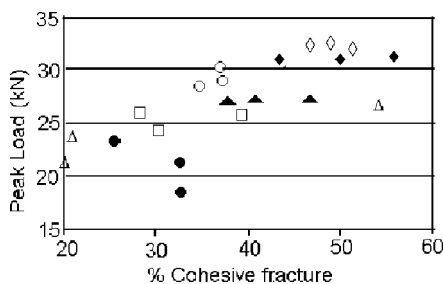


Figure 22 Correlation between (apparent) mode of fracture and peak load during tensile testing of corroded lap joints [214]. ◆: Hot AC anodized (4 s), ◇: Hot AC anodized (12 s), ▲: NaOH etched, △: NaOH etch + HNO<sub>3</sub> desmut, □: NaOH etch + H<sub>2</sub>SO<sub>4</sub> desmut, ●: Phosphate permanganate, and ○: FPL etched.

Surface contamination is a widespread problem in the adhesive bonding of some parts such as micro-assemblies, and therefore calls for a convenient method to assess the cleanliness of the adherends before introducing the adhesive to the microsystem. As pointed out by Woerdeman *et al.* [112], surface cleaning or preparation by means of solvents is the most common process step in many electronic manufacturing operations. Understanding the link between surface preparation and adhesion can lead to a reduction in the time required for development and testing of cleaning procedures. It can also lead to improved bondlines and enhanced manufacturability, enabling product realization for encapsulated components [112]. Molecular modeling has been employed to elucidate the behavior of a low molecular weight contaminant near an interface between a polymer adhesive and a substrate (see for example references [218–221]). Depending on the substrate-polymer and polymer-polymer interactions, as well as the molecular architecture of the contaminant and polymer, the contaminant can preferentially diffuse toward the interface [222]. When this happens, the contaminant molecules will displace the polymer from the interface, as illustrated in Fig. 23, resulting in a degradation of the adhesive bond strength [223]. Another molecular modeling has also been undertaken by Shanahan [224] to examine the role of diffusion in the wetting of a contaminated surface. Results of modeling indicate that a thin layer of a second liquid present on the substrate (the contaminant) can penetrate the sessile drop of liquid deposited on the solid surface and gradually change the effective interfacial free energy between the substrate and the drop [224].

Davis and Bond [152] have investigated the factors affecting the durability problem for the adhesively bonded structural joints using the “clean surface concept” approach. Most adhesive bond failures can be attributed to poor processes during fabrication, with lack of quality surface preparation being the most significant deficiency [152]. The best joint design in the world will not be durable if the surface preparation is inadequate. The influence of pretreatment surface conditions on the short- and long-term strength of adhesive bonds are presented in Table XVI. Short term strength is relatively easy to obtain with minimal surface preparation. If a simple lap shear test (ASTM D1002) is undertaken shortly after completion of the bonding process, acceptable lap-shear strengths can be obtained

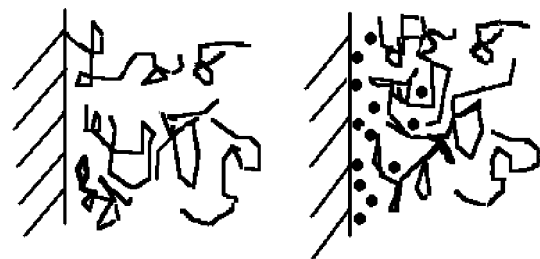


Figure 23 Schematic of a polymer adhesive/substrate interface in the absence (left) and presence (right) of surface contamination. In the latter case, the contaminant molecules can displace the polymer from the interface resulting in a degradation of the adhesive bond strength [112].

TABLE XVI The influence of surface condition on the short- and long-term strength of adhesive bonds [152]

Condition	Short-term effect	Long-term effect
(a) Contaminated surface	– Chemical reactions are inhibited – Bonds are weak	– Weak bond which fails soon after manufacture
(b) Clean surface without hydration resistance	– Short-term bonds are strong	– Gradual degradation leads to interfacial failure, – The joint strength will decay to zero.
(c) Clean and chemically active surface with hydration resistance	– Short-term bonds are strong	– Bond maintains integrity through its service life.

even with minimal preparation. However, long-term bond strength depends on the resistance of the chemical bonds to degradation over time. In many cases, poorly prepared metallic surfaces are due to hydrated oxides which displace the chemical bonds between the adhesive and the surface [152]. The consequence being that the adhesive bond fails along the interface some time after fabrication (adhesion failure).

As Woerdeman *et al.* [112] pointed out, surface analysis techniques, such as X-ray photoelectron Spectroscopy, Auger Spectroscopy, and secondary ion mass spectroscopy, are routinely employed to characterize surface properties of substrates, however these ultra-high vacuum techniques are not practical for probing liquid contaminants. However, the JKR contact mechanics technique has a number of unique advantages for examining microscale areas in a processing environment, as it is relatively inexpensive, versatile, easy to operate, and can be operated in ambient conditions [115].

Woerdeman *et al.* [112] have used the JKR method as a means to assess the level of contamination at an epoxy/aluminum oxide interface (see Section 3.4 for detail about this method). The aim of this study was to demonstrate the feasibility of the JKR contact mechanics for probing organic contamination on metal substrates. This was achieved by conducting JKR experiments in the presence and absence of an organic contaminant. The model contaminant was hexadecane, a non-polar hydrocarbon fluid of medium molecular weight. The hexadecane was chosen because it replicates typical machining fluids, is non-reactive with aluminum oxide surfaces, and should not readily dissolve into the adhesive system of interest. This was accomplished by measuring the interactions between an epoxy probe and aluminized substrate, both in the presence and absence of hexadecane surface contamination. Woerdeman *et al.* [112] performed JKR loading and unloading experiments, and of particular interest was the extent of adhesion hysteresis that resulted upon bringing the epoxy hemisphere into contact with the substrate. To be able to readily compare levels of contamination on samples of interest, they devised a scheme to extract the information embedded in the adhesion hysteresis curves in a quantitative fashion. Notwithstanding the specific interactions that have evolved inside the contact zone, the area under the unloading curve will depend upon parameters such as the maximum load achieved in the loading experiment ( $P_{\max}$ ), as well as the bulk modulus of the lens,  $K$ . With this in mind,

the adhesion energy is computed by first subtracting the area under the loading curve from the area under the unloading curve, which in this particular case, was fitted to two lines, as illustrated in Fig. 8 in reference [112]. This quantity,  $H'$ , is calculated using Equation 3 in reference [112].  $H'$  is subsequently normalized with respect to a normalization factor,  $N$ , where

$$N = P_{\max} a_{\max}^3 \quad (20)$$

giving rise to a newly defined “adhesion hysteresis parameter,”  $H$ , where

$$H = \frac{H'}{N} \quad (21)$$

Calculations of  $H$  are presented in Table XVII. Two replicate runs were made for the clean aluminum surface with the low modulus epoxy lens. These two values are very close to each other and very different from the value obtained on the contaminated surface. And with both epoxy systems,  $H$  was found to be a factor of two or three lower in the presence of the contaminant as opposed to when the contaminant was absent from the surface. With this quantitative distinction between “clean” and “contaminated” substrates, one could empirically determine the cutoff point for  $H(H_c)$ , below which the bond strength would be adversely affected in a given application. Success of this method hinges on the fact that the surface energy difference between the epoxy elastomer and the model contaminant is large; namely, the surface energy of amino-cured epoxide is 46.2 mJ/m<sup>2</sup> [225].

TABLE XVII Values of adhesion hysteresis parameter  $H$  for the interactions between a diglycidyl epoxy elastomer and an aluminum oxide substrate using the JKR contact mechanics approach [112]. Note that surface cleanliness can be estimated quantitatively by using the adhesion hysteresis parameter,  $H$

Epoxy elastomer	Air-plasma-cleaned aluminum	Hexadecane-contaminated aluminum
DER331/ED-900 epoxy: High Modulus system ( $K = 9$ MPa, from JKR theory)	1.17	0.383
DER332/ED-2003 epoxy: Low Modulus system ( $K = 3$ MPa, from JKR theory)	1.68, 1.73	0.867

Therefore, it is concluded that the JKR contact mechanics can be used to detect the trace amounts of surface contamination. This approach capitalizes on the difference in surface energy between the epoxy probe and organic contaminant. Using this approach, surface cleanliness can be estimated quantitatively by computing an adhesion hysteresis parameter,  $H$ , defined in this approach.

Hart-Smith [17] has investigated the surface assessment in bonded, co-bonded, and co-cured composite structures. As underlined in previous sections, the contamination prior to bonding is not merely an issue of cleanliness, but one of the reactivity and surface energy which relates to the wettability. Mahoney [226] has studied this problem. Surface contamination may cause insufficient wetting by the adhesive in the liquid state for the creating of a durable bond [17]. But these contaminants are not the only cause of such a condition. For example, composite laminates cured against an inert (inactive) surface are far harder for adhesives to wet than are the underlying surfaces exposed by abrasion. The nature of the adhesive also has an effect on the bond strength. It was observed that a composite peel-ply surface, to which one epoxy film adhesive does appear to bond securely if cured at 177°C, is not even wet by a room-temperature curing paste adhesive [17]. One reason for this is that the hot-bond adhesive becomes fluid during cure, while the paste adhesive maintains a high viscosity. The paste adhesive, when it is separated prematurely under a shear load, was embossed by a perfect replicate of every filament in the peel ply surface to which it had refused to bond. The hot bonded structures, on the other hand, had been used without failure for years. Studying the wettability problem, Schliekelmann [227] pointed out that it is necessary that the surface tension of the liquid adhesive should be lower than the critical surface tension of the adherend. He cited a four fold reduction in the adhesive energy (work of adhesion) of carbon-epoxy laminates due to the presence of water, explaining thereby why it is then so much more difficult for adhesives to bond than when everything is dry. He concluded [227] that the reliable surface pretreatment is abrasion of the CFRP composite surface by some means of sanding or (fine grit) blasting, citing evidence that this was recognized as long ago as 1976 [228].

A detailed study of the effects of grit blasting with different alumina grits on the surface characteristics of a mild steel and an aluminum alloy substrates by Harris and Beevers [52] has shown that in terms of surface energy the different sizes of Brown grit had no effect but with the Pink and White grits the large grit sizes generated surfaces with lower polar surface energy components and these changes correlated with a reduction in the Na presence in the surface chemical analysis. It was observed [52] that the durability response observed with mild steel substrates were evident from the tensile butt joint tests, which indicated that the surfaces produced by the coarser grit gave higher durability. This trend would be expected from a consideration of work of adhesion equations (see Section 3.3) (see for example [136, 225]), which suggest that the bonds on high polar energy surfaces would be more

sensitive to displacement by diffused water. Thus the rougher surfaces with high Na and polar surface energy values would exhibit more rapid degradation. The inability of the lap shear durability tests to detect these changes may be due to the lower sensitivity of the test method reported by Beevers [229]. Although the aluminum alloy exhibited similar changes in the surface energy and surface chemistry, the responses from the durability tests were opposite to those observed with mild steel, as reported by Harris and Beevers [52]. This may be due to the different degradation mechanisms between two substrates [52]. It is commonly observed that when bonded joints of aluminum alloy are exposed to hot, wet environments, loss of strength results from hydrolysis of the oxide layer rather than through thermodynamic displacement as in the case of mild steel. As Harris and Beevers suggested, It is possible that the surfaces formed by the coarser grit may result in a less stable oxide layer and/or a more rapid route for moisture ingress is created by the surface texture characteristics, for example, by capillary channeling.

Green *et al.* [153] have studied the effects of 13 surface pre-treatments (see Table XII) on the homopolymer polypropylene (PP) (monomer:  $\text{CH}_2 = \text{CH}-\text{CH}_3$ ) substrates using surface chemistry, topography and the lap shear test. It was reported that the adhesive bond strengths of these pretreatments varied widely following a similar pattern to that shown by the O:C ratios (see Table XII). The most effective pretreatments, based on joint strength, namely, corona, flame, fluorination, vacuum plasma and air plasma all showed both large increases in surface chemistry in the form of oxygen take-up and bond strengths, respectively. It was also found that the bond strength was not related to the surface topography of the pretreated samples, with both smooth and roughened surfaces creating joints having similar strength (see also Table XIII). It is therefore concluded from this that the micro-roughening effects of these pretreatments have little effect on adhesion of the joints especially with viscous adhesives such as polyurethanes [153].

It was observed [153] that corona discharge and flame both showed some of the highest bond strengths despite having the lowest O:C ratios of the five effective pretreatments investigated. However, from depth analysis it was observed [153] that the highest concentrations of oxygen content were within the first few nanometers of the surface and rapidly decrease with depth. This result suggests that the total amount of chemical modification is small compared to other more powerful techniques, yet the joint strength is comparable. The chemical modification was found to be localized to the near surface allowing a large number of effective bond sites to be created and high bond strengths to be achieved for a low overall functional content [153]. From the pretreatments examined by Green *et al.* [153], the new atmospheric plasma (i.e., Agrodyn<sup>TM</sup>) and the older fluorination pretreatments have been found to be the most effective at modifying the surface and creating a number of varying functional types for various adhesives to bond to. The comparison of the O:C ratios may be useful as a guide of the likelihood of a

strong joint being created [153]. However, the trends within the ratios show that various deep-penetrating pre-treatments such as low pressure and atmospheric plasmas induce high levels of deep-positioned oxygen functional groups. Due to their depth within the substrate they can not be of use in adhesive bonding, leading to the hypothesis that the O:C ratios can not be used as a yardstick to judge the performance of a pre-treatment under loading conditions due to purely the relative increased amount of oxygen of a pretreatment not increasing bond strength by similar ratio compared to other pre-treatment regimes [153].

The recently developed and patented Ciba laser pre-treatment (CLP) have been studied by Broad *et al.* [151]. As observed by these workers, the CLP process is a beneficial surface preparation technique for metals, which facilitates adhesively bonded joints with better durability. CLP provides also important ecological advantages over wet pretreatments [151]. A comparison with pickle-etching, considering the required energy, the pretreatment waste and the emissions, demonstrated the ecological benefits of CLP. In contrast to wet pretreatments, with CLP no bulk pretreatment waste materials arise. The emissions observed from pickle-etching are mostly acid containing water vapor. The emissions from CLP are mostly lower alcohols, such as ethanol or iso-propanol, and some break-down products. Furthermore, it was claimed [151] that the required energy input for the pretreatment with CLP is much lower than that of the energy required for pickle-etching.

Using the available laser technology, applications of CLP can range from small repair or small production applications to high-volume series production. Therefore, the advantages of the CLP pretreatment process can be summarized as [151]: (a) adhesively bonded joints with good durability, (b) ecological advantages, (c) short pretreatment times (d) compatible with short cycle times, (e) easy installation as in-line, (f) stable surfaces, (g) selective pretreatment possible, (h) low pretreatment costs.

## 8. Concluding remarks

An adhesive is a substance capable of holding adherends together either by chemical or mechanical attraction. The effectiveness of the adhesive bonding is dependent upon many variables including [11], (a) the polymeric composition of the adhesive, (b) surface preparation materials and method of surface pretreatment, (c) adhesive lay-up procedure, (d) fitting of the parts to be joined, (d) tooling, and (e) curing process. Adhesive bonding offers many advantages (i.e., ability to join dissimilar materials, higher stiffness, more uniform load distribution, cleaner lines for aerodynamic benefits, part consolidation, no holes drilled in adherends with less stress concentrations, and, generally, less labor cost) over the classical fastening techniques such as welding, riveting and mechanical fastening. The adhesive bonding has a high resistance to fatigue, and as a consequence the life-cycle maintenance costs are significantly reduced. The substantial reduction in weight

that can be achieved by the use of adhesive bonding is an important advantage, especially for lightweight structures. In joining lightweight composites, the adhesive bonding is the most appropriate joining technique.

Adherend surface pretreatment plays a critical role in developing adhesively bonded joints. For example, unsuitable surface pretreatment of composite substrates, such as inadequate surface roughening, environmental effects, peel ply chemical contamination, and other factors (both mechanical and chemical) can prevent adhesives from bonding properly to composites, resulting in interfacial failures [89b]. These failures occur at loads well below those of properly bonded joints that fail cohesively. Other failures can occur over time in service, as joints are exposed to harsh environments, including elevated temperature and humidity [84, 88b, 230–237].

The common misconception in surface preparation is that the only requirement for a good adhesive bond is a clean surface. A clean surface is a necessary condition for adhesion but it is not a sufficient condition for bond durability. Most structural adhesive work as a result of the formation of chemical bonds (mainly covalent, but some ionic and static attractive bonds may also be present) between the adherend surface atoms and the compounds constituting the adhesive [152, 203]. As pointed out by Davis and Bond [152], these chemical links are the load transfer mechanism between the adherends. Solvent degreasing is important, because it removes contaminant materials which inhibit the formation of the chemical bonds, and increase wettability and surface energy of the substrate. However, solvent degreasing, whilst providing a clean surface, does not promote the formation of acceptable surface conditions for longer term bond durability.

Surface pretreatment should not be termed “cleaning” nor should the chemicals used be termed “cleaning agents” as these expressions lead to confusion between the different activities which combine to form the whole surface preparation process. Contamination should be removed by solvent degreasing as the first step of the surface preparation process. Processing chemicals such as etchants require contact with the substrate, and their effectiveness is diminished if the surface is contaminated. In many cases, surface-modifying chemicals do not dissolve the contaminants, and an ineffective bond results if the solvent degreasing step is not performed adequately. The basic principles of surface pretreatment dictate a number of aspects which are often violated by process specifications even from reputable manufacturers [35, 238]. Davis and Bond [152] considered the following three basic steps for adequate surface pretreatment: (a) the surface must be free of contamination; removing surface contamination by degreasing, (b) the adherend surface must be a sufficiently fresh and chemically active to enable formation of chemical bonds between the adhesive and the adherends, typically by chemical etching or surface abrasion, and (c) the surface should be chemically modified to produce an interface resistant to environmental deterioration in service, especially by hydration. However, most thermosetting polymer matrix composite adherends do not need the chemical modification process as such a

surface is not as susceptible to hydration as metallic surfaces. Whereas the recommended surface preparation for thermoplastic composites is a light aluminum oxide grit blast in dry nitrogen [152]. The abrasion should just remove the surface of the resin without exposing bare fibers. This process may be effective on moulded surfaces and corona treated tear film surfaces, and has been shown to reduce silicone contamination when coated nylon tear films are used [160]. Dust should be blown off the prepared surface using a nitrogen gas stream. Because the epoxy surface bonds well to other epoxies, no chemical modification is required.

Polyolefins are the most frequently surface pretreated polymers. The corona treatment is usually used with polyolefins in film forms, whereas symmetrical mouldings such as bottles, flame treatment is favored. Corona and flame pretreatments are ineffective with fully fluorinated polymers; with these materials, sodium in liquid ammonia or sodium naphthalenide in an aprotic solvent are usually used. As pointed out by Brewis and Dahm [129], for plastics such as nylon-6.6, which possess suitable functionality, a physical method such as grit blasting is often effective. Grit blasting can be very effective at removing mold release agents such as silicones which would otherwise have a serious effect on adhesion, and the roughening will generally enhance adhesion.

Before testing the ability of different surface pretreatments to promote adhesion, a detailed description of the rheological and mechanical properties of the adhesive is needed. Change of adhesive properties (due to incomplete curing) can affect the results of the adhesion tests and screen out the effect of the pretreatment. In this context, Lapique and Redford [208] have studied the curing process of a room temperature curing adhesive paste (Araldite 2014). Fig. 24 shows a differential scanning calorimetry (DSC) curve of uncured sample (just after the mixing of the two components). The DSC curve for the unreacted epoxy shows an exotherm peak representing 197 J/g. This area is defined as  $A_0$  and will be used as reference.  $A_0$  is directly related to the amount on unreacted reactants. As the curing progresses the amplitude of the peak decreases and the area  $A(t, T)$  was measured. The ratio  $[1 - (A_0/A(t, T))]$  was defined as the conversion factor  $\beta$ . According to this definition, a conversion factor of 1 (or 100%) was related to a fully cured epoxy. Samples were cured at different temperatures (23, 45 and 64°C) and the conversion factor deter-

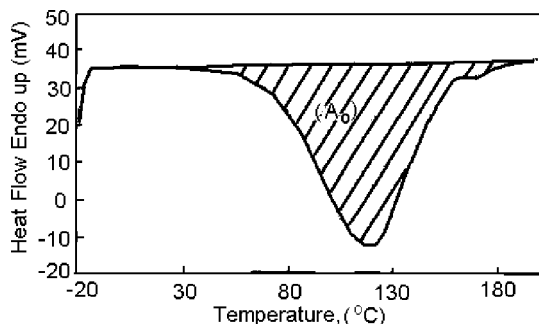


Figure 24 Differential scanning calorimetry (DSC) of scan of an uncured sample [208].

mined (see Fig. 25). Fig. 25 shows that the curing state can be characterized by three different conversion factors (once the plateau-like regime is reached) varying from 74% at 23 to 99% at 64°C. The plateau-like regime was reached after only 4 h at 64°C and the curing can be considered as complete. At lower curing temperatures, the adhesive is not fully cured when the plateau-like regime is reached. This suggests that in that regime the glass transition temperature  $T_g$  of the adhesive exceeds the curing temperature leading to vitrification.

The kinetics of the curing reaction has also been studied. A plot of the fraction of epoxy remaining with time showed [208] that the reaction follows a first order law [239, 240] at all curing temperatures until the transition to the plateau-like regime (see Fig. 25) is reached. Arrhenius plot of the rate coefficient with the inverse of the temperature, the activation energy was determined to be 34.6 kJ/mol (see Fig. 26). After a temperature dependent curing time, the first order law is no longer valid.

There is a strong correlation between the degree of conversion and the viscosity of the epoxy adhesive [241]. The viscosity measurement during curing at 23, 45 and 64°C has shown that there was a dramatic increase of viscosity [208]; this increase was associated with gelation. From a molecular point of view, this process is associated with both an increase of the molecular weight and an incipient creation of molecules with finite branches until a cross-linked structure is obtained [208]. Measurements show that the relationship between the conversion factor  $\beta$  and viscosity  $\eta$  can be described by (see Fig. 27)

$$\beta \alpha k(T) \ln \left( \frac{\eta - \eta_0}{\eta_0} \right) \quad (22)$$

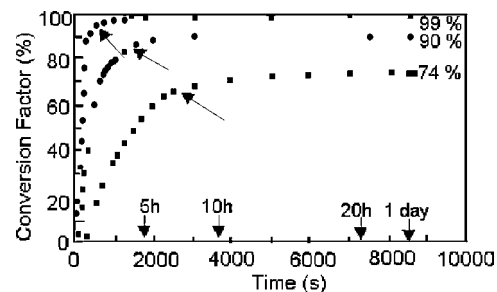


Figure 25 Curing of Araldite 2014 at different temperatures [208]. ■: Curing temperature 23°C, ●: Curing temperature 45°C, and ◆: Curing temperature 64°C.

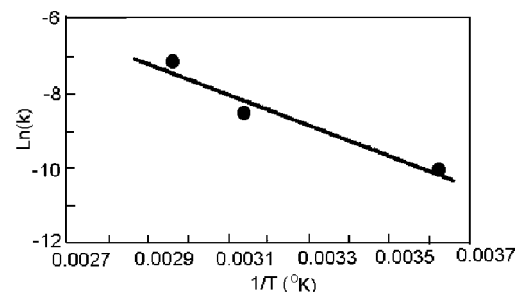


Figure 26 Arrhenius plot of rate coefficient. The activation energy was determined to be 34.6 kJ/mol [208].

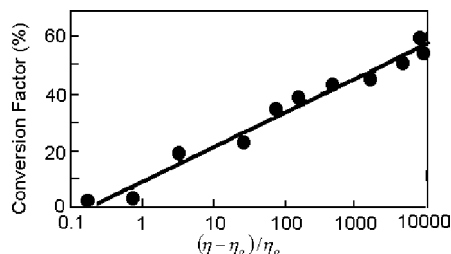


Figure 27 Conversion factor versus viscosity (log scale) for a sample cured at 23°C [208].

where  $\eta_0$  is the initial viscosity before the curing reaction starts.

Lapique and Redford [208] have also studied the effects of the curing process on the mechanical properties of the adhesive. According to the DSC measurements (see Fig. 25) the curing of the adhesive is completed after 4 h at 64°C. The measurement of the mechanical properties shows that 28 days at 23°C were needed to reach the same level of cure and that the properties of the adhesive during that period of time changed drastically. This confirms the assumption that the curing process was not stopped once the plateau-like regime was reached in Fig. 24 but only slowed down.

## References

1. R. A. FLINN and P. K. TROJAN, "Engineering Materials and Their Applications," 4th ed. (John and Wiley Sons, Inc., 1995) p. 608.
2. P. MOLITOR, V. BARRON and T. YOUNG, *Int. J. Adhes. Adhes.* **21** (2001) 129.
3. K. K. CHAWLA, "Composite Materials, Science and Technology," 2nd ed. (Springer, 1998).
4. E. PAUL DEGARMO, J. T. BLACK and R. A. KOHSE, "Materials and Processes in Manufacturing," 8th ed. (Prentice Hall) Chapt. 38.
5. "Modern Manufacturing Process Engineering," edited by B. W. Niebel, A. B. Draper and R. A. Wysk (McGraw-Hill, New York, 1989).
6. W. C. WAKE (ed.), "Synthetic Adhesives and Sealants" (Wiley, New York, 1987).
7. A. H. LANDROCK, "Adhesive Technology Handbook" (Noyes, Park Ridge, NJ, 1985).
8. S. R. HARTSHORNE (ed.), "Structural Adhesives: Chemistry and Technology" (Plenum, New York, 1986).
9. J. SHIELDS, "Adhesives Handbook," 3rd ed. (Butterworths, London, 1984).
10. S. L. ROSEN, "Fundamental Principles of Polymeric Materials," 2nd ed. (John Wiley and Sons, 1993).
11. "Fundamentals of Composite Manufacturing: Materials, Methods, and Applications," edited by A. B. Strong (Society of Manufacturing Engineers, Development Reference Publications Division, Dearborn, Michigan 48121, 1989).
12. D. K. SHAFFER, H. M. CLEARFIELD and J. S. AHEARA, in "Treatise on Adhesion and Adhesives," Vol. 7, edited by J. D. Minford, (Marcel Dekker, New York, 1991) p. 437.
13. H. M. CLEARFIELD, D. K. McNAMARA and G. D. DAVIS, "Adhesive Bonding" (Plenum Press, New York, 1990).
14. J. D. VENABLES, *J. Mater. Sci.* **19** (1984) 2431.
15. J. S. AHEARA and G. D. DAVIS, in Proceeding Adhesion 1987, Third International Conference (Plastics and Rubber Institute, York, UK, 1987).
16. W. BROCKMAN, O. D. HENNEMANN, H. KOLLEK and C. MATZ, *Int. Adhes. Adhes.* **6** (1986) 115.
17. L. J. HART-SMITH, *ibid.* **19** (1999) 181.
18. MEL M. SCHWARTZ, "Composite Materials Handbook," 2nd ed. (Mc Graw-Hill, 1992).
19. R. E. POLITI, "Recent Developments in Polyimide and Bis-maleimide Adhesives," High Temperature Polymer Matrix Composites, edited by T. T. Serafini (Noyes Data Corp., Park Ridge, NJ, 1987) p. 123.
20. N. ALLBEE, "Adhesives for Structural Applications" (Advanced Composites, November-December 1989) p. 42.
21. D. K. KOHLI, *Int. J. Adhes. Adhes.* **19** (1999) 231.
22. *Idem.*, in Proc. of 10th Int. European Chapter Conference of the SAMPE 55, 1989, p. 239.
23. *Idem.*, 39th Int. SAMPE Symposium, 11-14 April, 1994.
24. "Thermoplastics: Materials Engineering," 2nd ed., edited by L. Mascia (Elsevier Applied Science, London, 1989) p. 32.
25. B. GEORGE, Y. GROHENS, F. TOUYERAS and J. VEBRAL, *Int. J. Adhes. Adhes.* **20** (2000) 245.
26. E. DRAGONI and P. MAURI, *ibid.* **20** (2000) 315.
27. I. SKEIST, "Handbook of Adhesives," 2nd ed. (Van Nostrand Reinhold, New York, 1997).
28. D. B. YANG, D. WOLF, T. WAKAMATSU and M. HOLMES, *J. Adhes. Sci. Technol.* **9** (1995) 1369.
29. A. M. BROWSTEIN, US Patent 3,428,614 (1969).
30. B. M. MALOFSKY, Brit. Patent 1,528,626 (1978).
31. I. J. BACCEI, Brit. Patent 1,531,351 (1976).
32. D. SATES (ed.), "Handbook of Pressure-Sensitive Adhesives" (Van Nostrand Reinhold, New York, 1989).
33. I. SKEIST, Adhesive Compositions, in "Encyclopedia of Polymer Science and Technology," Vol. 1, edited by N. Bikales (Wiley, New York, 1971) p. 482.
34. A. ZOSEL, *Colloid Polym. Sci.* **263** (1985) 541.
35. COSTANTINO CRETON, "Materials Science of Pressure-Sensitive Adhesives, Materials Science and Technology," Processing of Materials, Vol. 18, edited by R. W. Cahn, P. Haasen and E. J. Kramer (Wiley-VCH, Weinheim, Germany, 1997).
36. B. SILLION, Polyimides and Other Heteroaromatic Polymers, in "Comprehensive Polymer Science," edited by G. Allen and J. C. Bevington (Pergamon, Oxford, UK, 1989) Vol. 5, p. 449.
37. H. D. STENZENBERGER, Polymer Matrices in "Carbon Fibres and Their Composites," edited by E. Fitzer (Springer, Berlin, Heidelberg, New York, 1985) Chapt. 2.
38. "Advanced Composite Materials," edited by L. A. Pilato and M. J. Michno (Springer-Verlag, Berlin, Heidelberg, New York, 1994).
39. H. R. BROWN, *Annu. Rev. Mater. Sci.* **21** (1991) 463.
40. R. R. MYERS, *Trans. Soc. Rheol.* **4** (1960) 43.
41. D. H. KAELBLE, *ibid.* **4** (1960) 45.
42. G. YASUDA, K. NINOMIYA and S. IDO, *Nippon Gomu Kyokaishi* **36** (1963) 1001.
43. G. YASUDA and S. IDO, *ibid.* **36** (1963) 1089.
44. "Viscoelastic Properties of Polymers," edited by J. D. Ferry (John Wiley and Sons, New York, 1980).
45. R. P. WOOL, in "Fundamentals of Adhesion," edited by L. H. Lee (Plenum, New York, 1991).
46. G. R. HAMED, *Rubber Chem. Technol.* **54** (1981) 576.
47. A. N. GENT and G. R. HAMED, Adhesion, in "Encyclopedia of Polymer Science and Engineering," 2d ed., Vol. 1, edited by J. Kroschwitz (Wiley, New York, 1985) p. 476.
48. F. J. MAYER, Bonding, in "Encyclopedia of Polymer Science and Engineering," 2d ed., Vol. 1, edited by J. Kroschwitz (Wiley, New York, 1985) p. 518.
49. A. W. ADAMSON, "Physical Chemistry of Surfaces," 5th ed. (Wiley, New York, 1990).
50. P. C. HIEMENZ, "Principles of Colloid and Surface Chemistry," 2d ed. (Dekker, New York, 1986).
51. R. F. WEGMAN, "Surface Preparation Techniques for Adhesive Bonding" (Noyes, Park Ridge, NJ, 1989).
52. A. F. HARRIS and A. BEEVERS, *Int. J. Adhes. Adhes.* **19** (1999) 445.
53. J. H. BROPHY, R. M. ROSE and J. WULFF, "The Structure and Properties of Materials," Vol. II, Thermodynamics of Structure (John Wiley and Sons Inc., New York, 1967).
54. "An Introduction to Composite Materials," edited by Derek Hull (University Press, Cambridge, UK, 1981).
55. A. KELLY, "Strong Solids," (Clarendon Press, Oxford, 1973).
56. J. COMYN, *Int. J. Adhes. and Adhes.* **12**(3) (1992) 145.
57. A. J. KINLOCH, "Durability of Structural Adhesives" (Elsevier Applied Science, Barking, UK, 1983).

58. T. G. GUTOWSKI, "The Mechanics of Composite Deformation During the Manufacturing Process. First Conference of Composite Materials" (American Society for Composites, Dayton, OH, 1986).
59. P. MOLITOR and T. YOUNG, *Int. J. Adhes. Adhes.* **22** (2002) 101.
60. P. G. DE GENNES, *Rev. Mod. Phys.* **57** (1984) 827.
61. L. LEGER and J. F. JOANNY, *Rep. Prog. Phys.* **55** (1992) 431.
62. N. EUSTATHOPOULOS, *Acta Mater.* **46** (1998) 2319.
63. S. MASON, in "Wetting Spreading and Adhesion," edited by J. F. Panday (Academic, New York, 1978).
64. G. PALASANTZAS and J. TH. M. DE HOSSON, *Acta Mater.* **49** (2001) 3533.
65. G. W. CRITCHLOW and D. M. BREWIS, *Int. J. Adhes. Adhes.* **15**(3) (1995) 173.
66. Y. GILIBERT and G. VERCHERY, in "Influence of Surface Roughness on Mechanical Properties of Joints," edited by K. L. Mittal (Adhesive Joints Formation, Characteristics, and Testing, Plenum Press, New York, 1982).
67. C. W. JENNINGS, *Amer. Chem. Soc. Div. Org. Chem.* **31**(2) (1971) 184.
68. J. P. SARGENT, *Int. J. Adhes. Adhes.* **14**(1) (1994) 21.
69. T. R. KATONA, *ibid.* **3**(2) (1983) 85.
70. A. F. HARRIS and A. BEEVERS, in Conf. Proc. Structural Adhesives in Engineering V, Bristol, Institute of Materials, 1998.
71. J. M. SYKES, Surface Treatments for Steels, in "Surface Analysis and Pretreatment of Plastics and Metals," edited by D. M. Brewis (London, Applied Science Publishers, 1982) p. 153.
72. D. E. PACKHAM, Roughness of Surfaces, in "Handbook of Adhesion," edited by D. E. Packham (Longman Group (FE) Ltd., New York, 1992).
73. M. SHAHID and S. A. HASHIM, *Int. J. Adhes. Adhes.* **22** (2002) 235.
74. M. J. DAVIS, A Call for Minimum Standards in Design and Application Technology for Bonded Structural Repairs. Proc. Symp. on Composite Repair of Aircraft Structures, Vancouver, 1995, p. 4-1, 4-15.
75. J. GUILLEMENT, B. BISTAC and J. SHULTZ, *Int. J. Adhes. Adhes.* **22** (2002) 1.
76. A. N. GENT, *J. Schultz, J. Adhes.* **3** (1972) 281.
77. D. MAUGIS and B. BARQUINS, *J. Phys. D* **11** (1978) 1989.
78. H. CHUN and A. N. GENT, *J. Polym. Sci. Part B*, **34** (1996) 2223.
79. A. D. ROBERTS, *Rubber Chem. Technol.* **52** (1979) 23.
80. P. G. GENNES, *Langmuir* **12** (1996) 4497.
81. A. AHAGON and A. N. GENT, *J. Polym. Sci. Phys. Ed.* **13** (1975) 1285.
82. D. MAUGIS, *J. Adhes. Sci. Technol.* **9** (1995) 1005.
83. A. N. GENT and G. R. HAMED, *Polym. Eng. Sci.* **17**(7) (1977) 462.
84. J. A. MARCEAU, Y. MOJI and J. C. McMILLAN, "A Wedge Test for Evaluating Adhesive Bonded Durability," 21st National SAMPE Symposium, Los Angeles, CA, 1976, p. 332.
85. M. L. WILLIAMS, *J. Appl. Polym. Sci.* **14** (1970) 1121.
86. D. MAUGIS, in "Contact, Adhesion and Rupture of Elastic Solids" (Springer Verlag, Berlin, 2000).
87. D. W. AUBREY, G. N. WELDING and T. WONG, *J. Appl. Polymer Sci.* **13** (1969) 2193.
- 88a. M. A. KRENCESKI and J. F. JOHNSON, *Polym. Eng. Sci.* **29** (1989) 36.
- 88b. W. D. BASCOM and R. L. COTTINGTON, *J. Adhes.* **20** (1976) 333.
- 89a. A. N. GENT and R. P. PETRICH, *Proc. Roy. Soc. London A* **310** (1969) 433.
- 89b. L. J. HART-SMITH, "The Curse of the Nylon Ply," Presented at 41st International SAMPE Symposium, 1996, p. 303.
90. H. SCHONHORN, *J. Polym. Sci., Polym. Lett.* **2** (1964) 465.
91. *Idem.*, *Macromolecules* **1** (1968) 145.
92. H. SCHONHORN and F. W. RYAN, *J. Polym. Sci. A-2* **6** (1968) 231.
93. H. ISHIDA and P. BUSSI, Morphology Control in Polymer Composites, in "Structure and Properties of Composites (Materials Science and Technology)," Vol. 13, edited by R. W. Cahn, P. Haasen and E. J. Kramer, VCH (Weinheim, New York, 1993) p. 339.
94. E. H. ANDREWS and A. J. KINLOCH, *Proc. R. Soc. London A* **332** (1973) 385.
95. *Idem.*, *ibid.* **A 332** (1973) 401.
96. M. TOYAMA, T. ITO and H. MORIGUCHI, *J. Appl. Polym.* **14** (1970) 2039.
97. M. SHERRIFF, R. W. KNIBBS and P. G. LANGLEY, *J. Appl. Polym. Sci.* **17** (1973) 3423.
98. K. N. G. FULLER and D. TABOR, *Proc. R. Soc. London A* **345** (1975) 327.
99. S. J. HITCHCOCK, N. T. CAROLL and M. G. NICHOLAS, *J. Mater. Sci.* **16** (1981) 714.
100. Y. TAMAI and K. ARATANIC, *J. Phys. Chem.* **76**(22) (1972) 3267.
101. C. HUH and S. G. MASON, *J. Coll. Interf. Sci.* **60**(1) (1977) 11.
102. F. G. YOST, J. R. MICHEAL and E. T. EISENMANN, *Acta Metall. Mater.* **43**(1) (1995) 299.
103. J. J. BIKERMAN, *J. Phys. Coll. Chem.* **54** (1950) 653.
104. R. N. WENZEL, *Ind. Eng. Chem.* **28**(8) (1936) 988.
105. A. CARRE and J. SCHULTZ, *J. Adhes.* **15** (1983) 151.
106. R. SHUTTLEWORTH and G. L. J. BAILEY, *Disc. Faraday Soc.* **3**(16) (1948) 16.
107. A. FALSAFI, M. TIRREL and A. V. POCIUS, *Langmuir* **16** (2000) 1816.
108. D. L. WOERDEMAN, N. AMOUROUX, N. PONSINENT, G. JANDEAU, H. HERVET and L. LEGER, *Composite A: Appl. Sci. Manuf.* **30**(1) (1999) 95.
109. K. R. SHULL, D. AHN and C. L. MOWERY, *Langmuir* **13** (1997) 1799.
110. M. DERUELLE, H. HERVET, G. JANDEAU and L. LEGER, *J. Adhes. Sci. Technol.* **12** (1998) 225.
111. H. R. BROWN, *Macromolecules* **26** (1993) 1666.
112. D. L. WOERDEMAN, J. A. EMERSON and R. K. GUINTA, *Int. J. Adhes. Adhes.* **22** (2002) 257.
113. M. K. CHAUDHURY and G. M. WHITESIDES, *Langmuir* **7** (1991) 1013.
114. D. AHN and K. R. SHULL, *Macromolecules* **29** (1996) 4381.
115. K. L. JOHNSON, K. KENDALL and A. D. ROBERTS, *Proc. Roy. Soc. London Part A* **324** (1971) 301.
116. H. HERTZ, Gesamelle Werke, Leipzig, 1895.
117. P. CHIN, R. L. MCCULLOUGH and W. L. WU, *J. Adhes.* **64** (1997) 145.
118. JANG-KYO KIM and YU-WING MAI, Interfaces in Composites, Vol. 13, "Structure and Properties of Composites (Materials Science and Technology)," edited by R. W. Cahn, P. Haasen and E. J. Kramer, VCH (Weinheim, New York, Cambridge, 1993) p. 239.
119. A. MAHOON, edited by A. J. Kinloch (Titanium Adherends in Durability of Structural Adhesives, 1983) p. 259.
120. E. P. PLUEDDEMANN, in Proc. Int. Conf. Composite Interfaces II, Interfaces in Polymer, Ceramic and Metal Matrix Composites, edited by H. Ishida (Elsevier Sci. Publ., New York) p. 17.
121. H. ISHIDA and J. L. KOENIG, *J. Coll. Interf. Sci.* **64** (1978) 555.
122. E. P. PLUEDDEMANN and G. L. STARK, 35th Ann. Tech. Conf. Reinf. Plast./Comp. (Society of Plastic Industries, Washington, D.C., 1980) p. 20B.
123. A. GARTON and J. H. DALY, *Polym. Comp.* **6** (1985) 195.
124. J. L. THOMASON, *ibid.* **11** (1990) 105.
125. H. C. TSAI, A. M. AROCHA and L. W. GAUSE, *Mater. Sci. Eng. A* **126** (1990) 295.
126. J. W. WILLIAMS, M. E. DONNELLAN, M. R. JAMES and W. L. MORRIS, *ibid.* **A 126** (1990) 305.
127. W. J. WHATLEY and F. E. WAWNER, *J. Mater. Sci. Lett.* **4** (1985) 173.
128. P. LANNON, E. ESPUCHE, H. SAUTEREAU and D. SAGE, *Int. J. Adhes. Adhes.* **19** (1999) 273.
129. D. M. BREWIS and R. H. DAHM, *ibid.* **21** (2001) 397.
130. BLACKMAN, KINLOCK and WATTS, *Composites* **25**(5) (1994).
131. J. WINGFIELD, *Int. J. Adhes. Adhes.* **13**(3) (1993) 151.
132. G. KEMPE and H. KRAUSS, Adhesion Bonding Techniques for Highly Loaded Parts of Continuous Carbon-Fiber Reinforced Polyetherketone (CF-PEEK/APC02). ICAS-92-6.9.1, 1992.
133. J. COMYN and XIAO MASCIA, *Int. J. Adhes. Adhes.* **16** (1996) 301.

134. G. W. CRITCHLOW and D. M. BREWIS, *ibid.* **15**(3) (1995) 161.
135. G. K. A. KODOKIAN and A. J. KINLOCH, *J. Mater. Sci. Lett.* **7** (1988) 627.
136. A. J. KINLOCH, "Adhesion and Adhesives" (Chapman and Hall, London, 1987).
137. A. BAALMANN, K. D. VISSING and A. GROSS, *J. Adhesi.* **46** (1994).
138. J. R. ARNOLD, C. D. SANDERS, D. L. BELLEVOU, A. A. MARTINELLI and G. B. GASKIN, in Proceeding of the 29th International SAMPE Technical Conference, Vol. 1, 1997, p. 345.
139. J. R. ARNOLD, C. D. SANDERS, D. I. BELLEVOU, A. A. MARTINELLI and G. B. GASKIN, in Proceedings of the 29th International SAMPE Technical Conference, Vol. 1, 1997, p. 345.
140. K. Y. BLOHOWIAK, J. H. OSBORNE, K. A. KRIENKE and D. F. SEKITS, in Proceedings of the 28th International SAMPE Technical Conference, 1996, p. 440.
141. F. J. BOERIO and R. G. DILLINGHAM, in "Adhesive Joints Formation, Characteristics, and Testing," edited by K. I. Mittal (Plenum Press, New York, 1991) p. 541.
142. British Aerospace Aircraft Group Weybridge-Bristol Division, 1984, Report No. AL/MAT/3864.
143. G. D. DAVIS, G. B. GROFF and R. A. ZATORSKI, *Surf. Inter. Anal.* **25** (1997) 366.
144. Lockheed-California Company, Prepared for National Air Development Center, 1983, Report No. NADC-84124-60.
145. A. MAHOON, in "Durability of Structural Adhesives," edited by A. J. Kinloch (Applied Science Publishers, London, 1983) p. 255.
146. E. SANCAKTAR and E. ZHANG, *ASME* **79** (1994) 65.
147. K. RAMANI, W. J. WEIDNER and G. KUMARI, *Int. J. Adhes. Adhes.* **18**(6) (1998) 401.
148. J. L. COTTER and A. MAHOON, *ibid.* **2** (1982) 47.
149. C. INGMAN and K. RAMANI, *ibid.* **17** (1997) 39.
150. J. R. ARNOLD, *et al.* "A Study of Titanium Surface Pretreatments for Bonding with Polyamide and Epoxy Adhesives," in Proceedings of the 29th International SAMPE Technical Conference, 1997.
151. R. BROAD, J. FRENCH and J. SAUER, *Int. J. Adhes. Adhes.* **19** (1999) 193.
152. M. DAVIS and D. BOND, *ibid.* **19** (1999) 91.
153. M. D. GREEN, F. J. GUILD and R. D. ADAMS, *ibid.* **22** (2002) 81.
154. D. K. SHAFFER, H. M. CLEARFIELD and J. S. MINFORD (eds.), "Treatise on Adhesion and Adhesives" (Marcel Dekker, New York, 1991) Vol. 7, p. 437.
155. V. BARRON, PhD thesis, University of Limerick, 1998.
156. J. R. ARNOLD, C. D. SANDERS, D. L. BELLEVOU, A. A. MARTINELLI and G. B. GASKIN, *Proces. of the 29th Int. SAMPE Technical Conference*, Vol. 1, 1997, p. 345
157. A. J. KINLOCH, "Adhesion and Adhesives" (Chapman and Hall, London, 1987) p. 123.
158. D. ARNOTT, P. PEARCE, A. WILSON, R. CHESTER, A. CAMILLERI and J. VAN DER BERG, The Effect on Mechanical Properties of Void Formation During Vacuum Bag Processing of Epoxy Film Adhesives, in Proc. Int. Aerospace Congress. PICAST 2-AAC 6, Melbourne, 1995, p. 811.
159. A. WILSON, M. KINDERMANN and D. ARNOTT, Void Development in an Epoxy Film Adhesive During Vacuum Bag Cure. Proc. Int. Aerospace Congress, PICAST 2-AAC 6, Melbourne, 1995, p. 625.
160. L. J. HART-SMITH, G. REDMOND and M. J. DAVIS, The Curse of the Nylon Peel Ply. 41st Int. SAMPE Symp. and Exhib. Brea, CA, Anaheim, 1996.
161. J. K. PARK, J. W. CHEN and K. MUKHERJEE, in Proceedings of the American Society for Composites 14th Technical Conference (Dayton, OH, 1999) p. 661.
162. P. D. MILLER, R. A. JEFFREYS and H. A. PRAY, Metal Progress Report, 1974, p. 61.
163. J. A. FILBEY and J. P. WIGHTMAN, in "Adhesion," edited by K. W. Allen, 12 ed. (Applied Science Publishers, London, 1987) p. 17.
164. W. BROCKMANN, O. D. HENNEMAN, H. KOLLEK and C. MATZ, *Int. J. Adhes. Adhes.* **6** (1986) 115.
165. Pasajell Data Sheets SEMCO Divison Products Research and Chemical Corporation 5454 San Francisco Road Glendale CA, 1997.
166. J. M. HILL, E. KARBASHEWSKI and A. LIN, *J. Adhesion Sci. Technol.* **9**(12) (1995) 1575.
167. M. STROBEL, M. J. WALZAK and J. M. HILL, *ibid.* **9**(3) (1995) 365.
168. K. L. MITTAL and A. PIZZI (eds.), "Adhesion Promotion Techniques; Technical Applications" (Marcel Dekker, New York, 1999).
169. I. SUTHERLAND, R. P. POPAT, D. M. BREWIS and R. CALDER, *J. Adhes.* **46** (1994) 79.
170. H. K. YASUDA, "Plasma Polymerisation" (Academic Press, USA, 1985).
171. V. BARRON and M. BUGGY, in Proceeding of the 23rd Annual Adhesion Society Conference Myrtle Beach SC, 2000, p. 540.
172. B. O. ARONSSON, J. LAUSMAN and B. KASEMO, *J. Biomed. Mater. Res.* **35**(1) (1997) 49.
173. R. FOERCH, J. IZAWA, N. S. MCINHYRE and D. H. HUNTER, *J. Appl. Polym. Sci.* **46** (1990) 415.
174. J. P. BRADEY, E. ESPUCHE, D. SAGE, B. CHABERT, Y. JUGNET and C. BATIER, *Trans. Minh. Duc. Polymer* **37**(8) (1996) 1377.
175. L. LAVIELLE, J. SHULTZ and J. NAKAJIMA, *J. Appl. Poly. Sci.* **42** (1991) 28.
176. R. FOERCH, J. IZAWA and G. SPEARS, *J. Adhes. Sci. Techn.* **5**(7) (1991) 549.
177. G. S. SHEU and S. S. SHYU, *ibid.* **8**(5) (1994) 1027.
178. M. SHOBEI, M. J. WALZAK, J. HILL, A. LIN, E. KARBASHEWSKI and C. LYONS, *ibid.* **9**(3) (1995) 365.
179. R. H. HANSEN, J. V. PASCALE, T. DE BENEDICHS and P. M. RENTZEPIS, *J. Polym. Sci. Part I*, **3** (1993) 991.
180. F. M. FOWKES, *Ind. Engng. Chem.* **12** (1964) 40.
181. Methods and Apparatus for Treating the Surface of a Workpiece by Plasma Discharge, US Patent 5837958 (1998).
182. M. W. POTTS, in Proceedings of the Polymer, Laminations and Coatings Conference (1993) p. 444.
183. J. DIGIACOMO, J. Proceedings Finishing'91 Conference Cincinnati, Ohio, 1991, p. 376.
184. F. DEMBLON, *Vide Couches Minces* **272**(Suppl 5) (1994) 394.
185. D. BRIGGS, *J. Mater. Sci.* **14** (1979).
186. I. SUTHERLAND, D. M. BREWIS and R. J. SHENG, *J. Surface Interface Anal.* **17** (1991) 507.
187. E. WURZBERG, A. BUCHMAN, E. ZYLERSTEIN, Y. HOLDENGRABER and H. DODIUK, *J. Adhes. Adhes.* **10** (1987) 337.
188. A. BUCHMAN, H. DODIUK, M. ROTAL and J. ZAHAVI, *Int. J. Adhes. Adhes.* **11** (1991) 3.
189. J. K. PARK and K. MUKHERJEE, *Mater. Manufact. Process* **13**(3) (1998) 359.
190. A. BUCHMAN and H. DODIUK-KENIG, in "Laser Surface Treatment to Improve Adhesion," edited by K. L. Mittal, Adhesion Promotion Techniques, Technical Applications, Marcel Dekker, New York.
191. H. FRERICHS, J. STRICKER, D. A. WESNER and E. W. KREUTZ, *Appl. Surface Science* **80** (1995) 405.
192. A. J. KINLOCH, The Service Performance of Structural Adhesive Joints. Haftung als Basis für Stoffverbunde Oberursel 1982.
193. D. M. BREWIS, *J. Adhes.* **37** (1992) 97.
194. J. P. COLEMAN and D. PLETCHER, *J. Electroanal Chem.* **87** (1978) 111.
195. J. BRINGMANN, K. EBERT, U. GALLA and H. SCHIEDER, *J. Appl. Electrochem.* **25** (1995) 846.
196. I. MATHIESON, D. M. BREWIS, I. SUTHERLAND and R. A. CAYLESS, *J. Adhes.* **46** (1994) 49.
197. D. M. BREWIS, I. MATHIESON, I. SUTHERLAND R. A. CAYLESS and R. H. DAHM, *Int. J. Adhes. Adhes.* **16** (1996) 87.
198. D. M. BREWIS, R. H. DAHM and I. MATHIESON, *J. Adhes.* **72** (2000) 373.
199. R. TOMAT and A. RIGO, *J. Appl. Electrochem.* **16** (1986) 8.
200. D. M. BREWIS, R. H. DAHM and I. MATHIESON, *Polym. J. Mater. Sci. Lett.* **16** (1997) 93.
201. W. A. LEES, in Proc. of the Bonding and Repair of Composites Seminar, Birmingham, UK, 1989, p. 17.



202. F. J. BOERIO, C. A. GOSSELIN, J. W. WILLIAMS, R. G. DILLINGHAM and J. M. BURKSRAND, in Proc. of the Symp. on Polymer Composites, Seattle, Washington, USA, 1983, p. 171.
203. A. J. KINLOCH, "Adhesion and Adhesives, Science and Technology" (Chapman and Hall, London, 1987) p. 30.
204. L. E. RANTZ, Proper Surface Preparation, Bonding Critical First Adhesive Age, May 1987.
205. W. WADE, R. MAMMONE and M. BINDER, *J. Appl. Polym. Sci.* **43** (1991) 1589.
206. P. RUMEAU, Thesis, no. 81-95, Lyon I, 1995.
207. M. R. WERTHEINER and H. P. SCHREIDER, *J. Appl. Polym. Sci.* **26** (1981) 2087.
208. F. LAPIQUE and K. REDFORD, *Int. J. Adhes. Adhes.* **22** (2002) 337.
209. J. P. SARGENT, *ibid.* **14**(1) (1994) 21.
210. S. THERY, A. LEGROS and P. BALLADON, Study of Parametrs Influencing the Mechanical Behavior of and Damage to Steel-Polymer Interfaces, in "Mechanics and Mechanisms of Damage in Composites and Multi-Materials, ESIS 11," edited by D. Baptiste (Mechanical Engineering Publications, London, 1991) p. 339.
211. S. J. HITCHCOCK, N. T. CAROLL and M. G. NICHOLAS, *J. Mater. Sci.* **16** (1981) 714.
212. C. BOCKENHEIMER, B. VALESKE and W. POSSART, *Int. J. Adhes. Adhes.* **22** (2002) 349.
213. L. KOZMA and I. OLEFIJORD, *Mater. Sci. Technol.* **3** (1987) 860.
214. O. LUNDER, B. OLSEN and K. NISANCIOGLU, *Int. J. Adhes. Adhes.* **22** (2002) 143.
215. A. J. KINLOCH and N. R. SMART, *J. Adhes.* **12** (1981) 23.
216. A. J. KINLOCH, H. E. BISHOP and N. R. SMART, *ibid.* **14** (1982) 105.
217. M. J. RIJKHOFF, R. BLEEKER and J. BOTTEMA, in Proc. of the Int. Symp. on Aluminum Surface Science and Technology, Antwerpen, 1997, p. 125.
218. K. S. SCHWEIZER and J. G. CURRO, *Phys. Rev. Lett.* **58** (1987) 246.
219. J. G. CURRO and K. S. SCHEWEIZER, *Macromolecules* **20** (1987) 1428.
220. *Idem.*, *J. Chem. Phys.* **87** (1987) 1842.
221. K. S. SCHWEIZER and J. G. CURRO, *Adv. Chem. Phys.* **98** (1997) 1.
222. B. K. FINK and R. L. McCULLOUGH, *Composites A: Appl. Sci. Manuf.* **30**(1) (1999) 1.
223. J. A. EMERSON, T. R. GUESS, J. G. CURRO, E. D. REEDY, E. P. LOPEZ and P. LEMKE, Investigation of the Impact of Cleaning on the Adhesive Bond and the Process Implications, SAND 2000-1042, May 2000.
224. M. E. R. SHANAHAN, *J. Coll. Interf. Sci.* **229** (2000) 168.
225. J. COMYN, "Adhesion Science" (The Royal Society of Chemistry, RSC Paperbacks, 1997) p. 98.
226. C. L. MAHONEY, Fundamental Factors Influencing the Performance of Structural Adhesives. Internal Report, Dexter Adhesives and Structural Materials Division, The Dexter Corporation.
227. R. J. SCHLIEKMANN, Adhesive Bonding and Composites, 4th Int. Conf. on Composite Materials, ICCM-IV, Tokyo, Japan, 1982, p. 63.
228. L. W. CRANE, *et al.*, Surface Treatment of Cured Epoxy Graphite Composites to Improve Adhesive Bonding, SAMPE J. 1976, Vol. 6.
229. A. BEEVERS, A Critical Appraisal of Durability Test Methods, SAE IV, Bristol, 1995, p. 137.
230. J. COGNARD, *J. Adhes.* **22**(2) (1987) 97.
231. *Idem.*, *ibid.* **20**(1) (1986) 1.
232. P. B. CROSLLEY and E. J. RIPLING, *J. Test. Evalu.* **19**(1) (1991) 24.
233. E. J. RIPLING, S. MOSTOVOY and C. BERSCH, *J. Adhes.* **3** (1971) 145.
234. F. SLOAN, *J. Comp. Mater.* **27**(16) (1993) 1606.
235. W. JOHNSON and L. M. BUTKUS, *Fatigue and Fract. Engin. Mater. and Struct.* **21**(4) (1988) 465.
236. L. J. HART-SMITH, "A Peel-Type Durability Test Coupon to Assess Interfaces in Bonded, Co-Bonded, and Co-Cured Composite Structures," McDonnell Douglas Paper MDC 97K0042, presented to MIL-HDBK-17 Meeting, Tucson, 1997.
237. R. A. JURF, "Environmental Effects on Fracture of Adhesively Bonded Joints," Adhesively Bonded Joints: Testing, Analysis, and Design, ASTM STP 981, p. 276.
238. "Starch and Dextrins in Prepared Adhesives," Chapter 20, edited by H. M. Kennedy and A. C. Fischer, p. 607; "Starch: Chemistry and Technology," 2nd ed., edited by R. L. Whistler, J. N. Bemiller and E. F. Paschall (Academic Press, Orlando, San Diego, New York, 1984).
239. J. W. SINCLAIR, *J. Adhes.* **38** (1992) 219.
240. P. W. ATKINS, "Physical Chemistry," 2nd ed. (Oxford University Press, 1982) (ISBN 0-19-855151-7).
241. J. J. IMAZ, N. MARKAIDE and M. J. JURADO, *Eur. Polym. J.* **28** (1992) 299.

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