

TREATMENTS OF COMPOSITE MATERIALS SURFACES FOR ADHESIVE BONDING

F. Mocanu, L. Bejan

Technical University "Gh. Asachi", Iasi,

INTRODUCTION

The use of advanced composite materials has increased significantly in the last 30 years. A variety of composite materials are now commonly used in the aircraft, automotive, marine and other industries. Adhesive bonding of composite materials is a joining method, which is attractive as an alternative or as a complement to more conventional methods like spot welding, riveting or bolting. The present paper discusses in detail mechanical, energetic and chemical treatments of composite material surfaces for adhesive bonding.

1. ADHESIVE JOINTS WITH COMPOSITE MATERIALS

The adhesive bonding technique has been used successfully in engineering designs in which structural components with similar/dissimilar material properties are bonded to each other. Adhesive bonding has been extensively studied over the last 40 years but principally for aeronautical and automobile applications, for which the adherents tend to be less than 2mm thick. Adhesive joining was an attractive joining technique because it saves weight up to 20% compared to conventional methods, does not create stress concentration and generally produces longer fatigue life in comparison to joints bonded using the other techniques. Adhesive bonding provides a smooth surface along which the load is transferred and removes probable high stress concentration around holes, stress raisers in the case of conventional methods [1].

An adhesive is defined as a polymeric substance with viscoelastic behavior capable of holding together by surface attachment to produce a joint with high shear strength. Some thermoplastic and thermosetting polymers are used as adhesives. The adhesives can be liquids, pastes and solids. The adhesive should wet the adherend and solidify under production conditions of time, temperature and pressure. The strength of the adhesive joints 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.

Advanced synthetic adhesives with a high strength have been developed as a result of intensive research in organic chemistry during the last decades and have been used in the bonding of polymeric and composite materials. Adhesives are normally epoxy resin, but could be acrylic, phenolic or polyurethane. They come in liquid, paste or film form and cure at room temperature or higher temperatures [1].

The composite materials are frequently manufactured as elements, which must then be joined to each other or to a metallic structure. Assemblies of elements using tapered lap joints of the some stacking sequence as the composite is the best method but it is long labour intense and expensive. Composite materials, be they metal matrix composites, polymer matrix composites, or ceramic matrix composites are joined by the same procedures that are well known for joining isotropic materials such as metals or polymers. This is to be expected since the process of transferring loads between joined components sets up stress patterns, which are more dependent on the component/joint configuration than on the material used to fabricate the article [2].

All forms of composite can be satisfactorily joined. Composite materials could be joining by adhesive bonding and by mechanical fastening. To utilize the full potential of composite materials as structural elements, the strength and failure of these bolted/bonded joints in laminated composites must be understood. Joining techniques used for metals, such as bolting and riveting, can be detrimental to the mechanical properties of the composite. Adhesive bonding is a convenient alternative way to joint these materials. Adhesive are often required when joining composite materials in order to make best use of their properties.

Is needed to prepare the mating surface by removing all traces of mold release agent or other contaminant from the composite. If the composite is to be bonded to a metal then the latter will also need

pretreatment to remove grease and any surface oxide layer. The failure of adhesive joints often takes place by cohesive fracture in the adhesive or by adhesive

fracture at the interface between the adhesive and the adherents. The fracture of an interface between two materials depends on the geometry, the constitutive properties of the adherents and the details of the bonding across the interface. The relationship between the normal cohesive stresses and the normal displacements across the interface dictates the failure of the joint loaded in an opening mode [3].

It is generally accepted that a bonded joint is stronger than a bolted joint and a well-designed bonded joint is stronger than a bonded-bolted joint.

2 TREATMENT OF COMPOSITE SURFACES FOR ADHESIVE BONDING

2.1. General considerations

The surface pretreatment of composite materials for bonding is very important in order to obtain good joint strength. Adherent surface treatment plays a critical role in developing adhesively bonded joints. Unsuitable surface preparation of substrates, such as inadequate surface roughening, environmental effects, peel ply chemical contamination and other factors mechanical and chemical can prevent adhesives from bonding properly to substrates, resulting in interfacial failures (failure between adhesive layer and adherent). These failures occur at loads well below those of properly bonded joints that fail cohesively (in adhesive layer).

A standard requirement for an adhesive to work is a clean surface. This simply reflects the fact that adhesion starts with interfacial interactions. If these interactions are too weak or screened the stress cannot be transferred at the interface, the adhesive layer cannot deform and the energy dissipation will be very small during the debonding process resulting in a low adhesion energy. However, the lower the stress at which the adhesive can deform extensively, the weaker the interactions needed for good adhesive properties. The common conception in surface preparation is that the only requirement for a good adhesive joint is a clean surface. Most adhesive work as a result of the formation of chemical bonds between the substrate surface and the layer adhesive. This chemical links are the load transfer mechanism between the

adherents of the adhesive joint. Surface treatments often involve chemicals which produce surfaces with different chemical compositions and these morphological changes influence the nature of the chemical bonds [1]. Reasons put forward for improved joints performance due to a surface treatment include the following:

- the elimination of "weak boundary layers" at the surface such as contaminants, low molecular weight species and loose, friable, surfaces;
- improved wetting of low-energy surfaces (for complete wetting the surface energy of the adhesive must be lower than the surface energy of the adherend);
- chemical modification such as the introduction of polar chemical groups;
- increase in surface roughness giving rise to improved mechanical interlocking or increased bondable surface area [1].

Surface treatment increases the joint strength in following:

- increasing surface tension;
- increasing surface roughness (an increase in surface roughness which allows the adhesive to flow in and around the irregularities on the surface to form a mechanical joint);
- changing result in the formation of a chemical bond between the polymer molecules in the polymer matrix composite [3].

The primary function of a fiber surface treatment is to improve the fiber surface wettability with the matrix and to create a strong bond at the fiber-matrix interface. Both are essential for effective stress transfer from the matrix to the fiber and vice versa. To example, for glass fibers are used chemical coupling agents to improve the fiber/matrix interfacial strength through physical and chemical bonds and protect the fiber surface from moisture and reactive fluids. The interfacial bond created by coupling agents allows a better shear stress transfer between fibers and matrix, which in turn improves the tensile strength as well as the interlaminar shear strength of the composite. Carbon fiber surface are chemically inactive and must be treated to form surface functional groups that promote good chemical bonding with the resin matrix.

Surface treatments also increase the surface area by creating micropores or surface pits on already porous carbon fiber surface. Increase in surface area provides a larger number of contact points for fiber-matrix bonding. Surface treatments for carbon fibers can be: oxidative or nonoxidative. Oxidative surface treatments produce acidic

functional groups (carboxylic, phenolic and hydroxilic) on the carbon fiber surface.

The treatment improves the surface properties depends on the acid concentration, treatment time and temperature. In one of nonoxidative treatments, the carbon fiber surface is coated with an organic polymer that has functional groups capable of reacting with the resin matrix. The preferred method of coating the fiber surface is electropolymerization, in which carbon fibers are used as one the electrodes in acidic solution of monomers or monomer mixtures. Improved results are obtained if the carbon fiber surface is oxidized prior to the coating process.

Is needed to prepare the mating surface by removing all traces of mold release agent or other contaminant from the composite. If the composite is to be bonded to a metal then the latter will also need pretreatment to remove grease and any surface oxide layer (for aluminium and titanium). Solvent decreasing 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 decreasing, whilst providing a clean surface, does not promote the formation of acceptable surface conditions for longer term bond durability. 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 result, if the solvent decreasing step is not performed adequately [1].

Authors, of this paper, considered the following three basic steps for adequate surface pretreatment:

- 1) the surface must be free of contamination (removing surface contamination) by decreasing;
- 2) the adherent surface must be a sufficiently fresh and chemically active to enable formation of chemical bonds between the adhesive and adherents (typically by chemical etching of surface abrasion);
- 3) the surface should be chemically modified to produce an interface resistant to environmental deterioration in service.

Some of special characteristics of composite materials need to be considered when treating their surfaces for adhesive bonding. Composite usually have very smooth, moulded surfaces composed mainly of the polymer matrix material. Surface energies of composites tend to be low, especially for the thermoplastic matrices such

as polyether-ether-ketone and polypropylene, making wetting of surfaces by an adhesive difficult. There is a danger that some treatment may cause delamination defects just below the surface or damage to the relatively brittle fibers. These defects may result in poorer mechanical properties of the composite [3].

Perhaps the biggest problem with composites is the wide ranges of contaminants that can be found on the surface and by their nature form a weak boundary layer in a bond. These contaminants include silicones from release agents and bagging materials, fluorocarbon release sprays and films, machining oils, fingerprints and components in the composite itself which have migrated to the surface, such as calcium stearate from self-releasing formulations, water and plasticizers.

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. A wide variety of chemical, mechanical and energetic surface treatments have been evaluated and reported in the literature for the treatment of plastics and metals adherents for bonding. Many of these techniques may also be suitable for the bonding pretreatment of composite materials as adherents. A selection of surface treatments on composite materials is shown in following.

2.2. Mechanical treatments

A mechanical treatment is used primarily to produce a clean macroscopically rough surface and remove some of existing oxide layer. The mechanical treatments are following:

2.2.1. Alumina grit blasting

The effect of alumina grit blasting is to modify the morphology of the surface and also to remove some surface contamination. The roughness introduced by treatment will also affect the wetting the composite. This method 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. The variables in grit blasting are the size of alumina grit, the blast pressure, the treatment time, the blast angle and the distance from the blast nozzle to the surface. Alumina gri blasting has been suggested as a good mechanical surface treatment for carbon/epoxy composite. Silicon carbide paper abrasion can be carried out dry or, more usually, in conjunction with a solvent which aids removal of any debris and contaminants. As

with alumina grit blasting, silicon carbide abrasion also causes visible damage to carbon and glass fiber in the composite. The surface energy and adhesion characteristics of the surface of substrate are dependent by following factors: the substrate material, the grit-blasting media purity and contamination and the grit-blasting media particle size. The bulk mechanical properties of the composite material can be affected by abrasive surface treatments like alumina grit blasting and silicon carbide abrasion. Strength is very low for joint with glass/polypropylene composite for treatment with silicon carbide washing where the mode of failure is adhesive [3].

2.2.2. Cryoblast

The cryoblast technique may remove surface contamination without causing large changes to surface morphology or fiber damage.

2.2.3. Sodablast

Sodablasting, using a suspension of sodium bicarbonate in water, has been developed as a cleaning technique. The disadvantage of the technique is that it used water and will therefore raise the water content of the composite. This may mean that the composite has to be dried before any bonding process.

2.2.4. Peel ply

One of the more common surface treatments for composite bonding is the peel ply (a peel ply is a layer of nylon or polyester fabric incorporated in the surface of a composite during its manufacture and which is stripped off the surface immediately before bonding). The variables for a peel ply treatment are: type of material, size of ply, type of weave and whether any release agent applied to the peel ply [1]. Typically, three forms of peel ply are used:

- a thin fiber-glass layer which is difficult to remove and will cause delamination damage in thin laminates;

- a nylon product. Nylon forms good chemical bonds with epoxy adhesive 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 laminates. The release agent is transferred to the joining surface and reduces the effectiveness of any adhesive joint formed with that now contaminated surface;

- polyester films. This forms uses heat setting or corona discharge treatment to glaze the surface of the fibers [3].

2.2.5. Tear-ply

Tear-ply exploits a laminate property and consists of a fabric, which is completely impregnated by the laminate matrix resin. It is mainly used for thermoset composites. The tear-ply must be carefully selected to enable it to be removed without any difficulty following the molding process. Superficially the surface of the laminates treated with either peel-ply or tear-ply appears very similar.

Abrasion and grit blasting techniques are not adequate methods of surface treatment but when combined with chemical or energetic treatment on can be obtained adhesive joints with good strength. Abrasion and solvent cleaning may be employed to degrease the surface and remove mold release agents from the adherend.

2.3. Energetic treatments

The energetic treatments are following:

2.3.1. Corona discharge

Corona discharge, namely exposing the substrate surface to excited atoms, ions and free radicals at atmospheric pressure has been widely used to treat composite materials surfaces for adhesive joints. The main effect of corona treatment is to introduce oxygen and nitrogen functionalities onto the composite surface, resulting in improved wetting of the surface. The corona treatments are often used to increase the number of functional groups on the surface available for bonding. This is especially important for the low surface energy thermoplastics such as polypropylene. Variables in corona treatment are the power output of the corona generator, the discharge medium, the geometry of the discharge apparatus, the treatment time and the distance of the sample from the corona. For polypropylene composite the formation of water soluble low molecular weight species on the surface may result in a weak boundary layer. For carbon/epoxy composite the best strength is obtained with corona treatment, which removes contamination and improves wetting without affecting the bulk properties of the composite. The corona discharge increases surface tension and some cases alters the surface chemistry by oxidizing the polymer matrix, which results in the increase in joint strengths.

2.3.2. Plasma

The plasma treatment involves a low-pressure plasma gas, which is electrically conductive and consists of excited atoms, ions and free radicals. After this treatment results an

improvement of the adhesion properties of the composite surface. Plasma treatments will cause chemical and texture changes to a surface. In the plasma process the surface is exposed to ionized gases, usually generated by radio frequency energy in low pressure chamber. The plasma region contains a high concentration of reactive species, such as ions and electrons, which are formed from the gas. Various studies have indicated that these energetic species interact with the surface and cause chemical changes (these changes are dependent upon the gas used to create the plasma). 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: surface cleaning, degradation of the polymer chains, removal of the material from the surface, formation of radicals on the surface, and respectively change of tacticity of the polymer chains. The main parameters in plasma treatment are the plasma medium, distance of the sample from the plasma and the exposure time. It was felt that the plasma treatment increases surface roughness and carbonyl, did not remove silicone release agent and was more controllable than acid etching because the chromic acid was very aggressive towards the resin and rapidly etched away the surface. Oxygen and nitrogen plasma will be effective bonding pretreatments for thermoplastic composites [2].

2.3.3. Flame

The treatment of a surface with a flame can oxidize the surface and if treated for long enough, the surface texture. An oxidizing flame is very similar to a gas plasma in that it contains excited species such as atoms, ions and free radicals, which oxidize the surface of the composite materials. The important variables in flame treatment are the type of gas, the ratio of gas to air or oxygen, the flow rate of the gas/air mixture, the exposure time and the distance from the surface to the flame. All types of flame gave similar improvements in shear strength and that the improvement was thought to be due to increased oxygen content at the surface.

2.3.4. Excimer laser

The variables in excimer laser etching are the energy density, laser wavelength and the number of laser pulses. This treatment has reported for the bonding of polyetherimide and polycarbonate. When applied to composite surfaces, excimer laser radiation preferentially etches the organic matrix and causes minimal fiber damage. Surface contaminations such as fluorocarbons and silicones are completely removed.

2.4. Chemical treatments

The chemical methods may occur following changes: removal of weak material, roughening, and introduction of functional groups into the polymer [1].

Perhaps the simplest method of removing contaminants from a surface is to tissue wipe with a solvent. The effectiveness of the treatment will depend on the contaminant and the solvent used. There is the possibility that, rather than removing the contaminant; the process will just spread the contamination over the surface [1].

Because joining 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.

Contamination on a composite surface can also be removed using a detergent in conjunction with some form of agitation. This technique might cause problems because of the use of water. For carbon/epoxy composite very low strength is obtained with solvent or detergent cleaning and this is associated with adhesive failure. Strength is also low for joint with glass/polypropylene composite for treatment with detergent washing where the mode of failure is adhesive. The most important chemical treatments are following:

2.4.1. Solvent cleaning

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 substrates; this must be performed in a controlled atmosphere to prevent surface to-contamination. 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. The type of solvent is also important. 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.

Chromic/sulfuric acid is a widely used treatment for polypropylene and should also be effective for glass/polypropylene composites [1].

2.4.2. Primer

Primers may be applied to the composite surfaces for one or more of the following reasons:

to protect the substrate surface until joining is carried out, to increase surface wettability, to block pores of porous surface thereby preventing adhesive escaping, for corrosion inhibition, to form chemical bonds with the adherend and the adhesive. Commercial primers are usually chlorinated polyolefins in a solvent such as toluene.

CONCLUSIONS

Analyzing and comparing all the surface treatments methods one can draw the following conclusions:

1) a variety of surface pretreatments have been used with various degrees of success to increase surface tension, increase surface roughness, change surface chemistry and increase bond strength and durability of composite adhesive joints;

2) the efficiency of a surface treatment depends on the nature of the adherend and on the depth of treatment. There is often a compromise between the functionalisation and the degradation of the surface. Selection of surface pretreatments for composite materials including: cost, environmental impact and stability of the treated surface in service;

3) the intention of surface treatment is to modify the chemistry or morphology of a thin surface layer without affecting the bulk properties. The effectiveness of any surface treatment is dependent upon the type of substrate and the extent of the treatment. For instance, solvent cleaning some substrates will remove surface contaminants but the same solvent on the other substrates may interact with the surface and bulk causing morphological changes. Etching treatments, such as with acid or by laser techniques, may cause chemical modification at low treatment levels, but at high treatment levels may introduce large surface texture changes. Electrical discharge treatment may result in a temperature rise on a surface and therefore can cause surface texture changes due to localized melting;

4) a clean surface is a necessary condition for adhesion but is not a sufficient condition for bond durability. Solvent decreasing does not promote the formation of acceptable surface conditions for longer term joint durability;

5) typical composite surface treatments include traditional abrasion/solvent clearing techniques for thermoset composites, while

thermoplastic composites require surface chemistry and surface topographical changes to ensure strong and durable joint strengths;

6) for thermoplastic composites the primary aim of the surface treatment is to increase the surface energy of the composite substrate as much as possible. Surface treatments decrease water contact angle, increase surface tension and as a result increase joint strength;

7) with the abrasion and solvent wipe, grit blasting gave strong and durable joint strength for thermosets but very little degree of success with thermoplastic composites;

8) acid etching has produced similar results to abrasion and grit blasting, in that an increase in bond strength is recorded for thermoset polymer composites; little or no effect was recorded for thermoplastics;

9) on used an oxygen plasma surface treatment this gives a surface, which resulted in better bond strengths than alumina grit blasting, but similar strengths to chromic acid etching;

10) the flame treatment is widely used in the surface modification of thermoplastics;

11) peel ply following by the grit blasting offers the best overall mechanical performance and best durability for the composite adhesive joints and the dry peel ply is the worst (grit blast in addition to peel ply provides the most durable joins);

12) most thermosetting polymer matrix composite supports not need the chemical modification process as such a surface is not susceptible to hydration;

13) for thermoplastic composites the recommended surface preparation is a light aluminum oxide grit blast in dry nitrogen.

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