The Effect of Nylon and Polyester Peel Ply Surface Preparation on the Bond Quality of Composite Laminates

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Abstract

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The preparation of the surfaces to be bonded is critical to the success of composite bonds. Peel ply surface preparation is attractive from a manufacturing and quality assurance standpoint, but is a well known example of the extremely system-specific nature of composite bonds. This study examined the role of the surface energy, morphology, and chemistry left by peel ply removal in resulting bond quality. It also evaluated the use of contact angle surface energy measurement techniques for predicting the resulting bond quality of a prepared surface.

The surfaces created by preparing three aerospace fiber-reinforced composite prepregs were compared when prepared with a nylon vs a polyester peel ply. The prepared surfaces were characterized with contact angle measurements with multiple fluids, scanning electron microscopy (SEM), and x-ray electron spectroscopy. The laminates

were bonded with aerospace grade film adhesives. Bond quality was assessed via double cantilever beam testing followed by optical and scanning electron microscopy of the fracture surfaces.The division was clear between strong bonds (G_{IC} of 600-1000J/m^2 and failure in cohesion) and weak bonds (G_{IC} of 80-400J/m^2 and failure in adhesion).

All prepared laminates showed the imprint of the peel ply texture and evidence of peel ply remnants after fabric removal, either through SEM or XPS. Within an adhesive system, large amounts of SEM-visible peel ply material transfer correlated with poor bond quality and cleaner surfaces with higher bond quality. The both sides of failed weak bonds showed evidence of peel ply remnants under XPS, showing that at least some failure is occurring through the remnants. The choice of adhesive was found to be significant. AF 555 adhesive was more tolerant of peel ply contamination than MB 1515-3.

Although the bond quality results varied substantially between tested combinations, the total surface energies of all prepared surfaces were very similar. Single fluid contact angle measurements/water break tests were therefore not predictive of bond quality, and are recommended against. The multiple fluids used allowed the construction of wettability envelopes, a more detailed look at the surface energy profile. The envelopes of nylon and polyester prepared systems were noticeably different, but while potentially useful for detecting changes or errors in surface preparation of known systems, they were not valid for predicting bond quality in new systems. Ultimately, it was determined that wetting is a necessary but not sufficient condition for bonding.

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DEDICATION

to my daughters, Ingrid and Linnea

Chapter 1

INTRODUCTION

1.1 Motivation

Joints represent one of the greatest challenges in the design of structures in general and of advanced fiber-reinforced polymer composite structures in particular. Joints entail interruptions in the geometry of a structure and often, material discontinuities. The latter almost always produce localized areas of high stress. Monolithic structures with neither joining nor assembly would therefore be ideal [4], but real world applications and technological limitations most often require some sort of joint. As composite materials rapidly replace metal parts in racing cars, wind turbine blades, and aerospace applications to utilize their exceptional specific strength, specific stiffness, and corrosion resistance, a more complete understanding of the factors involved in creating an effective composite joint becomes critical.

In principle adhesive joints are preferable to mechanically fastened joints, and can in fact be one of the strongest parts of the structure when properly designed and executed [5], even stronger than the parent structure itself [6]. In composite materials the holes required for mechanically fastened joints are of particular concern, as not only do they create local stress concentrations [2], but they also damage the fiber reinforcement capabilities [5]. Their design is also substantially more complex than in metals, due to the existence of different failure modes, the almost infinite possible composite material and fiber patterns combinations, and complex 3D stress and strain distributions causing occasional failure at loads not predicted by either perfectly elastic or perfectly plastic assumptions [7]. Bonded joints possess better fatigue resistance and vibration damping than mechanically fastened joints, and are more structurally efficient [8]. They eliminate the need for additional fastener parts, reducing part count and weight [9]. The continuous nature of the bond produces a stronger and stiffer structure with more uniform stress distribution [5], and advantage can be taken of ductile response of the adhesive to reduce stress peaks [10]. Local stress concentrations are therefore avoided.

Despite all of the advantages to using bonded composites, historically aircraft designers faced with loss of life in the event of bond failure in service have generally avoided bonded construction in primary structures [5]. This is because of a lack of reliable inspection methods and the requirement for close dimensional tolerances in fabrication. Adhesive joints tend to lack structural redundancy and are highly sensitive to manufacturing deficiencies, including poor bonding technique, poor fit of mating parts, and sensitivity of the adhesive to temperature and environmental effects such as moisture [11]. Assurance of bond quality has been a continuing problem in adhesive joints. The durability of bonded repairs is known to be variable [12]. While IR, ultrasonic and X-ray inspection may reveal gaps in the bond, no technique can guarantee that a bond that appears to be intact does, in fact, have adequate load transfer capability [13] [14] [15] [12].

Most joint design principles are irrelevant if the adhesion between the adherends is poor. Integrity of a bond hinges on strong primary chemical bonding and, to a lesser degree, mechanical factors [?]. Surface preparation is the most important factor in bond quality [13][12], because it can remove contamination from the environment or left from processing and it can create chemically active surfaces [2]. An adhesive/adherend system that consistently creates strong bonds can still fail miserably if mistakes are made preparing the surface. Premature failure at low load is almost always attributable to bad surface preparation [16]. It is therefore of the utmost importance that surfaces be properly prepared in order to create strong bonds. Unfortunately, composite surface preparation encompasses a highly system-specific [13] complex array of techniques developed through trial and error [17], with often inconsistent results and unclear reasons for success or failure. This study examines one common surface preparation technique, peel ply removal, in depth in order to identify factors responsible for its varying resulting bond quality.

1.2 Report Organization

This report will use a review of the relevant literature to provide an overview of the chemistry of epoxies that make up the adhesives and matrixes in carbon reinforced composite materials, theoretical background of surface thermodynamics and adhesive theory, a description of bond failure modes, and a review of the techniques used in preparing composite surfaces for bonding in Chapter 2. The proposed research will be outlined in Chapter 3. Sample and testing considerations and methods will be described in Chapter 4. The investigation results will be detailed and discussed in Chapter 5. Chapter 6 will analyze the the results of the study globally, discussing the overall outcomes of the study. Areas with potential for further work will be suggested in Chapter 7, and finally conclusions will be summarized in Chapter 8.

Chapter 2

BACKGROUND AND LITERATURE REVIEW

2.1 Composite Fundamentals

The materials of interest to this study are the carbon-reinforced (both woven and unidirectional) epoxy matrix composites used in aerospace. The focus here is on secondary bonding processes. These materials require surface preparation before bonding, and are then joined using epoxy-based adhesives.

2.1.1 Chemistry of Base Epoxy Resins

The resins used in the carbon fiber prepreg and the adhesives of interest to this study are epoxy-based, as that is most common in advanced composite materials [13]. They consist of an epoxy resin that hardens to give a thermosetting polymer by step-growth polymerization or addition polymerization [2]. Epoxies generally out-perform most other resin types in terms of mechanical properties and resistance to environmental degradation, which leads to their almost exclusive use in aircraft components [13] [1]. These resins are formed from a long chain molecular structure with two oxirane rings, a chemical group consisting of an oxygen atom bonded to two carbon atoms that are already bonded in some way, as their reactive moiety at each end. Epoxies have the largest variety of structural adhesives because of the substantial number of

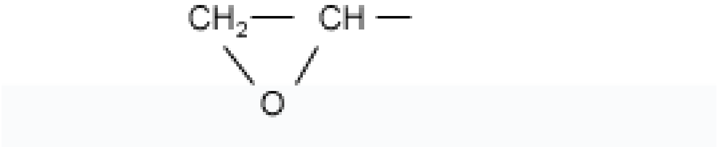


Figure 2.1: The idealized chemical structure of a simple epoxy [1]

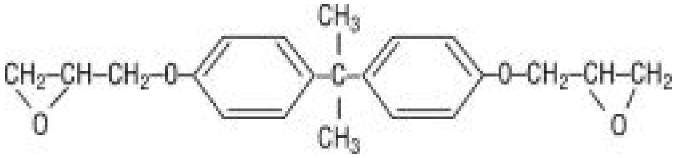


Figure 2.2: Idealized chemical structure of a typical epoxy [2]

crosslinking reactions to which oxirane groups are sensitive [2]. The simplest epoxy is a three-member ring structure known by the term 'alpha-epoxy' or '1,2-epoxy'. The idealized chemical structure is shown in Figure 2.1 and is the most easily identified characteristic of any more complex epoxy molecule.

The typical epoxy molecule, as shown in Figure 2.2, also contains two ring groups at its center which are able to absorb both mechanical and thermal stresses better than linear groups and therefore give the epoxy resin very good stiffness, toughness and heat resistant properties.

Epoxies are also advantageous because the liquid resin and the curing agents form low viscosity easily processed systems, and they have high adhesive strength, mechanical properties, electrical insulation, chemical resistance, and water resistance [2].

2.1.2 Epoxy Resin Additives

Unless epoxy resins are modified, they can be very costly, have overly high viscosity and be too rigid for some applications. To resolve these issues, diluents, fillers, and/or flexibilizers can be added, or the resins can be mixed with other resins.

Diluents, which are added in amounts usually less than 10 phr to reduce the viscosity of a resin, are usually reactive fluids such as phenyl glicidyl ether, butyl glycidyl ether, or acetylene oxide. If they are used in systems, such as those in this study, that are cured under vacuum care must be taken to remove the resulting volatiles. Diluents do generally have an adverse affect on the physical properties of the epoxy and retard cure. Fillers such as sand or asbestos, which reduce cost and curing shrinkage, give lower coefficient of expansion, and reduce exotherms, are primarily used in tooling and casting applications, and are uncommon in the aerospace applications related to this study [18].

The highly cross-linked structure of epoxy resins causes them to absorb insignificant amounts of energy during the fracture process [19], and therefore be very brittle. The cured epoxy resins have fracture energies (G_{IC}100 to 200 J/m^2) two orders of magnitude lower than do thermoplastics and other high-performance materials [20]. So most of the research has been focused on improving the relatively poor fracture properties of epoxy resins, either by reducing the cross-linked density of the epoxy network or by modifying commercially available epoxy resins with secondary components. In the literature, the modifiers have been classified into four main groups: low molecular weight liquid rubbers, engineering thermoplastics, reactive ductile diluents, and inorganic/hybrid particles.

Plasticizers and flexibilisers are used in epoxies to improve the flexibility and toughness of resins. Elastomers are added in order to create an epoxy adhesive that is capable of absorbing energy, which can happen through one of two mechanisms. If the elastomer is soluble in the uncured epoxy but not in the cured, toughening occurs by phase separation. The discrete pockets of the elastomer phase are then uniformly dispersed in the cured epoxy resin. These small, well-bonded rubber particles leave the matrix essentially unchanged but now able to absorb energy and blunt cracks [2]. These epoxies will then have two glass transition temperatures, and have significantly smaller increases in extensibility than flexibilized epoxies [1]. If instead the epoxy is flexibilized the elastomer is soluble in the resin both before and after cure, and has a single lower glass transition temperature. In this method, a reduction in modulus results in decreased lap shear properties is exchanged for higher flexibility and extensibility [1].

While very effective at increasing the toughness of epoxies, the above additions often also have the effect of decreasing their modulus or tensile strengths and creep resistance [21]. Elastomer modification is also only effective in polymers with low crosslinking, and avoided in the highly-crosslinked epoxies which compose most advanced thermoset resins used in aerospace [22]. Engineering thermoplastics offer improved toughness without such dramatic detrimental effect, with significant reduction of stiffness only at temperatures near the glass transition temperature of the thermoplastic [23]. Nylon has been used for such toughening, as the epoxy resin crosslinks the nylon through the reaction of oxirane group with amide nitrogen in nylon chain [24]. Toughening occurs through the mechanisms of (1) primary crack bridging, (2) crack bifurcation and crack path alteration, (3) formation of steps and welts and secondary crack bridging, (4) ductile fracture of the particles, and (5) initiation of secondary cracks [25].

When thermoplastics such as polyether sulfone [26] or poly(ether imides) [27] were originally used with purely mechanical blending with no chemical reaction, they were ineffective. Hedrick et al, however, resolved the problem of poor interfacial adhesion between the thermoplastic modifiers and the epoxy by engineering amine-terminated polysulphone oligomers and mixing at elevated temperature to allow for chemical reaction [28]. The resulting homogeneous mixture undergoes spinodal decomposition during cure, and a two-phase microstructure is formed [29]. Thermoplastics increase the toughness of epoxies through the mechanisms of plastic yielding or drawing and tearing of thermoplastic rich phases [23].

2.1.3 Cure Kinetics of Epoxy Resins

The primary advantage of epoxies is their low shrinkage during cure, which minimizes internal stresses. Curing occurs quickly and easily at a temperature dependent on the choice of curing agent. Alcohols, mercaptans, anhydrides, or Lewis acids can act as curing agents for epoxy resins, or they can be polymerized anionically as can be seen in Figure 2.3 [1] [13]. The most common curing agent used with epoxy resins is based upon an amine, which can react at room temperature without a catalyst. The primary aliphatic amine is the most common basis for a curing agent at room temperature, but aromatic amines can also react, though much more slowly than at elevated temperatures [2]. The epoxies used in this study cure at 121^o C (250^o F) and 176^o C (350^o F), and therefore are hardened with aromatic amines.

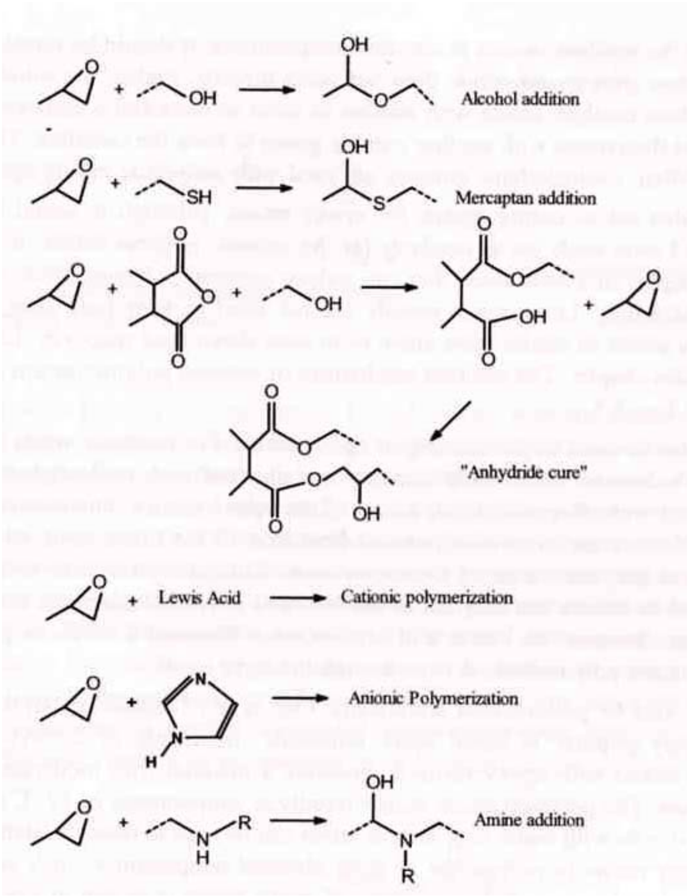


Figure 2.3: Chemistry of curing reactions for epoxy resins [1]

The overall state of an epoxy reaction is characterized by the fraction of epoxides that have been reacted, which is referred to as the degree of cure and usually assigned the letter α. The degree of cure and its rate of change, $\delta\ \alpha/\delta$ t, are the main parameters studied in cure kinetics investigations.

Amine-cured epoxy resins are governed by an autocatalytic reaction. The epoxy group reacts with a primary amine to produce a secondary amine, which then reacts further to form a tertiary amine [30]. The by-products of this epoxy-amine reaction are hydroxyl groups, which further catalyze and accelerate the production reaction and react with the epoxy rings to form ether linkages. Due to the high curing temperatures required by the aromatic amines speeding the epoxide-hydroxyl reaction, and the frequent significant excess of epoxy with respect to amine, this etherification becomes more important in aerospace epoxy curing than in other systems and complicates the mathematics of cure kinetics considerably [31].

The most frequently used mathematical model for the autocatalytic reaction is semiempirical and was developed by Kamal and co-workers [32].

$$\frac{\delta\alpha}{\delta t} = (K_1 + K_2\alpha^m)(1-\alpha)^n \tag{2.1}$$

where K_1 and K_2 are the rate constants and m and n are the reaction orders. The variable exponents are temperature dependent and allow for a good fit to data, but this equation does not explicitly take into account the etherification reaction [32].

2.2 Adhesive Theory and Surface Thermodynamics

In this work the consideration of epoxies is in the context of secondary bonding. The cured carbon fiber reinforced epoxy laminates are bonded to each other using an engineered epoxy adhesive in a second curing step. Adhesion is a complex set of interactions that is not completely understood. Fundamentally, two surfaces (in this study, epoxy) are brought together and intermolecular forces are engaged across a significant portion of the area of an adhesive interface. The inherent roughness and contaminatibility of surfaces prevents the situation from being quite so simple, however. At least one of the surfaces must be liquid (the adhesive), which is applied to a solid surface (the adherend), and the adhesive interface is created upon cure of the adhesive [33].

The adhesive interfacial strength can then be considered a measure of the quality of the resulting bond. In general, there are two variables available for improvement of the interfacial strength: 1) the chemistry of the adhesive, and 2) the chemistry or morphology of the surface [33]. In order to determine how best to structure these elements, an understanding of the mechanisms of adhesion and the surface thermodynamics involved in bonding is required.

2.2.1 Mechanisms of Adhesion

There are differing mechanisms through which adhesion occurs, any or all of which can be involved in bonding to a varying degree. The mechanisms of adhesion include 1) electrostatic, 2) diffusion, 3) adsorption, and 4) mechanical interlocking.

Electrostatic Mechanisms

Derjaguin asserts that nearly all adhesion phenomena could be explained by electrostatics [1]. The basis of the theory is that an electropositive material donates charge to an electronegative material, thus creating an electrostatic bi-layer at the interface. The strength of the adhesive bond then comes from the force necessary to overcome the Coulombic forces to move the charged surfaces away from one another. The work to break the adhesive bond is then

$$W_B = 2\pi\sigma_o^2 h_B \tag{2.2}$$

where W_B is the work to break the bond, σ_o^2 is the surface charge density, and h_B is the distance of separation at electrical breakdown in the air gap formed when the two materials are separated [1].

Smith and Horn provided the work that showed most definitively that there can be an electrostatic component to adhesion. They showed that a change was formed when silica and mica were brought into contact, meaning that charge had been transferred between the two materials [34]. The large difference in electronegativity between silica and mica is likely why this could be detected, while it has not been in bonds of dissimilar polymers [35]. Electrostatics can likely play a role in adhesion up to determining the strength of an adhesive bond, but only in cases of large material electronegativity differences. It is therefore unlikely that elecrostratics are a large component of the adhesion in the epoxy matrix-epoxy adhesive bonding of composite joints.

Diffusion Mechanisms

In most cases the adherend and adhesive have very different properties, and the point of their contact provides a stress concentration. In the case of diffusive bonding, two materials soluble in one another forming a solution when brought into close contact, an interphase exists in which properties of one material change gradually into the properties of the other. In this situation, ultimate adhesion is obtained [1]. The criterion for solubility is the solubility parameter,

$$\delta = (\frac{E_{coh}}{V})^{-1/2} = (\frac{\Delta H_v - RT}{V})^{-1/2} \tag{2.3}$$

where E_{coh} is the cohesive energy of the material (the amount of energy necessary to take all of the atoms or molecules in a mole of material and separate them to an infinite distance), ΔH_v is the molar heat of vaporization, R is the gas constant, T is the temperature (K), and V is the molar volume [2]. In a solution for which there are no specific chemical interactions, the enthalpy of solution of materials 1 and 2 is given by

$$\delta H_{soln} = \phi_1 \phi_2 (\delta_1 - \delta_2) \tag{2.4}$$

where σ_i is the mole fraction of component i. This equation predicts no exothermic reactions. The most negative value of ΔH_{soln} possible is 0, the point where the solubility parameters of the materials is the same [1]. Therefore, the best adhesion occurs when two materials have equal solubility parameters.

Voyutskii is the main proponent of diffusion theory for autohesion of polymers; the intrinsic adhesion of polymers to themselves. In order for the solubility parameters to be similar and diffusion to occur, the chain segments of the polymers in both adhesive and substrate possess sufficient mobility and be mutually soluble, as well as being amporphous [36]. Vasenin [37] developed quantitative models or diffusion theory beginning with Ficks law and ending with a relation between peel energy P, the time of contact t_c, and molecular weight M of the polymers used:

$$P = k_4(\frac{2N\rho}{M})^{2/3} D_d t_c^{1/4} \tag{2.5}$$

where D_d is a constant that characterizes the mobility of the macromolecules, N is Avagadros number, and k_4 is a constant that may be expressed in terms of molecular characteristics of the polymers involved. This model does not take into account the energy dissipated by viscoelastic means and plastic deformation during a fracture test, but provides good agreement with the experimental data. These factors are most likely contained in the constants [2]. Anand has proposed, however, that the contribution of diffusion to intrinsic adhesion is minimal compared to that from the formation of interfacial secondary bonds, since the dependence of the measured joint strength on parameters such as time of contact and polymer molecular weight may readily be explained by their effect on the kinetics of wetting [38].

Adsorption (Acid-Base)

The idea that materials will adhere because of interatomic and intermolecular forces established between atoms and molecules in the surfaces when the adherend and adhesive are brought into sufficiently close contact is the most widely applicable theory of adhesion. Secondary bonds (van der Waals and hydrogen) are most common, but chemisorption (covalent, ionic, or metallic bonds) may also occur. In certain circumstances, interfacial molecular complex structures may even be formed. There is a great deal of experimental work that shows secondary bonds to be the only mechanism of adhesion in many different adhesive joints, and that establishing primary bonding across the interface requires the use of special techniques such as incorporating certain side groups along the polymer chain of the adhesive, the use of certain phenolic and organometallic primers, or simultaneously bonding and crosslinking elastomeric adhesives against a reactive surface [2]. Pritchard found an example of hydrogen bonding playing an important role in the adhesion of nylon cords dipped into a complex adhesive mixture of rubber and resorcinol-formaldehyde, as the resorcinol-formaldehyde was adsorbed onto the nylon surface via hydrogen bonds through the phenolic groups [2]. Hydrogen bonding has also been shown to play an important role in the autohesion of polymers which have been subjected to surface oxidation by immersion in certain acids or exposure to corona discharge [2].

Donor-acceptor bonds (or acid-base interactions) are an important subset of interactions that occur at interfaces. Materials may fit one of three descriptions of acid-base capability:

1. Proton donors/electron acceptors (acids): partially halogenated molecules, sil-

ica, Fe_2O_3, Fe_3O_4, and others

2. Proton acceptors/electron donors (bases): esters, ketones, ethers or aromatics, calcium carbonate, amorphous hydroxides of iron oxide, etc
3. Act as both (1) and (2): amides, amines, alcohols, $\alpha-Al_2O_3$, boehmite, bayerite, etc

Fowkes [39] believed that the primary interactions at interfaces were due to dispersion, not polar forces, and that the remaining interactions were acid-base. He promoted the idea that polar forces were not involved in interfacial phenomena and expressed the surface energy into its component parts, modifying the Owens-Wendt equation for the work of adhesion

$$W_A = 2(\gamma_1^d \gamma_1^d) + W_A^{AB} \tag{2.6}$$

where W_A^{AB} is the component of the work of adhesion due to acid-base interactions, which Fowkes defined using the work of Drago as

$$W_A^{AB} = kN^{AB}(E_A E_B + C_A C_B) \tag{2.7}$$

where N^{AB} is the number of acid-base pairs that interact in the interphase or at the interface, K is a proportionality constant that corrects for units and E and C are the electrostatic and covalent contribution to the enthalpy of interaction experimentally developed by Drago. Fowkes then demonstrated that the work of adhesion increases with the acidity or basicity of the substrate and probe liquid (the predictor of acid-base interactions) [40]. Though there are few studies that have connected the acid-base character of interfaces with the actual forces of adhesion between them, there are experimental results implying the dominance of the acid-base interaction in some cases [2]. Examples include that basic materials bond well to silica (an acidic surface) and acidic materials bond well to glass (which is made basic due to additives to the glass). Secondary bonding should be more than sufficient for quality bonds. Fowkes, for example, calculated that including dispersion forces alone, the strength of polyethylene/steel butt tensile joints should be more than 157000 psi. The reason that this is not seen in practice is the presence of environmental effects such as humidity. In the presence of water, systems depending on dispersive components of secondary bonds become unstable. If covalent primary bonds were at the interface, however, water would first have to hydrolize those bonds before it could act on the interface [1].

Mechanical Interlocking

Rough surfaces also increase bond strength due to the increase in surface area in contact they represent. If the area of contact is increased by a large amount, the total energy of surface interaction increases by an amount proportional to the surface area [2]. Surface interactions are responsible for the success of bonds, and the sum of those interactions will scale as the area of contact.

Mechanical abrasion is known to increase measured joint strength, but there is little indication of the creation of the ink-bottle shaped cavities that would allow mechanical interlocking to be the major mechanism of adhesion by preventing the cured adhesive from pulling away from the surface. In industry, the major purpose of grit-blasting is rather to clean the substrate; allowing better wetting and removing any weak boundary layer [1].

Surface roughness also aids the kinetics and thermodynamics of wetting. Bascom et al showed that open pores will fill ahead of the advance of the primary film and random surface scratches may increase the spreading rate of some liquids by as much as 50% [41]. A liquid that would not normally wet a surface may spread along fine pores, scratches, and other inhomogeneities by capillary action. Bascom and Patrick suggested that this effect might cause redistribution of the adhesive even when the initial application is under pressure [42].

If an adhesive placed on a rough surface can flow into nooks and crannies, the two materials are left in intimate contact along a complicated path. A crack propagating through the bond does not have an abrupt plane of stress transfer found if two smooth surfaces have been bonded, but rather encounters a lock and key situation in which the adhesive in a pore cannot move past the overhang of the pore without plastically deforming. Plastic deformation consumes energy and makes the bond strength appear higher. This effect was best demonstrated by Arrowsmith in his work varying the surface roughness of copper [43].

The distance a pore is penetrated by an adhesive is given by the equation

$$x^2(t) = r\gamma_{LV}\cos\theta_\infty/(2\eta)(t - a/c + ae^{-ct}/c) \tag{2.8}$$

where r is the radius of the pore $\theta(t)$ is the time dependent contact angle, η is the viscosity of the adhesive, and a and c are adjustable parameters [11]. Although the depth penetrated increases with pore diameter, it does not increase as quickly as pore volume. The smallest pore radii then allow for the most complete removal of air.

Perrins and Pettett were able to confirm mechanical interlocking controlled adhesion of electroplated copper to polypropylene, because the interfacial component of adhesion could be completely removed with proper surface pretreatment while the mechanical component could only be minimized. Most importantly, their work allowed the contributions from mechanical interlocking and chemical interfacial effects to the intrinsic adhesion to be distinguished [44].

Adhesion may be obtained with smooth surfaces, however, as shown by the examination of adhesion between two perfectly smooth mica surfaces by Tabor et al [45] and adhesion to optically smooth rubber surfaces by Johnson et al [46]. Though there may be some mechanical interlocking aspect to bonding, it seems that surface roughening creates higher bond strengths primarily by increasing the degree of interfacial contact and more extensive energy dissipative deformations being initiated in the adhesive.

Theoretical Criteria for Adhesion

Pocius [1] summarized the significance of these mechanisms of adhesion as seven fundamental criteria for the creation of strong bonds:

1. The adhesive and adherend have the same solubility parameter to allow diffusion.
2. The adherend has micromorphology and the adhesive has low enough viscosity

to completely fill these features to maximize mechanical interlocking.

3. The adhesive and adherend must come into intimate contact, minimizing interfacial flaws.
4. The adhesive should have surface energy less than the critical wetting tension of the adherend so that wetting can occur (and intimate contact will exist).
5. The adhesive and adherend have opposite character in order for acid/base interactions to take place.
6. In adverse environmental conditions provide for interfacial covalent bonding, as secondary bonds will not be sufficient.
7. Weak boundary layers are removed or modified to be cohesively strong.

2.2.2 Interphases and Weak Boundary Layers

Rather than molecularly distinct boundaries between parent materials in a resulting adhesive bond, the literature supports regions of transition between the adhesive and adherend material [47][48]. In other words, there is an interphase rather than true adhesive interfaces. Interphases are generally classified as transcrystalline growth, crosslinked adlayers, interdiffusion, and molecular interdigitation (the gripping caused by long-chain molecules reaching into the opposite material) [1]. They could be as thin as 1nm, or as thick as several micrometers. The surface energy considerations and interface energetics are still important, however, as they represent the driving forces for formation of interphase regions [47]. Transcrystalline growth is unlikely to be involved in epoxy systems, but the other three interphases may be represented.

All of the considerations for adhesion are highly surface-specific, so an unexpected boundary layer can be of great consequence. Bikerman described how failure could occur via a fracture within a weak interfacial layer between two materials. He considered seven classes of weak boundary layers, variations on air pores, impurities, and reactions [49]. Though the Bikerman model was simple and criticized in the past, it is now admitted that many cases of poor adhesion can be attributed to these weak interfacial layers [50].

Robertson discovered that a boundary layer only becomes a weak boundary layer causing premature bond failure if it exceeds a critical thickness. In his study of polystyrene and poly(methyl methacrylate), this was 1μ m. He theorized that this could be because of the fracture path waviness, and the ability of a craze to disguise the position of the weakness from the stress field ahead of the craze front by bearing load. The critical thickness therefore depends on the molecular weight of the boundary layer, falling to less than 100Å for non-polymeric materials. His other theory was that the material of the thin layer had become discontinuous and dispersed as droplets in the primary material. The droplets would not be able to diffuse in that material, and so would stay as globules in a narrow band at the surface. These globules would enhance the initiation of secondary fractures ahead of the main crack, blunting it. Crack propagation would then require more energy, and likely slow. The crack would then propagate faster in the primary material and not exhibit the expected tendency to fracture in the weaker layer material. Different areas of Robertsons fracture surfaces supported each of these mechanisms, so he concluded that they might work together to result in the high fracture toughness observed [51].

2.2.3 Surface Thermodynamics

The interactions and mechanisms of adhesion described above occur in a very shallow band on the surface of the materials. Molecules at the surface of a solid are missing the interactions of atoms in the plane above them that they would have if in the bulk. In order to increase the force in the plane of the surface and counteract the imbalance of forces at the surface due to these unrequited valences, the atoms move further apart. The resulting difference in energy between the molecules at the surface and the molecules in the bulk is the surface energy. The surface energy of a material is related to its bulk mechanical properties. For example, higher surface energy materials have higher stiffness, E, according to the relationship [1]

$$E = \frac{32\gamma}{r_o} \tag{2.9}$$

where E the stiffness modulus, γ is the surface energy, and r_o is the equilibrium distance.

Surface tension and surface energy are identical for liquids [2]. The former is usually given in units of dynes/cm or N/m and the latter in units of mJ/m$\hat{2}$. The interaction of two surfaces depends on the density of molecules on the surface, the equilibrium distance between them (the intermolecular spacing), and an attractive constant. The total energy from their presence depends on intermolecular spacing and intermolecular forces. If a material breaks (or a crack is propagated), the work done on the sample is dissipated in creating two new surfaces. This can be expressed as the work of cohesion [1]

$$W_{coh} = 2\gamma \tag{2.10}$$

If instead two dissimilar materials are split from intimate contact, the energy expended would be the sum of the energies of the two surfaces created (γ_1 and γ_2), minus the intermolecular forces present when they were in contact (γ_{12}). This work of adhesion is expressed by the Dupre equation [2]:

$$W_a = \gamma_1 + \gamma_2 - \gamma 12 \tag{2.11}$$

The work of adhesion is a thermodynamic parameter and therefore is not affected by factors such as rate, thickness of the adhesive, or other physical characteristics of the bulk.

Contact angle measurements are an important tool in determining surface energy. The Young Equation [2] relates the contact angle measured to the tensions at the three-phase contact point shown in Figure 2.4 as

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} cos\theta \tag{2.12}$$

where γ_{sv}, γ_{sl}, γ_{lv} are the solid-vapor, solid-liquid, and liquid-vapor surface energies, respectively.

In these terms the Dupre equation (equation 2.11) becomes

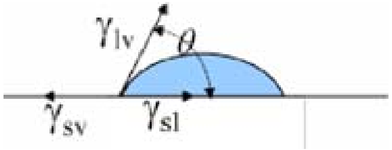


Figure 2.4: Contact angle, surface energy relationship [2]

$$W_a = \gamma_1 + \gamma_2 - \gamma_{sl} \tag{2.13}$$

The surface energy of a solid in a vacuum may be considerably higher than γ_{sv}. The solid-vapor interfacial energy and the true surface energy are related by

$$\gamma_{sv} = \gamma_s - \pi_e \tag{2.14}$$

where π_e is the equilibrium spreading pressure and γ_s is the true surface free energy of the solid. Equation 2.14 can then be expressed in terms of contact angle by use of the Young Equation [2] to become:

$$\gamma_s = \gamma_{sl} + \gamma_{lv}\cos\theta + \pi_e \tag{2.15}$$

The equilibrium spreading pressure is a measure of the energy released through adsorption of vapor on the surface of the solid, and therefore is important when the solid surface energy is high and the liquid surface energy is low.

By combining equations 2.12 and 2.14, two easily determined quantities (θ and γ_{lv}) can be used to determine the thermodynamic parameter, W_a [1]:

$$W_a = \gamma_{lv}(1 + \cos\theta) \tag{2.16}$$

When the contact angle of the liquid is greater than 0^o, the liquid is non-spreading. When $\theta = 0^o$, the liquid wets spontaneously and spreads over the surface at a rate dependent on viscosity, roughness, and other factors. The criteria for spontaneous wetting to occur can therefore be expressed as

$$\gamma_{sv}\gamma_{sl} + \gamma_{lv} \tag{2.17}$$

Or by defining the equilibrium spreading coefficient

$$S = \gamma sv - \gamma sl - \gamma lv \tag{2.18}$$

where wetting will occur spontaneously and completely when S 0 [2]. Zisman was able to use contact angle measurements to determine a criterion for wettability known as the critical wetting tension γ_c. He found that for liquids that form a homologous series such as n-alkanes on a non-wetting surface, a linear relationship exists between the energy of a surface and the cosine of the contact angle made by a liquid on it. When plotted this line can be extrapolated to $cos\theta = 1$, thereby predicting the liquid surface tension required for spontaneous wetting. A contact angle measurement can be used to determine the critical wetting tension through the relationship

$$\cos\theta = 1 + b(\gamma_c - \gamma lv) \tag{2.19}$$

where b is the slope of the line [52][53][54]. Quasi-linear relationships are found for a wide range of liquids. Upon measurement of both homologous and non-homologous series of liquids on a number of polymeric surfaces Dann found that different liquid series give different values of critical surface tension, and that the linear relationship between the cosine of the contact angle and the surface tension of the liquid is normally a curve of a power form [55]. Kitazaki and Hata found that γ_c is dependant on the type of liquid used and proposed measurement of a different γ_c for a series of dispersion force, hydrogen bonding, and polar liquids [56]. Dann also demonstrated that when only dispersion forces exist, the critical surface tension equals the dispersion force component of the surface free energy of the solid, so measurement of such a series provides a method for determining the true surface free energy of the solid [55].

In general, the surface is assumed to be perfectly rigid and smooth, as both surface roughness and chemical inhomogeneity on the surface can cause variance in measurement [57]. To describe a solid as ideally rigid and insoluble is a very good approximation in many low temperature systems. However, at high temperatures the major characteristic of wetting is reactivity. Many liquid/solid couples are then far from chemical equilibrium. The resultant interfacial reactions therefore can strongly modify the interface chemistry, structure, and topography, and in turn affect both spreading kinetics and the ultimate degree of wetting. Ceramic and metal surface properties, for example are extremely sensitive to contamination such as oxygen from the furnace atmosphere [58].

Also in contrast to low temperature systems, in which the vertical component of surface tension is resisted by elastic distortions of the solid (which are usually negligible), when the substrate is not perfectly rigid and inert the vertical force causes deformation of the solid at the triple point (where the solid-liquid, solid-vapor, and vapor-liquid boundaries meet). Then, equilibrium at the junction requires motion of the triple line (the line of contact) both horizontally and vertically [59][60][61][62]. For high temperature systems that have been studied, such as molten metals or oxides on ceramics or metals, the experimental temperatures are typically $0.2 - 0.5T_m$ of the substrate, which will lead to some local diffusion or solution-precipitation. Under these conditions, a small ridge will eventually develop at the triple junction. The perturbation will propagate until complete equilibrium ultimately ensues [63].

At these high temperatures before cure the viscosity of the adhesive is low. The result of this is that during reactive spreading the drop radius is equal to the reaction product radius, i.e. the positions of the triple line and of the radial reaction front are identical [64]. While liquids and solids at these high temperatures tend to interact with strong primary bonding, it has recently been shown that the chemical reactions that occur at interfaces under increased temperature do not necessarily imply an improvement and can even have a detrimental effect on wetting [65].

The spreading time to reach wetting equilibrium in reactive systems is almost always different than that of non-reactive systems, but it is not consistently higher or lower. This means that the rate of spreading is not controlled by viscous resistance, but by the interfacial reaction itself [58]. This work has been done on ceramics or metals, and not on polymeric composites, but it is reasonable to assume that some of the same considerations apply and that care should be taken when extrapolating room temperature contact angles to high temperature systems.

By comparing the rate of the chemical reaction at the triple line to the rate of diffusive transport of reactive solute from the drop bulk to the triple line, two limiting cases of reactive spreading can be defined; adsorption at the liquid side of the interface-active elements and replacement at the solid-side of the interface of the initial substrate by a 3D reaction product [58].

In the first case the transport within the droplet is comparatively rapid. The reaction does not change the global drop composition significantly (the chemical environment of the triple line is constant with time, and a steady configuration is established at the triple line during wetting. In this situation, the rate of reaction and hence the triple line velocity are constant with time and the drop base radius R is then written as

$$R - R_o = K_1 t \tag{2.20}$$

Where R_o is the initial drop base radius and K_1 is a system constant, independent of the drop volume [66].

In the second case, the rate of lateral growth of the reaction product at the triple line is limited by the supply of reactant from the drop bulk to the triple line. This occurs when local reaction rates are comparatively high. Because the contact angle decreases continuously during wetting, the reduction in transport within the droplet will lead to a continuous decrease in the reaction rate and, as a result, in the rate of movement of the triple line itself. Therefore, time-dependent spreading rates are expected in this case [66]. On the other hand, Saiz, Cannon, and Tomsia [67] have proposed that in many reactive cases the large decrease observed in wetting angle is a consequence of adsorption, and that frequently observed slow spreading rates and wetting hysteresis are often controlled by the dynamics of a triple line ridge.

Two types of kinetic wetting behaviors have been identified; the linear spreading controlled by the reaction kinetics at the triple line, and the nonlinear spreading controlled by diffusion in the drop bulk. In the latter case, the spreading rate correlates linearly with the instantaneous contact angle. These types of spreading behaviors have only been verified qualitatively [58]. Identifying the relevant driving forces is a critical, unresolved issue in treating kinetics.

Wetting is a complex combination of surface composition and the macro- and micromorphology [68], and these issues raise some questions about the validity of contact angle measurements. In general, however, the simplicity and usefulness overcome the limitations of the method. They are especially valid as a tool of comparison for the changes of a surface within a set or differences between sets.

Another use for the critical wetting tension of a solid surface is to characterize its chemistry. Zisman demonstrated that surfaces composed primarily of CH_2 groups had a higher critical wetting tension than those composed primarily of CH_3. Similar relationships were found between CF_2 and CF_3, as well as for partially fluorinated hydrocarbons and partially chlorinated hydrocarbons [52].

Good and Girafalco [69][70] defined a thermodynamic parameter in order to describe the interfacial free energy in terms of the surface free energies of pure phases. This parameter, ϕ, is known as the interaction parameter:

$$\phi = \frac{W_A}{(W_{coh,1} W_{coh,2})^{1/2}} \tag{2.21}$$

Inserting the definition of W_{coh} (equation 2.10) and the Dupre equation (equation 2.11) in order to express ϕ in terms of surface free energies γ for two phases 1 and 2 gives

$$\phi = \frac{\gamma_1 + \gamma_2 - \gamma_{12}}{2(\gamma_1 \gamma_2)^{1/2}} \tag{2.22}$$

which can be rearranged to

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\phi(\gamma_1 \gamma_2)^{1/2} \tag{2.23}$$

The attractive constants for a number of liquids are known which allows ϕ to be determined, and the interfacial energy between the two phases can then be calculated. These results give credence to the idea that molecules can act at interfaces in the same way they interact in their own bulk material, and that calculations of those forces are straightforward [1]. Furthermore, the true surface free energy of the solid can be obtained by combining its previous definition with the Good-Girifalco relationship

$$\gamma_s = \frac{\gamma_{lv}(1 + \cos\theta)^2}{4\phi^2} \tag{2.24}$$

Setting $\theta = 0$ it is evident that the relation of γ_s to γ_c [2] is

$$\gamma_c = \phi^2 \gamma_s \tag{2.25}$$

Fowkes hypothesized the additivity of components; the surface free energy of a pure phase can be represented as the sum of contributions from dispersion and polar force components:

$$\gamma_a = \gamma_a^D + \gamma_a^P \tag{2.26}$$

where the latter term incorporates all the non-dispersion force components [39]. Investigation into this theory of fractional polarity lead Owens and Wendt [71] to propose the somewhat controversial hypothesis that the surface tension between a solid and liquid is given by the sum of the solid-vapor and liquid-vapor surface tensions minus the geometric means of the polar and dispersive components

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2(\gamma_{sv}^D \gamma_{lv}^D)^{1/2} - 2(\gamma_{sv}^P \gamma_{lv}^P)^{1/2} \tag{2.27}$$

and that the work of adhesion can be similarly expressed

$$W_A = 2(\gamma_{sv}^D \gamma_{lv}^D)^{1/2} + 2(\gamma_{sv}^P \gamma lv^P)^{1/2} \tag{2.28}$$

Combining this with the Youngs Equation (equation 2.12) yields the prediction of wetting if

$$\gamma_{lv} \leq (\gamma_{sv}^{D}\gamma_{lv}^{D})^{1/2} + (\gamma_{sv}^{P}\gamma - lv^{P})^{1/2} \tag{2.29}$$

By setting

$$\gamma_{lv} - (\gamma_{sv}^{D}\gamma_{lv}^{D})^{1/2} - (\gamma_{sv}^{P}\gamma_{lv}^{P})^{1/2} = 0 \tag{2.30}$$

if γ_{sv}^{D} and γ_{sv}^{P} are known for a solid surface, values of γ_{lv}^{D} and γ_{lv}^{P} for liquids that would just completely wet and spread spontaneously on it can be calculated. A wettability envelope can then be constructed by plotting γ_{lv}^{P} vs γ_{lv}^{D}. [2] Future liquids can then be evaluated for use on that surface; if a given (γ_{lv}^{P},γ_{lv}^{D}) pair falls within the envelope, the liquid will spontaneously wet. The wettability envelope predicts when wetting of a liquid will occur on a solid, which is a necessary condition for strong bonds.

2.3 Surface Preparation of Composites for Bonding

As was briefly mentioned in the discussion of surface roughening above, many surfaces need to be treated before bonding to give optimum results. Surface pretreatments are usually employed in order to remove or prevent the formation of a weak boundary layer, maximize the degree of intimate molecular contact between adherend and adhesive, ensure the intrinsic adhesion forces across the interface yield the joint strength and service life required, generate a specific surface topography on the adherend, assist in the hardening of the adhesive, and/or to protect the surface of the substrate prior to the bonding operation [2][12]. The levels of intimate molecular contact and intrinsic adhesion forces are fundamentally increased by increasing the surface free energy or introducing surface groups which have the potential for acid-base interactions or stronger primary bonds. Because surface energy in amine-cured epoxies is governed primarily by the presence of hydroxyl groups, which may later form covalent bonds with epoxy-based adhesives, this can be accomplished in the systems of interest by increasing the oxygen and nitrogen content on the adherend surface [64].

The majority of the work on bonded structures to date is for metallic structures, as the use of composites is relatively new. Some aspects of preparing, bonding, and testing metals translate easily to composites, but others do not. For the most part, surface preparation methods are largely different. This is primarily because polymers have very low surface free energies and require pretreatment to obtain good or even reasonable adhesive joint strengths. Typical rubber-toughened epoxy, the most relevant example, has a surface free energy of 45.5 mJ/m^2, in distinction to metals that generally have energies greater than 500 mJ/m^2. Even surfaces that have relatively high energies and can bond without treatment often demonstrate their highest bond strengths when some form of pretreatment is used as it can eliminate contamination [1].

In the case of primary bonded structure in commercial aircraft, the composite system used is epoxy matrix carbon fiber prepreg with an epoxy adhesive. While modification of surface energy can still be useful, the chemical and thermodynamic similarity of these materials mean surface preparation is largely focused on the cleaning of contamination and prevention of a weak boundary layer. Epoxy has very low oxidation compared to aluminum, for example, but extended exposure to the air is still a concern. These surfaces can absorb water from the air, making available ions unavailable to the adhesive for chemical bonding [2]. The simplest surface preparation technique is the use of a solvent wipe. Other techniques of more use in composites are corona discharge, flame treatment, gas plasma, abrasion, and peel ply removal.

2.3.1 Methods of Surface Preparation

The most basic and minimal surface pretreatment is the use of a solvent wipe such as methyl ethyl ketone solvent wipes. More commonly used alone for metals than composites in industry, solvent wipes are primarily a method of cleaning the surface of greases, oils, and other handling contaminants to restore the original as-fabricated surface [72]. Solvents may be used more effectively in liquid or vapor degreasing baths, rather than wiped [2]. While useful to metals, this is usually not sufficient pretreatment for composites as the weak boundary layers usually quickly reform [1].

One of the most common surface treatments for polymers is corona discharge treatment. It is especially effective for low-density polyethylene, but can be used for many polymers including epoxies [73]. Essentially, powered electrodes create a corona of ionized gas (usually air) near a polymer as it is run over a drum covered with an insulating dielectric material [1]. Reactive sites are introduced as the surface is oxidized, improving interfacial contact and the possibility of higher intrinsic adhesion. The role of hydrogen bonds across the interface in adhesion is therefore emphasized. The material being treated determines the amount of time needed for treatment. If the polymer contains low molecular weight additives, for example, it is necessary to treat longer. Overtreatment is also a concern, as then surface regions begin to degrade generating a classic weak boundary layer and overwhelming the advantage of cleaning off a previously existing one [2].

A very similar technique to corona discharge is flame treatment. Again, a polymer is moved past and treated by a nonequilibrium, excited gas phase. In this case, it is a flame of natural gas. As in corona discharge treatment, the primary effect of flame treatment is to oxidize the surface [1]. This process is controlled through the position of the component relative to the flame, the air:gas ratio, the air/gas flow rate, and the exposure time. It can be difficult to optimize this method, as some of the elements have very narrow effective ranges, and flame treatment can readily lead to degradation of the polymer's surface regions[2].

The final plasma treatment useful in raising the energy of low energy surfaces is glow discharge or simply gas plasma treatment; exposure to an inert ionized gas at reduced pressure. The energy of the plasma is enough to break carbon-carbon bonds, on the order of 10s of electron volts [1]. This surface pretreatment cleans the surface, increases the surface free energy of the laminate, introduces chemically active species such as oxygen to the surface, and increases the polar surface energy component [2]. In early work, noble gasses such as argon and xenon were used [74][75], though nitrogen is also viable. Oxygen has also been used as an ablative gas, and surfaces have been perfluorinated by using fluorinated gases [1]. This surface preparation technique is represented extensively in academic literature [76][64][77][78][79][80][81][82][44-46], but is still uncommon in industry due to the expense of operating a system at less than atmospheric pressure.

In recent years, techniques for atmospheric pressure glow discharge have been developed. These are nonthermal discharges generated by the application of high voltages across small gaps wherein a nonconducting coating prevents the transition of the plasma discharge into an arc. The very practical technical significance because in contrast with low- or high-pressure plasma is that there is no need for in-chamber processing to ensure that a specific pressure level is maintained for appropriate and consistent surface modification. Atmospheric plasma designs are therefore easily incorporated in production lines, and are widely used in the web treatment of flexible packaging, fabrics, monofilaments, and yarns [83].

Abrasive surface pretreatments most commonly take the form of hand sanding or grit blasting. In grit blasting, high-pressure air is used to shoot grit at the surface, removing material and providing texture. Either form of abrasion theoretically cleans the surface and breaks open the long, relatively inert interlocked chains the polymer matrix forms during cure, creating a fresh surface that is able to form strong ionic or covalent bonds with the adhesive [84]. The surface energy is increased even after corrections are made for surface roughness [85], The polar component of the surface energy and the surface oxygen content can be increased, perhaps by generating free radicals that allow bonding of oxygen containing functional groups at the surface to oxygen from the air [85][64]. There can also be advantage to the roughening of the surface, but only if the structures produced are small enough to enable capillary action and draw the adhesive into the microstructure. This is much less likely to happen in hand sanding than in grit blasting [1]. Unfortunately, many grit blasting setups can actually add contamination to the system through machine oils or re-circulated media, and hand-sanding tends to simply spread existing contamination around in practice [12]. It often therefore requires solvents or even dry wiping [12] before or as a secondary step. Over-abrasion is a very real concern as well. Large grit can cause subsurface microcracking in the resin, and it is possible to erode too much of the surface and expose and even damage the fibers of the composite. While less likely in hand sanding, over-abrasion is still possible and both techniques are very sensitive to operator differences [2].

The final method of surface preparation for composites is the removal of a peel ply fabric that has been cured with the composite part. Peel ply treatment is very reproducible without the operator variation inherent in abrasion techniques, and ideally it does not require secondary surface preparation. It avoids the morphological problems of abrasive treatments, while being an effective way to clean the surface, increase fresh fracture, and reduce the polymer surface layer thickness which is known to improve adhesion [57], without risk of exposure and damage to the reinforcing fibers. Enhanced roughness from the peel ply surface treatment increases the surface area and thus the observed surface energy for wetting [86]. In practice, peel ply treatment has been adopted as an effective and efficient method for the manufacturing of primary bonded airplane structure. It has therefore been selected as the focus of the current study, and is examined in more detail in the next section.

2.3.2 Peel Ply Surface Treatment

Peel ply is a woven synthetic fabric added as the last layer in the lay-up and cured to the composite part to be bonded. During cure, the epoxy in the part becomes viscous and impregnates the peel ply between the fibers and in gaps where warp and weft meet. A cross-section of this layup can be seen in Figure 2.5. The peel ply is then removed from the surface immediately prior to bonding. Peel ply has been used

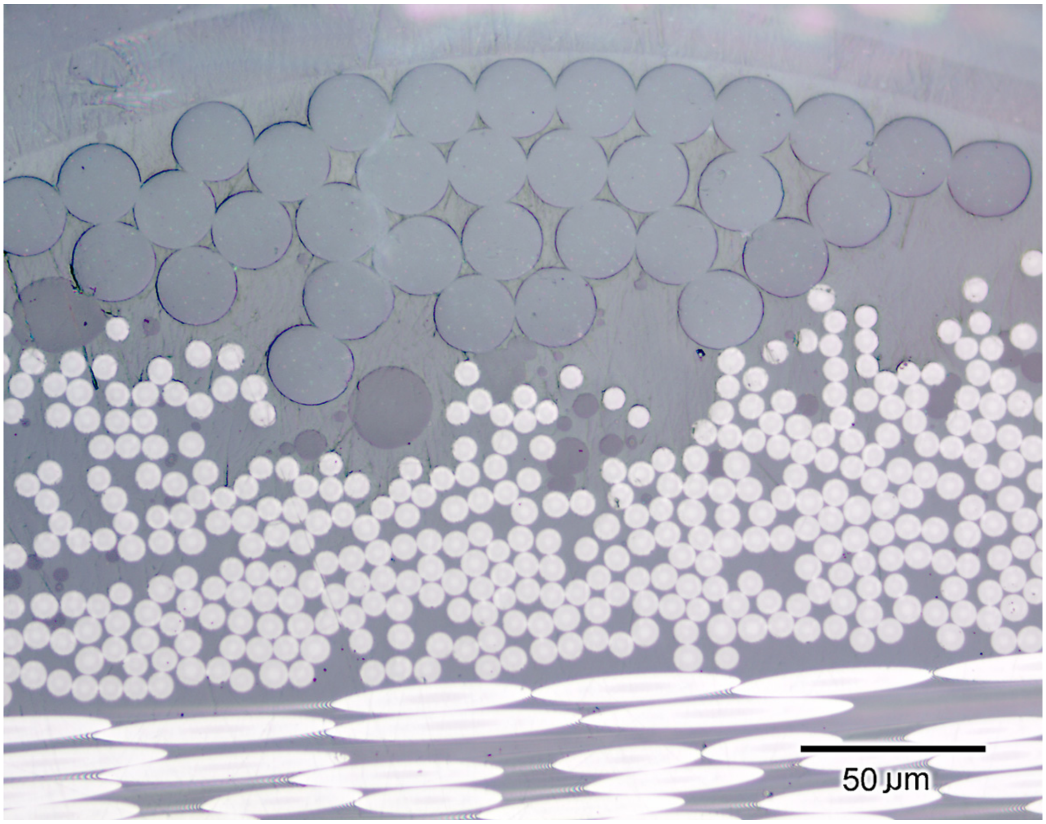


Figure 2.5: Cross-Section of Prepared Laminate with Peel Ply Intact

on fiberglass composites since the 1960s to protect their surfaces from contamination between initial part cure and bonding [87]. More recently the technique has been developed for use as a direct preparation for adhesive bonding rather than simply protective sacrificial layer. While consistent for known systems, it is not as predictable as abrasion methods of surface preparation. The characteristics of a surface created by peel ply removal are directly influenced by how the peel ply separates from the laminate.

The possible modes of separation can be seen in Figure 2.6, and are either 1) the fracture of the epoxy resin between the peel ply and the underlying carbon fibers, due to strong bonding of the peel ply to the composite matrix during cure (dark blue), 2) interfacial fracture between the peel ply fabric fibers and the epoxy matrix, if the strength of the chemical bond formed between the peel ply and the matrix is insufficient (pink), 3) peel ply fibers may fracture and leave material on the composite surface (green), or 4) there may be interlaminar failure in the composite (turquoise).

In the first mode, a fresh epoxy surface is created that should be chemically active and easily bonded between channels, and the channels themselves are clean. Though ideal, this is rarely the only mode of fracture present [88]. In the second mode, the chemistry of the surface created may be affected by the nature of the peel ply material surface. Peel ply coatings or fiber surface treatments may be transferred to the surface to be bonded and affect the future bond. The broken epoxy peaks left between peel ply channels are compositionally identical regardless of peel ply material, because the bulk epoxy is too far from the peel ply fiber to be affected by its composition [57]. The third mode may occur if the bond between the peel ply and epoxy is stronger than the peel ply fibers, and the fourth if the interlaminar strength of the laminate is low or the peel ply is removed incorrectly. The last two options are not acceptable for the creation of bondable surfaces.

In practice, the mode of fracture is at least visibly the second; the peel ply leaves a negative image of its texture on the composite adherend after removal [86], which can be seen in Figure 2.6. Visibly smooth channels then characterize the surface where the peel ply fibers once lay and broken epoxy sites along fine-scale peaks between imprints of fibers. This is because during cure the composite matrix resin does in

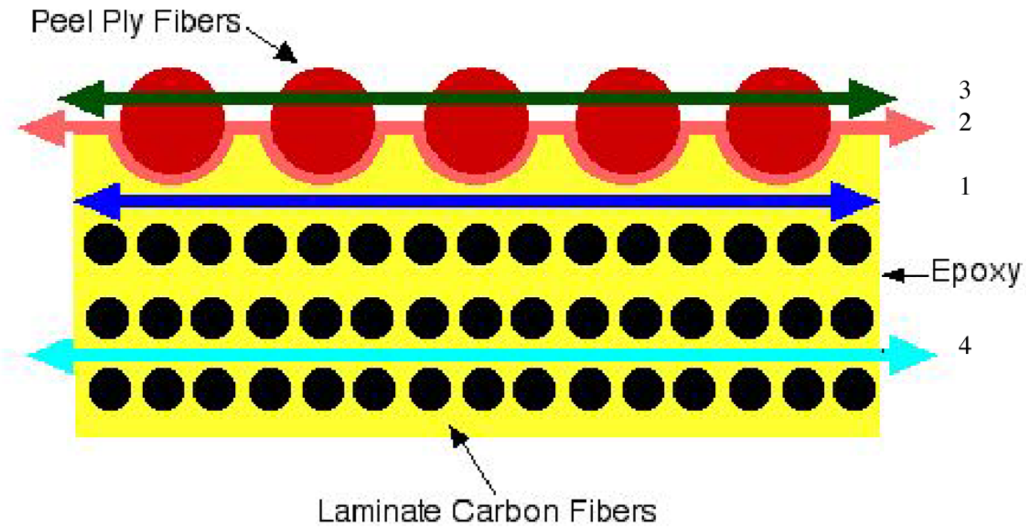


Figure 2.6: Fracture Modes in Peel Ply Removal

fact flow into the peel ply to some degree [89], even encapsulating fibers [90] and mechanically griping the peel ply. These mechanical interlocks are then fractured upon removal and fresh, active epoxy is exposed. Despite the obvious transfer of the peel ply texture to the adherend surface, the specific weave does not have a strong impact on fracture toughness/failure mode as coarser or finer weaves of the same peel ply material have produced similar results [88].

During bonding, the channels can once again enhance the mechanical mechanisms of bonding, acting as mechanical traps for adhesive flow to become mechanically interlocked with the adherend [91]. Although adhesion to peel ply-prepared surfaces could be dominated by this mechanism, the other criterion of adhesion must not be ignored. Surface wetting must have occurred or else intimate contact could not exist between the adhesive and the adherend layers.

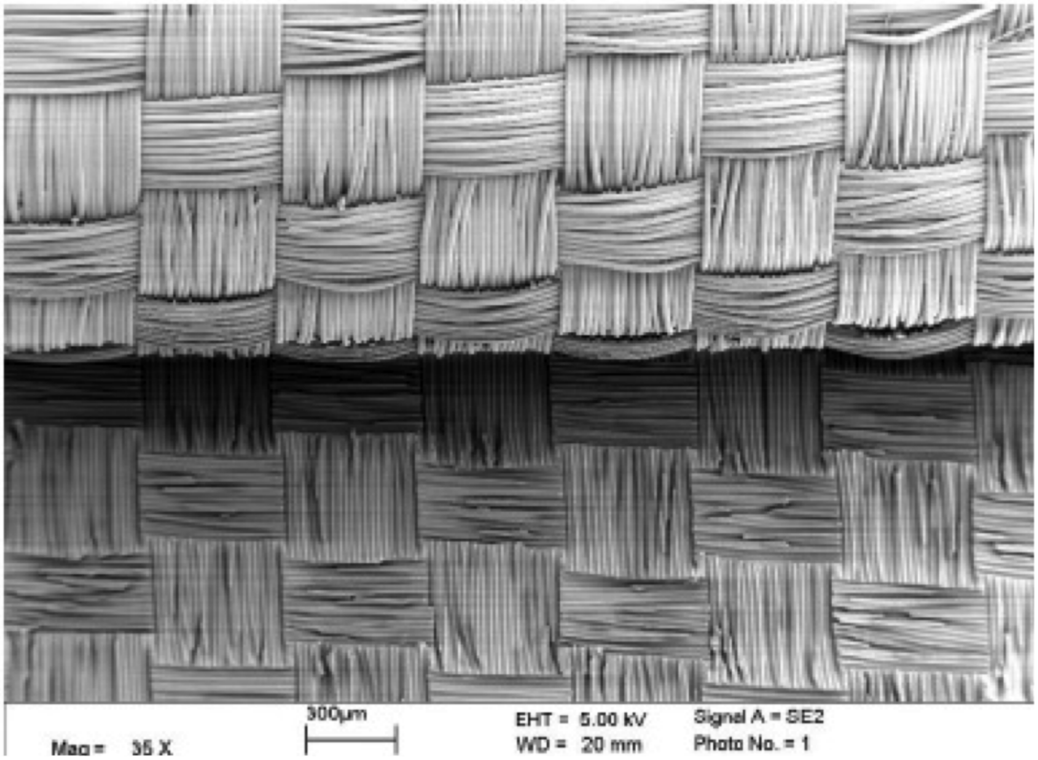


Figure 2.7: Composite surface after post-cure removal of peel ply

In addition to the obvious morphological effect of peel ply surface preparation there is evidence that the combination of peel ply and adherend matrix materials can have compositional effects as well. The polyester and nylon formations are the two primary choices for peel ply fabrics. With either choice, with the peel ply removal technique only the very outermost surface layer of the adherend chemistry is altered.

Polyester is a thermosetting polymer, and therefore mostly inert with respect to the composite adherend. The fiber is heat set or corona discharged to glaze its surface, allowing release from the epoxy because of its slickness [92]. The use of polyester peel ply has been found to add higher concentrations of aromatics, oxygen aliphatics and phthalates to the surface chemistry as shown by time-of-flight secondary ion mass spectroscopy (ToF-SIMS) [86], and a higher oxygen content by x-ray photoelectron spectroscopy (XPS) [89].

Nylon peel plies, in contrast, are thermoplastic polymers, which are not as chemically inert and will bond to epoxy. As was described in the section on epoxy resin additives, thermoplastics including nylon are used as an additive in epoxies and mixed at elevated temperature (such as the cure cycle) to allow for chemical reaction [28]. Gorton studied the interaction of nylon with epoxy resins in adhesive blends, and found that the epoxy resin crosslinks the nylon through the reaction of oxirane group with amide nitrogen in nylon chain [24]. These studies on the reaction of nylon with epoxy have all been done in the context of nylon incorporated into uncured epoxy, however clean nylon peel plies have therefore been known to destroy composite parts on removal, as can be seen in Figure 2.8.

In the cases that nylon peel ply does not stick and destroy the part, it usually has an applied release agent to promote separation from the adherend. This release can also transfer to the adherend surface [92]. Siloxane release agents are obvious offenders, resulting in poor bonds due to silicon contamination [89]. Low-energy fluorocarbons are used in certain release agents, and are possible sources of contamination. ToF-SIMS has revealed more nitrogenous species such as NH, CNO, and C_6H_12NO on surfaces prepared by nylon peel ply Benard:2005uq.

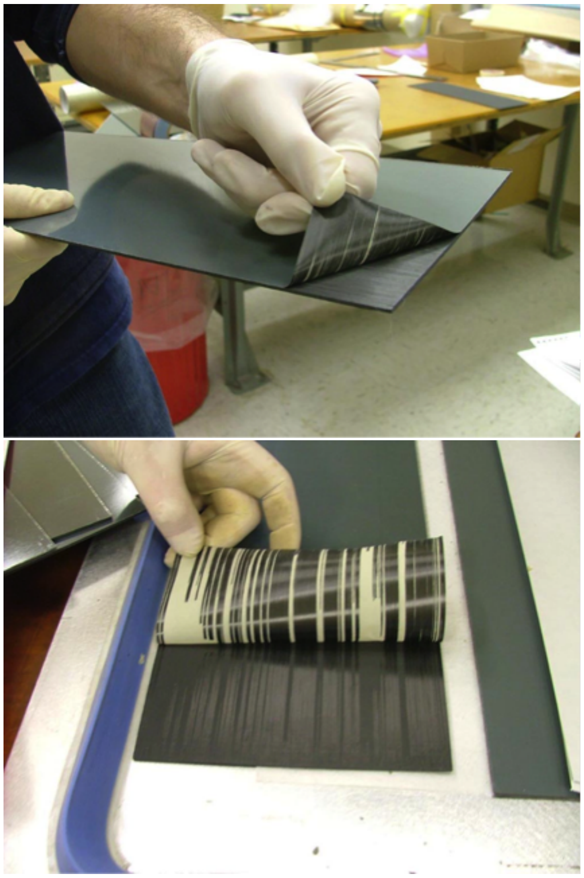


Figure 2.8: Examples of laminates damaged during removal of some nylon peel plies

Because the surface roughness and chemistry changes resulting from peel ply surface preparation would dominate the tiny energetic effects of any exposed fiber reinforcement [93], the small differences that might be observed between carbon- or fiberglass-reinforced composites become insignificant. The choice of fiber is irrelevant for peel ply surface preparations, and results are solely dependent upon the matrix resin and peel ply itself [57][93]. As with all components of composite systems, a universal peel ply probably does not exist. Each combination of composite resin, adhesive, and peel ply must be tested [94]. Peel ply type, surface preparation and testing method will all affect the apparent strength of an adhesive bond [93].

2.3.3 Previous Surface Preparation Studies

Work has been done examining the efficacy of these surface preparation methods specifically for composites. Chin and Wightman [72] examined several techniques including methyl ethyl ketone (MEK) solvent wipes, grit blasting, peel ply, and gas plasma. Bond quality was determined by double lap shear and wedge testing, and the surfaces were examined with scanning electron microscopy (SEM), profilometry, contact angle analysis, x-ray photoelectron spectroscopy (XPS), and ion scattering spectroscopy (ISS). MEK wipes were found to have negligible effect on the surface chemistry or in removing contamination. They saw improvement in bond quality from the as received samples under all other treatments, most strikingly for peel ply and gas treatment. Grit blasting and oxygen plasma treatments effectively removed contamination from the surface while peel ply prevented it from occurring. Any remaining contamination was detrimental to bond strength. Oxygen plasma also further oxygenated the surface, ensuring a highly polar and wettable surface for bonding.

Over-abrasion during grit blasting lowered bond strength and created bonds that were less resistant to hot/wet conditions.

Abrasive treatments were examined in more detail by Parker and Waghorne [95]. They investigated grit blasting and sanding through XPS and single lap shear tests. Because the adherends in this study were molded against coated fabrics and tools, contamination from liquid release and release fabric was of particular concern. It has been suggested that abrasion after peel ply (which might otherwise be difficult to remove) use would allow release-coated peel plies to be used, but this study found that while both abrasive methods improved bonding by lowering the levels of silicon and fluorine contamination found on the surface, neither fully removed it. The lack of consistency with these methods, especially hand sanding, was also highlighted.

Although groups such as Matienzo et al [96] have suggested that the mechanical interlocking mechanism for adhesion may be improved and exploited by the increase in surface roughness created by techniques such as peel ply and surface abrasion, the work of Pocius and Wenz [97] has eliminated this effect. Instead, a surface free of contamination is the critical factor in bond quality, and exaggerated surface roughness can even be detrimental to bond quality as it can trap air or other vapors and act as interfacial flaws.

Schonhorn and Hansen found glow-discharge treatments to be very effective for low-energy surfaces, increasing joint strength rapidly initially and then remaining nearly constant [74][98]. Although the mechanism for this success was originally mistakenly attributed to increased crosslinking increasing the strength of the weak boundary layer, it was later found to work via cleaning and oxygenating the surface [99].

Hart-Smith did extensive work [10][100][101][92] on release fabrics, peel plies, and abrasion, and found that fracturing the surface resin was key to attain the most improved bond quality. Nylon peel plies that had been coated to allow release (the uncoated nylon peel plies tested damaged the laminate surface on removal) were detrimental to bond quality, as the coating transferred to the adherend. Uncoated polyester peel plies created surfaces that bonded well. Light grit blasting was the most consistently reliable method. Due to the system-sensitive nature of peel ply surface preparation, and the universality of grit blasting, he concludes that grit blasting is the superior technique.

As a result of the fact that most studies on surface preparation of composites are taking place within highly competitive industries, published material in recent years is somewhat slim. Even many current articles [10][15][100][101][92] are primarily regurgitations of work that was done 20-30 years ago when it comes to peel ply. A review of the literature can leave one believing that all peel ply prepared surfaces must be grit blasted to be safe, for example, which does not reflect the fact that the aerospace industry is confidently using peel ply preparation alone in carefully determined composite systems.

This study examines the outstanding issue of inconsistency in peel ply surface preparation in order to clarify the factors involved in material transfer and the conditions under which such weak boundary layers cause bond failure. This will increase the understanding of a surface pretreatment that is known to be effective in certain systems, and is an important part of a larger body of work currently underway to study pretreatment techniques.

2.3.4 Concurrent Work

Recently, new studies into composite surface preparation were performed by Bardis and Kedward [11][84][102][103]. They examined surfaces prepared with release films and plies, peel plies, and grit blasting, and bonded using paste and film adhesives. Bond quality was examined using a variety of mechanical test methods. Much of the focus of this study was on testing methods; the floating roller peel test was determined to be inappropriate for composites, the double cantilever beam (DCB) test was found to be most useful for comparing bonds, and a new traveling wedge test was developed as a simpler replacement for the DCB. While single lap shear tests were found to agree with mode I fracture tests for the untreated surfaces, they did not for those that had been grit blasted. This confirmed earlier assertions in the literature that mode II tests are not well suited to test adhesive bonds. The results on wedge testing were inconclusive. Release films were once again confirmed to create poor bonds due to the transfer of the coatings. Grit blasting improved performance in cases where failure was adhesive without it, but reduced bond quality when failure was otherwise cohesive, and increased the scatter in the results.

Benard et al [104][57][86][93][105] have been investigating surface roughening as a method to increase bond quality. By examining polyester and polyamide peel plies in 176^o C cure systems they have corroborated the results of Bardis and Kedward [84] that roughening a surface that has been prepared by peel ply removal is only an asset when bonds were poor without doing so, and can actually be detrimental when bonds are already strong. The enhanced roughness inherent in peel ply treatment alone increased the surface area and thus the observed surface area for wetting. They found that peel ply fiber does interact with the adherend surface to a degree, with time-of-flight secondary mass spectroscopy (ToF-SIMS) revealing higher concentrations of aromatics, oxygen aliphatics, and phthalates on polyester-prepared surfaces and more nitrogenous species on nylon-prepared surfaces. They also took contact angle measurements of the prepared surfaces, and found that the surfaces that bonded the best had the lowest angles.

Kieronski, et al [91] found that peel ply surface preparation can increase the role of the mechanical interlocking mechanism of bonding. The adhesive can flow into the channels left behind by the peel during bonding and become mechanically interlocked with the adherend. They also found tiny ductile wisps of damaged peel ply remaining in the channels, depending upon the composite material system and cure processing temperature.

Lloyd Smith at Washington State University is running a partner study to this, focusing on the long-term environmental degradation of bonds created with peel ply, grit blasting, and sanding pretreatments. His tests on a few of the systems this study is investigating will add a durability aspect to some of the issues investigated herein.

Chapter 3

RESEARCH PROPOSAL

It is proposed that a key factor in the success or failure of peel ply surface preparation is the existence and quantity of material transferred from the peel ply to the matrix epoxy and remaining after peel ply removal. From literature review it is known that extreme cases of material transfer from poor peel ply choice harm bond quality, but the potential of less obvious peel ply transfer ruining bond quality has not been investigated. Surface energy measurements are one of the available tools for analysis of these prepared surfaces before bonding, and it is further proposed that surface energies may be a potential predictive tool for bond quality of new composite system combinations in order to widen the matrix of choices available to industry. The effectiveness of such measurements for bond quality prediction will therefore be examined. Literature review also suggests that the wettability envelope technique shows theoretical promise for judging a surface with little investigation to date.

> Hypothesis: Peel ply fiber remnants exist on most peel ply prepared composite surfaces to varying degrees, are a key factor in premature bond failure, and may be exposed via wettibility envelopes.

3.1 Research Goal

It is proposed that the inconsistency of peel ply surface preparation bond quality between composite material systems may be the result of differing peel ply debris transferred to the surface. The goal of this research is to examine the prepared composite surfaces of key representative systems in order to determine how the surface created by peel ply affects bonding, taking special note of peel ply remnants. The current study further provides an opportunity to examine the usefulness of prepared surface wettability envelope construction for a prediction of resulting bond quality.

3.2 Research Scope

The scope of this research is limited to the exemplar systems of:

- Carbon fiber reinforced epoxy matrix preimpregnated composite laminates
    - Toray 3900 resin with t800 fibers
    - Cytec 970
    - Cytec MxB (glass fiber)
- Epoxy-based film adhesives
    - Cytec Metal Bond (MB) 1515-3
    - 3M AF 555
    - Henkle Hysol EA9696
- Woven peel ply fabrics

  - Precision Fabrics Group (PFG) Polyester 60001
  - PFG Nylon 52006
  - PFG Polyester 60001 Silicon Release Blue (SRB)

3.3 Research Objectives

Into order to attain the research goal, prepared surfaces and their consequences in representative systems will be examined. The secondary research goal means that as surface energy measurements are utilized, their effectiveness in predicting bond quality will be analyzed. This will be achieved through the following objectives.

3.3.1 Identify characteristic composite systems of varying bond quality

Bond quality after peel ply surface preparation varies dramatically based on the complete composite system. A matrix of adhesive/adherend/peel ply materials in use in the aeronautical industry in which certain combinations produce strong bonds and others do not will be chosen, and the bond quality of the combinations will be determined qualitatively and quantitatively.

3.3.2 Confirm and characterize peel ply remnants in every studied composite system

The hypothesis that peel ply prepared surfaces beyond those known to produce problem surfaces also hold debris will be tested. The chemistry, morphology, and surface energy of peel ply prepared surfaces will be characterized before bonding in each system of interest.

3.3.3 Compare surface energy measurements and wettability envelopes in systems of varying bond quality

Surface energy measurements have previously been used, and wettability envelopes hold theoretical promise, for prediction of bond quality of a peel ply prepared system. Measurements will be taken and envelopes constructed and compare between systems to determine whether they expose the differences between systems that bond well and poorly.

3.3.4 Compare surfaces and bond quality created using standard materials with those created using a pre-contaminated peel ply

One of the exemplar laminates will be used with both a clean and a pre-contaminated (siloxane coated) Polyester 60001 peel ply. Resultant surface morphology and bond quality will be compared in order to develop a baseline for a "contaminated" surface.

3.4 Material Selection

To reflect the materials currently used in aerospace, carbon fiber-reinforced epoxy prepreg strips formulated to Toray 3900, Cytec 970, or Cytec MxB were selected. Epoxy-based film metal bond (MB) 1515-3 or adhesive film (AF) 555 were used to bond Cytec 970 and Toray 3900. Cytec MxB was bonded with epoxy-based film Henkel EA9696. Test samples were made of Toray 3900 with MB1515-3, Toray 3900 with AF555, Cytec 970 with MB1515-3, Cytec 970 with AF555, and Cytec MxB with EA9696. The array of tested composite systems can be seen in Table 3.1.

Table 3.1: Material systems used in this study

Laminate	Cytec 970	Toray 3900	Cytec MxB
Cure Temperature (°C)	176	176	121
Adhesive	MB1515-3 or AF555	MB1515-3 or AF555	EA9696
Peel Ply	Nylon 52006 or Polyester 60001	Nylon 52006 or Polyester 60001 or Polyester 60001 SRB	Nylon 52006 or Polyester 60001

Table 3.2: Peel ply fabrics from PFG used in this study and their weave characteristics

Fabric Code	60001	52006/51789	60001 SRB
Filament Material	Polyester	Nylon	Polyester
Warp (ends/mm)	2.75	6.30	2.75
Fill (picks/mm)	1.97	4.06	1.97
Peel Ply Thickness (mm)	0.13-0.15	0.11-0.14	0.13-0.15
Comments		Very Fine	Siloxane Coated

The peel ply fabrics used were from Precision Fabrics Group (PFG), Inc, and included Polyester 60001, Nylon 52006, and Polyester 60001 SRB. The first two were selected to represent differing peel plies currently in use in aerospace, and the last was a siloxane coated Polyester 60001 selected to show the results of known contamination. Their characteristics are listed in Table 3.2. All peel plies were stored at ambient conditions (20^o C and 50% ± 10% RH).

Chapter 4

SAMPLE PREPARATION AND TESTING

Unidirectional ten-ply laminates $[0]_{10T}$ were laid up using each of the selected preimpregnated laminate materials, covered with a layer of polyester, nylon, or precontaminated peel ply fabric, and then vacuum bagged.

All laminates underwent standard 2 hour, 0.58 MPa cure cycles in an autoclave with full vacuum maintained through out the cure cycle. Cytec 970 and Toray 3900 were cured at 176^o C, and Cytec MxB at 121^o C. The ends of the laminates were removed for surface characterization with the peel ply intact. After trimming the laminate panels to dimensions specified in Figure 4.1, peel plies were removed and the laminate panels were bonded with MB 1515-3, AF 555 (176^o C), or EA 9696 (121^o C).

A strip of non-porous fluorinated ethylene propylene (FEP) release film was placed between the halves to be bonded to create an initial debond for fracture toughness testing, as also seen in Figure 4.1. Bonded samples were cured using the same parameters as the laminates. Finally, the bonded panels were cut into specimens for double cantilever beam testing according to Figure 4.1.

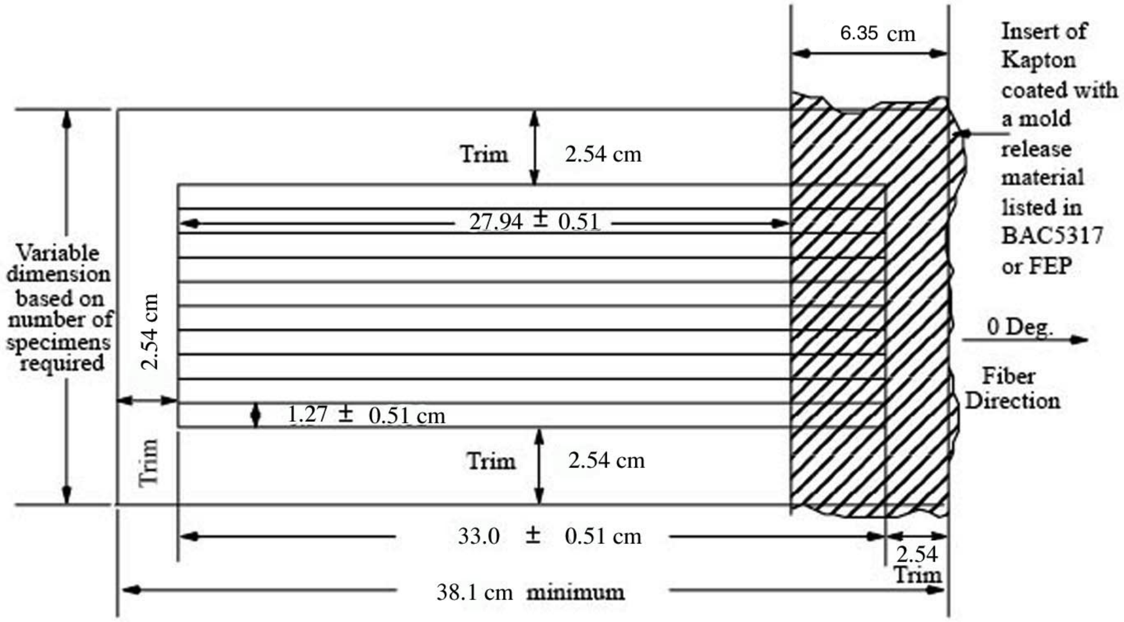


Figure 4.1: DCB specimen and panel geometry and dimensions, plan view

4.1 Test Selection

4.1.1 Mode of Failure

The mode of failure is defined by the location in the bonded sample where failure propagates. ASTM D5573-99 (2012) Standard Practice for Classifying Failure Modes in Fiber-Reinforced-Plastic (FRP) Joints defines the following types of failure which can be seen in Figure 4.2 [3]:

adhesion failure the crack propagates at the adhesive-adherend interface, leaving no evidence that any adhesive or FRP have transferred to the opposite surface. This is considered unacceptably poor bonding.

cohesion failure the crack propagates within the adhesive, leaving adhesive on both fracture surfaces. This is the preferred form of failure. If the crack propagates very close to the adhesive-substrate interface this may be specified to be a thin-layer cohesive or interphase failure.

fiber-tear failure the crack propagates exclusively within the FRP matrix, characterized by the appearance of reinforcing fibers on both ruptured surfaces. If the failure occurs within the FRP substrate near the surface and leaves resin matrix visible on the adhesive, but few or no glass fibers are transferred from the substrate to the adhesive this may be called light-fiber-tear failure.

stock-break failure the crack propagates through the FRP substrate outside the adhesively bonded joint region, often occurring near it.

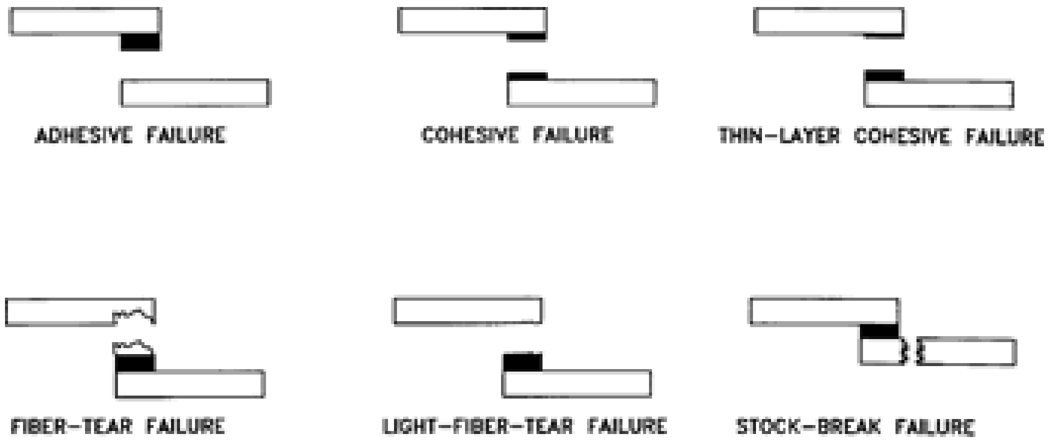


Figure 4.2: Failure modes in fiber reinforced polymers [3]

It is desirable from a bonding perspective that the failure occur anywhere other than the adhesive/adherend interface. It demonstrates that a strong bond has formed between adhesive and adherend and the joint is limited by material characteristics, not bond quality. Mixed mode failure is a combination of any of the above modes, and is often due to contamination in the adhesive or the adherend that changes the crack path. This change in failure mode can also be the result of the type of test being used or improper testing procedure.

Despite the fact that bonded joints are often designed for shear (Mode II) loads, it has been established that the traditional lap shear tests are not reliable indicators of bond durability in cases of prolonged loading, variable temperatures, or environmental exposure [12][106][2]. Cleavage, or Mode I, fracture testing has therefore become standard, and is used as the measure of bond quality in this study through double cantilever beam testing.

4.1.2 Double Cantilever Beam

Double Cantilever Beam (DCB) was selected as the fracture test method. Samples were cut from the bonded laminate panels to approximately 33 cm x 1.3 cm, and included a 6.4cm initial "crack" where the FEP prevented bonding during cure. Testing was performed according to ASTM D5528-01 standards using a servo hydraulic test frame with a 200N load cell and 25 mm/min ramp rate.

Of the four common data reduction methods for calculating the critical strain energy release rate G_C (area, modified beam, compliance, and load), this study used the area method. As the applied load is increased during testing it will eventually reach P_1, the load required to cause the starter crack originally of length a_1 to extend. The propagation is arrested at length a_2 , and the load drops to P_2 and the load point displacement increases to δ_2 at which point the applied load is removed. The area between the loading and unloading curves represents the decrease in stored strain energy caused by the crack extension [107]. The strain energy release rate required to cause crack propagation (G_C) can for the brittle fracture behavior of this study be approximated as:

$$G_{IC} = \frac{P_1 a_2 - P_2 a_1}{2b\delta} \tag{4.1}$$

G_C was calculated, and resulting fracture surfaces were examined to determine the mode of failure. The specimens were of constant cross-section and designed to avoid non-linear behavior according to ASTM D5528 [108], so calculations are based on linear behavior.

When examining the results of mechanical testing a step-function will be seen in the Mode I fracture toughness (G_C) of bonds that experience cohesion vs adhesion failure. While bonds that fail in adhesion will show increasing G_C values as bond quality increases, bonds that fail in cohesion will have substantially higher G_C values that do not vary substantially. This is because if a piece fails in cohesion it is the strength of the adhesive that is ultimately being tested. In the aerospace industry only cohesive failure is acceptable, regardless of the G_C value obtained by a system that fails in adhesion.

4.1.3 Scanning Electron Microscope

In this study, microscopy was performed using a JEOL JSM-7000F scanning electron microscope (SEM). Samples were sputter coated with a platinum target. SEM was used to examine the surface morphology and debris of prepared adherends imaged immediately upon removal of both the polyester and nylon peel ply. Post-fracture analysis was done by SEM as well, examining the surfaces of both the adherend and the adhesive to distinguish between interfacial failure and thin-layer cohesive failure and to expose if there were small patches of interfacial failure in a primarily cohesive failure (or vice versa).

4.1.4 X-ray Photoelectron Spectroscopy

This research used a Surface Science Instruments M-Probe spectrometer for non-destructive XPS analyses, in which environment pressure does not exceed $1x10^{-}8$ torr. Survey scans and high-resolution XPS spectra over the C (1s) peak were recorded to find chemical composition using nominal pass energies of 150 and 50 eV, respectively. Analyses are over an elliptical spots with major axes of approximately 1.7 mm and minor axes of approximately 0.4 mm, to depths of between ten and twenty atom layers (10nm) of the sample surface. The samples in this study are non-conducting, therefore a low energy electron load-gun set at 4.0 eV was used for charge neutralization of the samples. All spectra measurements were corrected for the charging by setting the hydrocarbon C (1s) peak to 285.0 eV. Adherend surfaces were examined for residue following nylon and polyester peel ply preparation, and post-bond fracture surfaces were examined to confirm fracture mode.

4.1.5 Contact Angle Measurements

Contact angles were found with a Ram-Hart Tilting Contact Angle Goniometer 100-00 115 with overall magnification 23x and working distance 57mm. Ten measurements were taken on each adherend immediately after nylon or polyester peel ply removal with each of the three fluids: deionized water, dimethyl sulfoxide (DMSO), and formamide. These fluids represent varied surface energies and all form non-zero contact angles on the surfaces of interest. These measurements were used to determine the polar and dispersive surface energies for calculation of a wettability envelope using equation 21 in a computer program originally written by Mark Tuttle [109] and modified by Brian Clark [94], both of the University of Washington.

Chapter 5

INVESTIGATION RESULTS

5.1 Bond Quality

In order to meet the first research objective, the specified exemplar systems were mechanically tested in their varying combinations to establish the quality of the bonds created. All combinations of Toray 3900 or Cytec 970 laminates prepared with Polyester 60001 or Nylon 52006 peel ply and bonded with MB 1515-3 or AF 555 adhesives were used to represent materials currently used in industry. Cytec MxB was chosen as a representation of a 121C cure system, prepared with both peel plies, and bonded with EA 9696. Toray 3900 was also prepared with siloxane coated Polyester 60001 SRB in order to present a clear example of known contamination, and bonded with both of the 176C cure adhesives. All were then tested via the double cantilever beam method, and bond quality was found.

The determination of bond quality was two-fold. A numerical strain energy release rate required to propagate a crack through the bond is given by the DCB test, but the mode of failure (the location and path of crack propagation) must be determined as well as the quantifiable strength of the bond. Quantitative comparisons are important, but a bond of high strength with crack propagation along the adherend/adhesive interface is still considered a "poor bond." The aerospace industry wants the materials to fail rather than the bond interface, as the materials are more easily controlled and modified. The results of this mechanical testing follow.

5.1.1 Quantitative Measure of Bond Quality

The strain energy release rate of the bonded laminate, determined by Mode I DCB testing is the quantitative measure of bond quality for this study. In DCB load-displacement plots the initial linear portion of the curve shows where the specimen is being loaded through the pre-cracked region up to the peak of the curve, where the crack begins (the initial peak loading). The second linear portion tracing back to zero load and displacement shows the unloading of the specimen. Examples of these plots can be seen in Figure 5.2 and Figure 5.1. Figure 5.1 displays a representative set of curves from the testing of Cytec 970 laminates prepared with Nylon 52006 peel ply and bonded with AF 555, but also reflects the basic results of preparation with Polyester 60001 as well as the testing of Toray 3900 laminates bonded with AF 555 after preparation with 60001 or 52006. All displayed stick-slip crack propagation and the high initial peak loading indicative of cohesive failure. Figure 5.2 is a representative set of curves from the DCB testing of Cytec 970 laminates prepared with Polyester 60001 and bonded with MB 1515-3, but also reflects the results of MB 1515-3 bonding of Nylon 52006 prepared surfaces of either laminate. All displayed low initial peak loading values indicative of adhesive failure. The Toray 3900 surfaces prepared with Polyester 60001SRB were similar, with even lower initial peak loads. The actual values for measured fracture energies, G_C, of the bonded samples are presented in Table 5.1. There was a division between the G_C values of a ”strong” bond

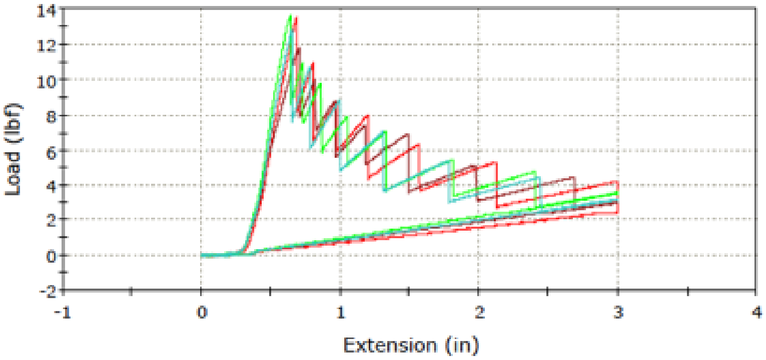


Figure 5.1: DCB load-displacement plot for Cytec 970 laminates prepared with Nylon 52006 and bonded with AF 555.

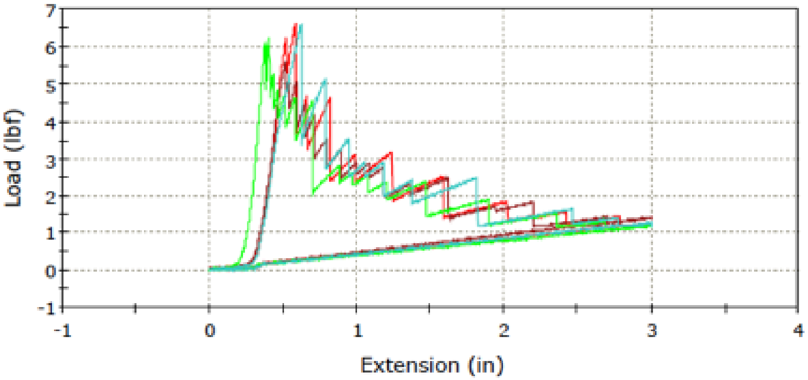


Figure 5.2: DCB load-displacement plot for Cytec 970 laminates prepared with Polyester 60001 and bonded with MB 1515-3.

Table 5.1: Summary of average G_C data for laminates prepared with various peel plies and bonded with AF 555, MB 1515-3, or EA 9895. Specimen id # reflects the laminate formulation / PFG peel ply / adhesive used.

Specimen ID#	G_C (J/m^2)	StdErr (J/m^2)
970/MB/60001	242	9
970/AF/60001	638	2
970/MB/52006	190	15
970/AF/52006	734	4
3900/MB/60001	812	35
3900/AF/60001	910	35
3900/MB/52006	122	15
3900/AF/52006	911	80
3900/AF/SRB	93.9	1.2
3900/MB/SRB	86.0	6.0
MxB/EA/60001	386	8
MxB/EA/52006	653	10

and those of a "weak" bond. This is very clear when examining the results in order of decreasing G_C as in Figure 5.3. Tested bonds either measured between 100 and 400 J/m^2, or between 600 and 1000 J/m^2. The characterization of these ranges as "good" and "bad" is supported by viewing observing the change in bond quality when exchanging one element of the system. For example, the use of MB 1515-3 adhesive rather than AF 555 in the Cytec 970/60001 system causes the G_C to drop from 638 to 242 J/m^2.

The AF555 adhesive seems to work well in all configurations tested. Strong bonds were created with both Toray 3900 and Cytec 970, using both the polyester 60001 and the nylon 52006 peel plies. MB 1515-3 was much less successful; it's use only created a strong bond in the Toray 3900/60001 system. The Henkle Hysol 9696 bonded well to the nylon 52006 prepared MxB laminate, but not the polyester 60001.

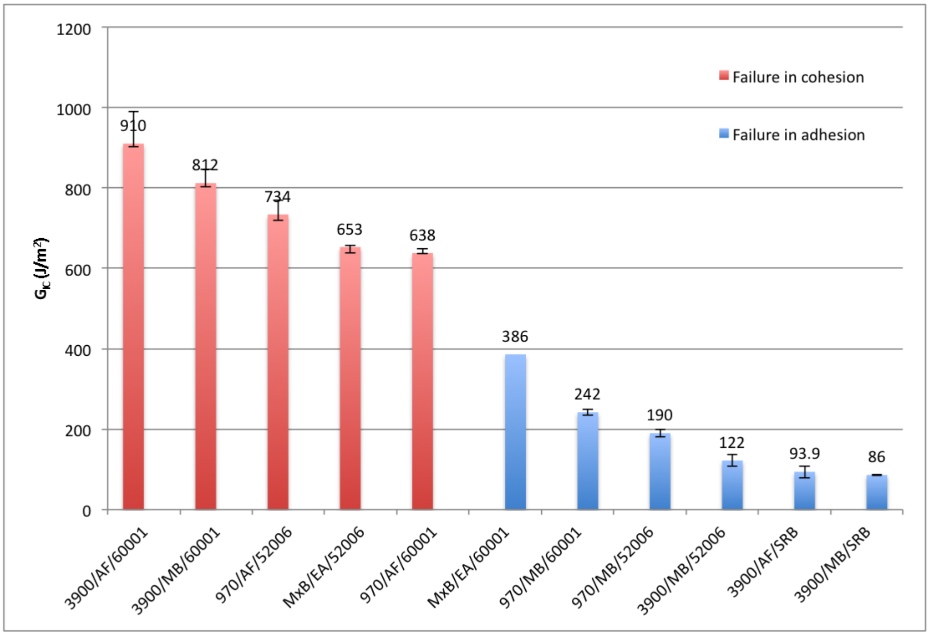


Figure 5.3: All systems as tested by DCB in order of decreasing G_C.

Figure 5.4 portrays a direct comparison of G_C from preparation with each peel ply within each adherend/adhesive system. There was a marked decrease in G_C in the Cytec MxB system when prepared with the polyester 60001 peel ply rather than the nylon 52006. The reverse was true in the Toray 3900/MB 1515-3 system; only the polyester 60001 peel ply preparation created a strong bond. Clearly both the adhesive and the peel ply used can change the fate of a composite system.

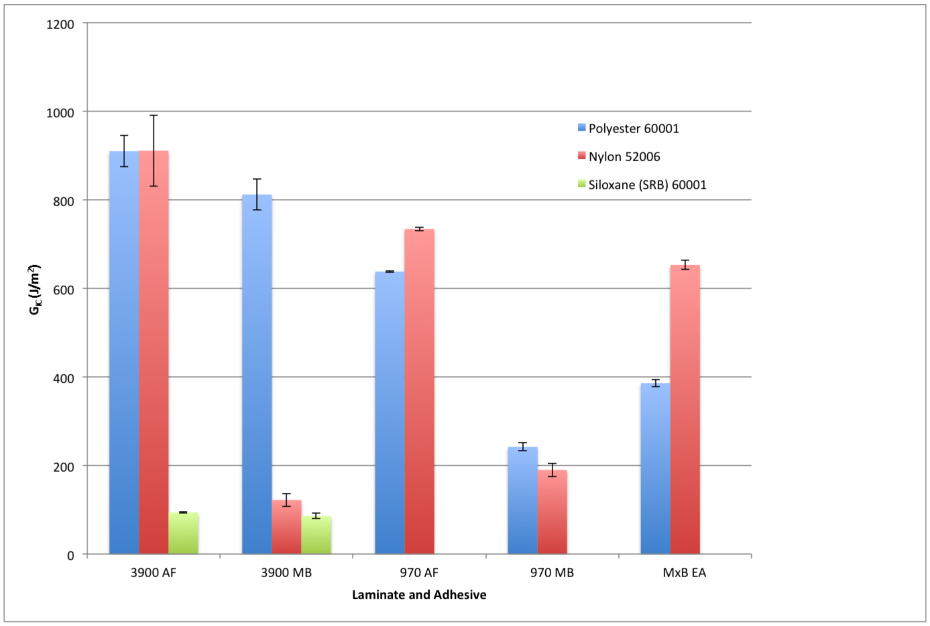


Figure 5.4: G_C of all systems as tested by DCB.

5.1.2 *Failure Mode*

The mode of failure is critical to determining whether a surface preparation is successful at creating high quality bonds in the aerospace industry, as only failure in cohesion is acceptable (and brings with it high G_C values as determined by the adhesive formulation). The mode of failure also determines whether comparison of G_C results is valuable; only within adhesion failure is such a comparison meaningful, as the G_C of interlaminar failure or failure in cohesion is actually a test of the materials rather than the bond in question. The bond resists crack propagation more than the adhesive or laminate. Table 5.2 displays the average G_C value for each system along with the fracture surface and fracture mode. The mode of fracture is expressed as the percentage cohesive failure determined by standard optical and scanning electron microscopy methods, so C0 is total failure of adhesion and the lowest quality while C100 is completely failure in cohesion and the most desirable. In this study the qualitative results were clearly separated; failure was either completely in adhesion, completely in cohesion, or almost completely in cohesion with a few samples exhibiting small areas of interlaminar failure (also considered a "good" bond).

Table 5.2: Comparison of G_C data and failure mode for laminates prepared with various peel plies and bonded with AF 555, MB 1515-3, or EA 9895. Specimen ID# reflects the laminate formulation / PFG peel ply / adhesive used. Cases that had 95% failure in cohesion had 5% interlaminar failure.

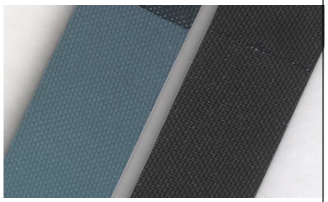
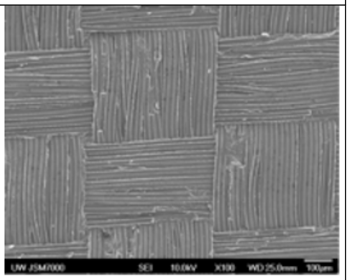
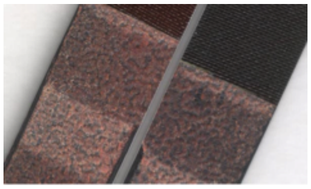
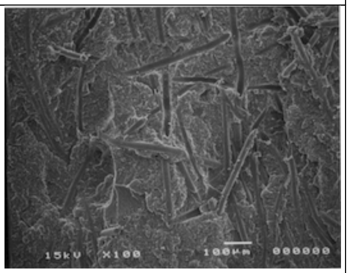
Specimen ID#	G_C (J/m^2)	Fracture Mode (%Cohesive)	Fracture Surface	SEM of Fracture Surface
970/MB/60001	242	C0		
970/AF/60001	638	C95		

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Table 5.2 – *Continued from previous page*

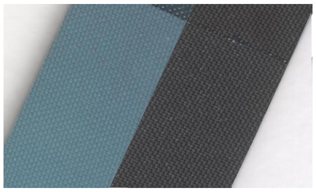
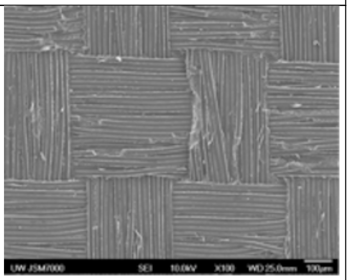
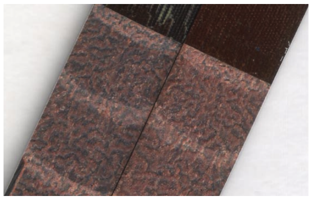
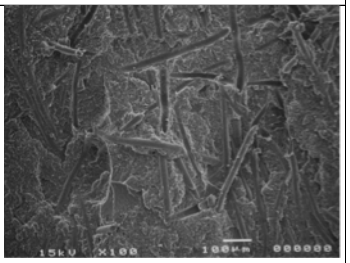
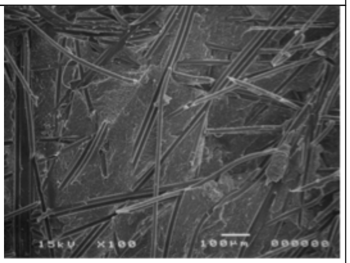
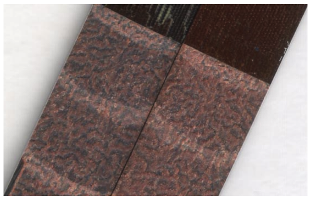
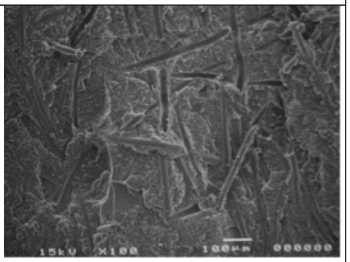
Specimen ID#	G_C (J/m^2)	Fracture Mode (% Cohesive)	Fracture Surface	SEM of Fracture Surface
970/MB/52006	190	C0		
970/AF/52006	734	C100		
3900/MB/60001	812	C95		
3900/AF/60001	910	C100		

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Table 5.2 – *Continued from previous page*

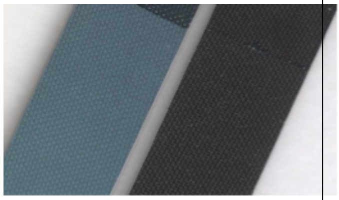
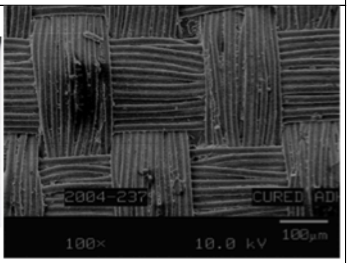
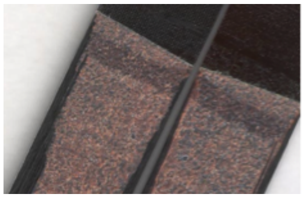
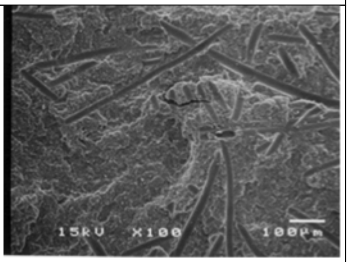
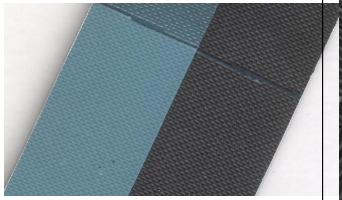
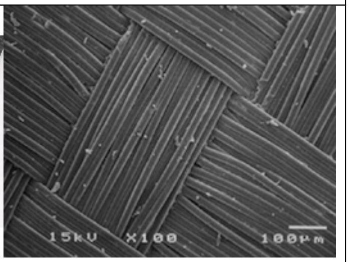
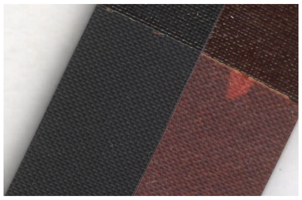
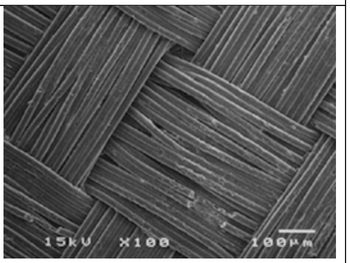
Specimen ID#	G_C (J/m^2)	Fracture Mode (% Cohesive)	Fracture Surface	SEM of Fracture Surface
3900/MB/52006	122	C0		
3900/AF/52006	911	C95		
3900/MB/SRB	86.0	C0		
3900/AF/SRB	93.9	C0		

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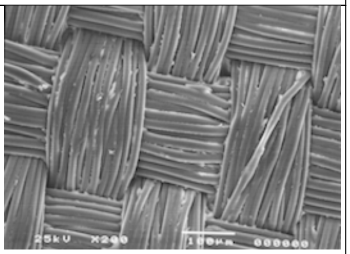
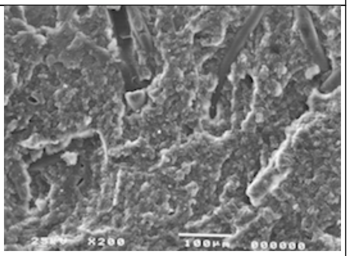
Table 5.2 – *Continued from previous page*

Specimen ID#	G_C (J/m^2)	Fracture Mode (% Cohesive)	Fracture Surface	SEM of Fracture Surface
MxB/EA/60001	386	C0		
MxB/EA/52006	653	C100		

Examination of the failure surfaces shown in Table 5.2 gives the mode of failure. The samples that have adhesive on both sides failed in cohesion, with the crack running through the adhesive. Those that have adhesive remaining on only on side of the fracture failed in adhesion, with the crack running along the adhesive/adherend interface. The scanning electron microscopy images confirm the modes seen though the optical stereoscope. The SEM images also demonstrate that at least superficial wetting is occurring in all samples, as the adhesive took on the form of the imprint left by the peel ply on the laminate surface during the initial cure cycle. As was mentioned in the literature review, peel ply channels can increase the spreading rate of an adhesive and pull it across the surface. The imprint is so exact, with some roundness to the top edges of the false "fibers" that lifted out on failure, that it is possible the peel ply created surface is enough to help with some mechanical interlocking as suggested by Kieronski [91], especially in the corners where warp and weft had met. Obviously in this study any mechanical interlocking mechanism was not sufficient to overcome the other factors resulting in poor bonding. The adhesive "positive" was still able to lift away.

As expected, the higher strength bonds were those that failed in cohesion. The systems in the higher G_C group failed entirely in cohesion or mostly in cohesion with some interlaminar failure. This is considered acceptable as well, as the substrate material rather than the bond failed. Comparing the Toray 3900 laminate systems prepared with clean and siloxane coated Polyester 60001 clearly shows the detrimental affect of contamination on G_IC. Rather than failing in cohesion as with the clean, the siloxane-coated Polyester 60001SRB prepared surfaces created bonds that failed in adhesion with the lowest G_IC values of all. 970/MB/60001, 970/MB/52006, 3900/MB/52006, 3900/MB/SRB, 3900/AF/SRB and MxB/EA/60001 all failed entirely in adhesion. They can therefore be compared as in Table 5.3. The surfaces prepared with polyester 60001 created stronger (though still inadequate) bonds than those prepared with nylon 52006 within these systems. Table 5.4 and Table 5.5 offer a simplified view of bond quality results. In the Toray 3900 and 970 systems, bond quality of laminates produced with nylon peel plies was very sensitive to the adhesive used. AF 555 bonded well to the nylon prepared surfaces; whereas a dramatic decrease in fracture energy was observed when nylon-prepared surfaces were bonded

Table 5.3: Comparison of G_C data of systems that failed in adhesion

Specimen ID#	G_C (J/m^2)
MxB/EA/60001	386
970/MB/60001	242
970/MB/52006	190
3900/MB/52006	122
3900/AF/SRB	93.9
3900/MB/SRB	86.0

Table 5.4: Failure mode of PF 60001 polyester prepared surfaces

	Cytec MxB	Cytec 970	Toray 3900
Henkle EA9898	Adhesion	—	—
AF555	—	Cohesion	Cohesion
MB 1515-3	—	Adhesion	Cohesion

Table 5.5: Failure mode of PFG 52006 nylon prepared surfaces

	Cytec MxB	Cytec 970	Toray 3900
Henkle EA9898	Cohesion	—	—
AF555	—	Cohesion	Cohesion
MB 1515-3	—	Adhesion	Adhesion

with MB 1515-3. The fracture mode also changed from cohesive (AF 555) to adhesion (MB 1515-3). Cytec MxB, however, produced strong bonds when prepared with nylon peel ply, but not with polyester.

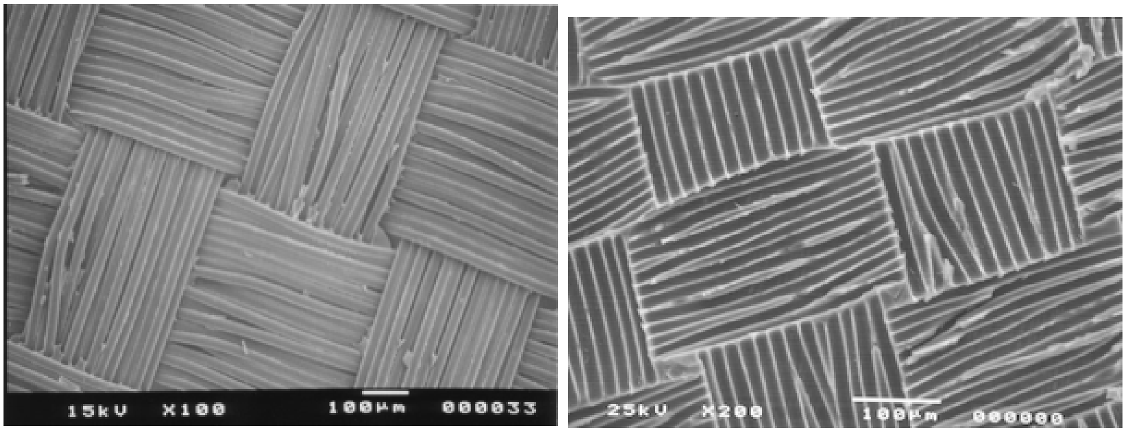
5.2 Surface Characterization

5.2.1 Examination of Removed Peel Ply Fabric

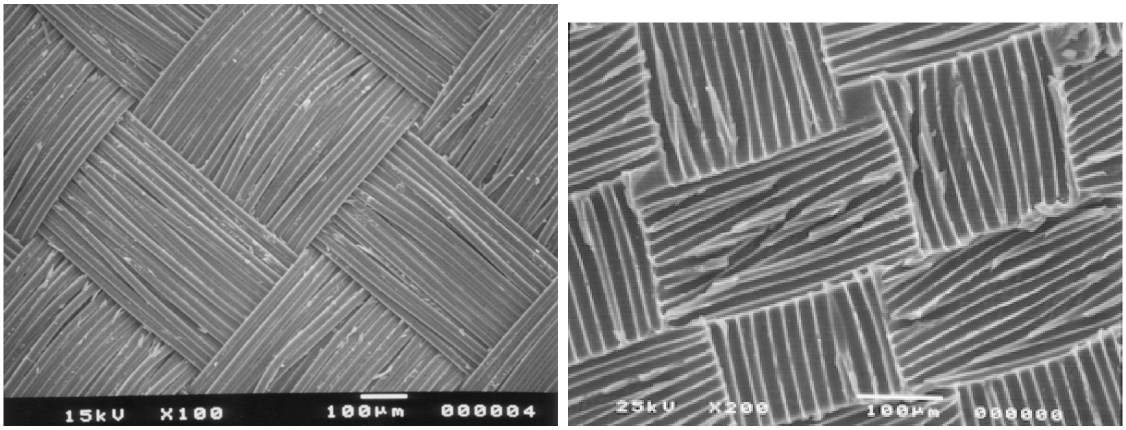
The texture of the peel ply fabric directly controls the laminate surface topography when the predominate mode of fracture during peel ply removal is along the interface between the peel ply filaments and the epoxy matrix (mode 2 in Figure 2.6). This effect can be seen in Figure 5.5 as an imprint of the peel ply fabric onto the surface of the laminate, and was observed in all laminates.

The peel plies removed from the laminates were examined in the SEM and example cases from the Toray 3900 system are displayed in Figure 5.6. In all cases the matrix epoxy clearly impregnated the peel ply fabric, even completely encapsulating fibers in some cases (example in the center of Figure 5.6 a). Areas of epoxy remain between fibers and especially at intersections of warp and weft of the removed peel ply (as seen in the bottom right of Figure 5.6 b), showing regions of fractured epoxy must remain on the laminate surface.

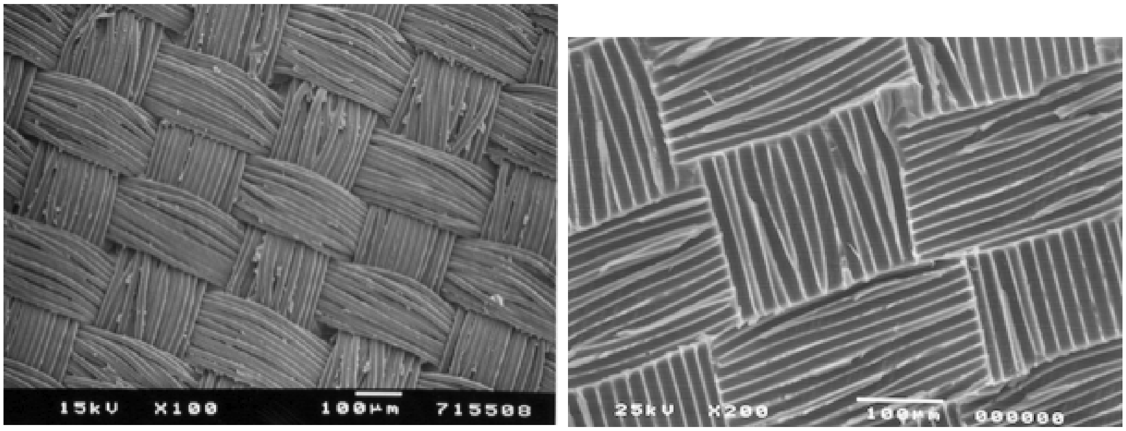
Of particular interest in examining these removed peel plies, is the existence of damage to the peel ply filaments. In the Toray 3900 system, the filaments of the Polyester 60001 peel ply appear similar to the filaments in the as received peel plies with very few areas of damage. There are some small light "nicks" sporadically along the fibers, and rare small areas of "peeling." The filaments in the Nylon 52006 peel ply have a more tortured appearance; the surfaces are not clean and smooth, but rather ragged and torn. There are many areas of the fiber surfaces where nicks and strips were exfoliated from the filaments. Some of the fibers, or possibly just their coating, in the siloxane coated Polyester 60001SRB peel ply even look as though they have cracked. The state of the peel ply fabric fibers suggest that the transfer of material during cure may not have just been epoxy seeping into the peel ply to be torn away; the peel ply may have lost material to the surface as well.



(a) Polyester 60001 fabric (b) 60001-prepared laminate

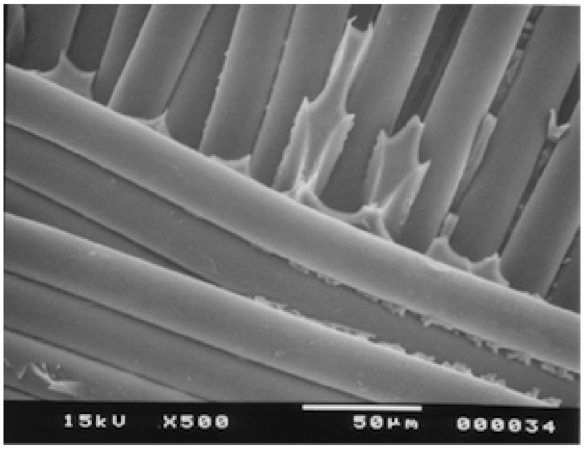


(c) Polyester 60001 SRB fabric (d) 60001 SRB-prepared laminate

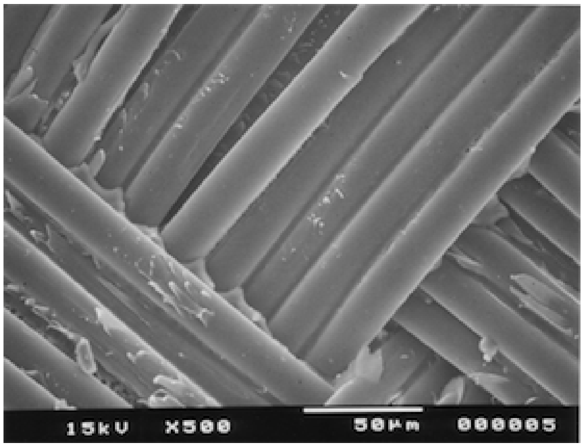


(e) Nylon 52006 fabric (f) 52006-prepared laminate

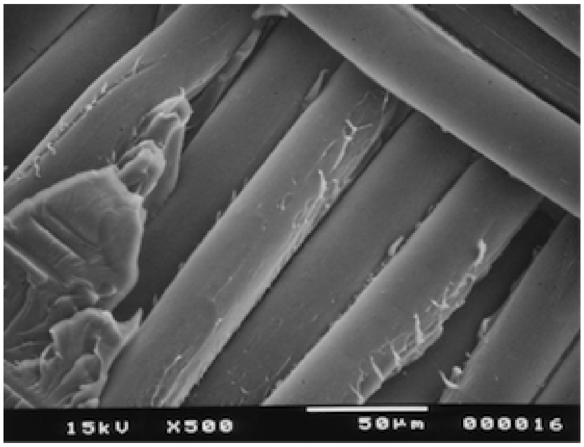
Figure 5.5: Removed peel ply fabric and Toray 3900 laminate surfaces after separation in preparation for bonding



(a) Polyester 60001



(b) Nylon 52006



(c) Polyester 60001 SRB

Figure 5.6: SEM micrograph of peel ply after removal from cured Toray 3900 laminate, illustrating fractured epoxy and the damage to the peel ply filaments the nylon peel ply.

5.2.2 Surface Character Initial Results

In order to investigate the possible transfer of material from the peel plies, the laminate surfaces were examined via SEM after peel ply removal and before bonding, as can be seen in Table 5.6.

Table 5.6: Laminate Surfaces After Peel Ply Removal

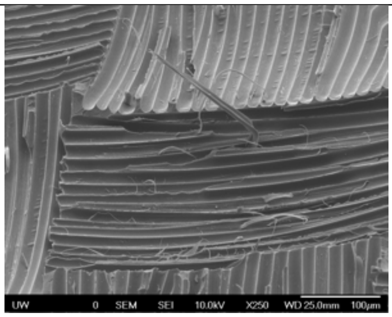
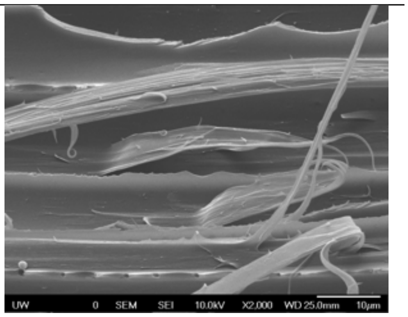
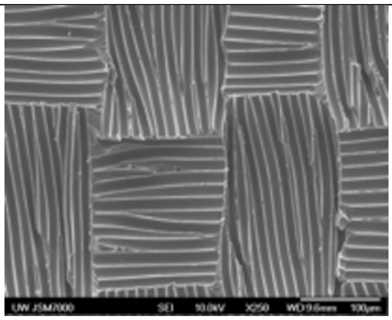
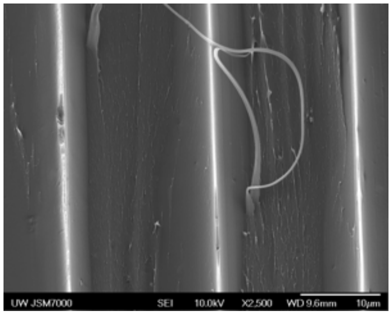
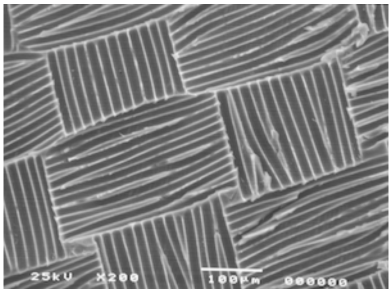
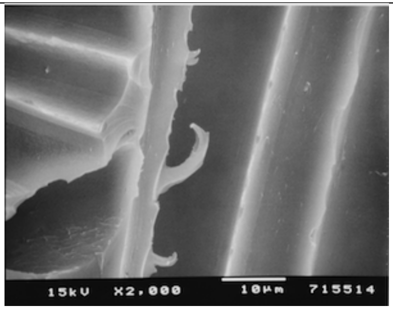
Specimen ID#	Laminate Surface 250x	Laminate Surface 2000x
970/60001		
970/52006		
3900/60001		

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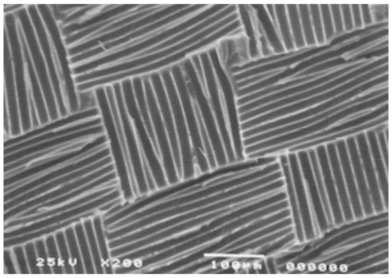
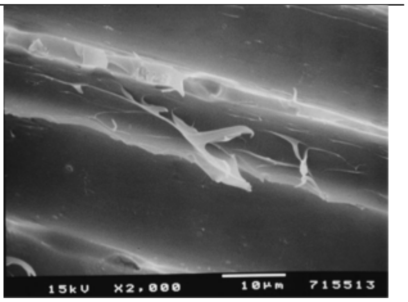
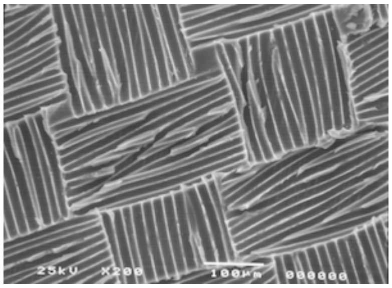
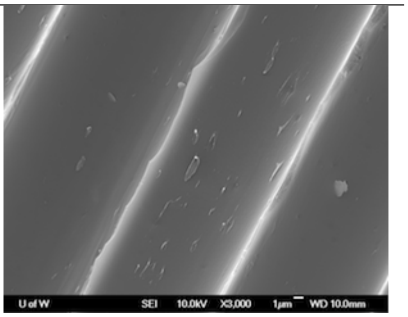
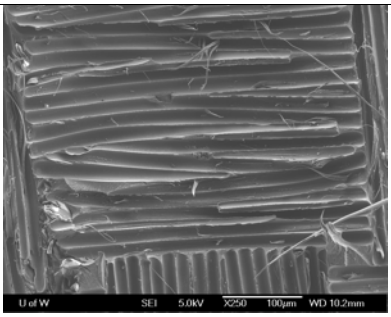
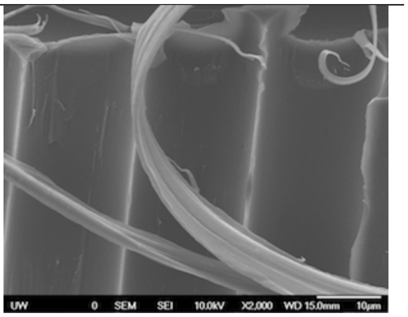
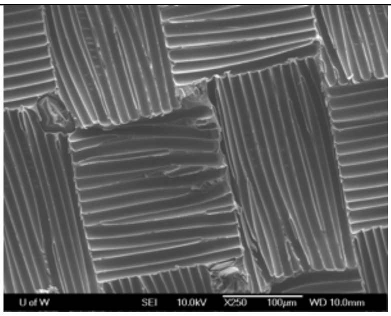
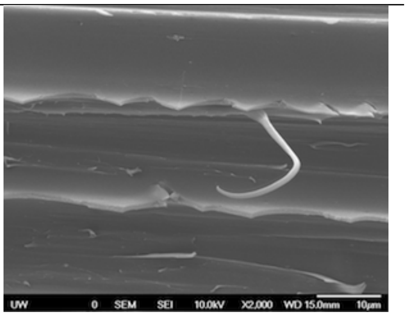
Table 5.6 – *Continued from previous page*

Specimen ID#	Laminate Surface 200x	Laminate Surface 2000x
3900/52006		
3900/SRB		
MxB/60001		
MxB/52006		

2000x magnification reveals at least some transfer of peel ply to all surfaces. As suggested by Figure 5.6, the laminates in the Toray 3900 systems show evidence of peel ply remnants. In fact, all surfaces studied were affected to some degree, with some cases are more severe than others. The Cytec 970 and MxB laminates prepared with Polyester 60001 are particularly striking. Large strips are visible, as well as many small hairy filaments sticking up along the length of the channels. Peel ply remnant strands stretch and curl over the surface of the laminate.

The character of the debris left behind matches the damaged areas still attached to the peel ply fibers observed after removal in Figure 5.6. This form of fracture from the fibers makes sense in the context of peel ply manufacture. The fabrics are drawn, aligning the polymer chains. Bits of the outer layer peeling off from deeper peel ply fiber material is a reasonable result of this structure. Peel plies are also subjected to heat treatments and solvent baths, leaving the peel ply fibers with differing material properties at different diameters, and potentially a more separable outer layer.

Looking at the prepared surfaces at higher magnification also in Figure 5.6 supports the hypothesis, as it shows that even those prepared surfaces that initially appeared clean have some peel ply remnants left behind. There are clear examples of ductile fracture in the channels. These are transferred material from the thermoplastic peel plies, as the thermoset epoxy matrix would only exhibit brittle fracture.

5.3 Surface Energy

The surfaces left behind by peel ply treatment clearly differ in more than texture. Simply the quantity of large peel ply remnants left on the surface can't completely explain the bonding results, as the 60001SRB prepared surfaces would be expected to have the most obviously cluttered surface since they had the lowest GIC values. Some of these surfaces even looked relatively clean at lower magnifications while creating bad bonds, and 250-2000x SEM is not a practical check of a surface in the field. The third research objective was implemented in order to more fully explain the differences in bond quality: comparison of surface energy measurements and wettability envelopes between the surfaces that created varying bond quality. This also provided the opportunity for assessing these methods as predictive techniques for untested composite system combinations and quality assurance techniques.

5.3.1 Single Measurement Contact Angle Results

A lower contact angle means a higher surface energy, and according to theory better adhesion [1]. Contact angles were measured on all prepared surfaces with ethylene glycol. Even an initial review of the contact angle averages in Table 5.7 shows that these measurements are not useful for judging surfaces. While some results were expected, such as Polyester 60001SRB-prepared surfaces having the largest contact angle signifying very little wetting behavior, they largely did not correlate with bond quality results. Toray 3900 prepared with the Nylon 52006 peel ply had a smaller angle than when prepared with the Polyester 60001. This should mean it has a higher

Table 5.7: Ethylene glycol single measurement contact angles

Specimen ID #	Avg Angle (deg)	St Dev
970/60001	15.6	7.5
970/52006	20.2	4.6
3900/60001	32.3	5.6
3900/52006	20.8	4.1
3900/SRB	56	3.0
MxB/60001	12.3	6.7
MxB/52006	31.7	8.7

surface energy and theoretically should wet and bond better than the Polyester 60001-prepared surface. The bonds failed when bonded with MB 1515-3, however, but the 60001-prepared surfaces created strong bonds. Similarly, Cytec MxB prepared with Polyester 60001 had a substantially lower contact angle than when prepared with Nylon 52006, but the former failed in adhesion while the latter was strong enough to fail in cohesion, the opposite of the theoretically expected result.

In addition to single contact angle measurements and surface energy calculations, a quick ”water break” test is sometimes performed in the field to test the quality of preparation and for contamination before bonding. Acknowledging the inaccuracy of this method, DMSO has been suggested as a replacement fluid particularly for these epoxy-based systems since its polar and dispersive surface energies are close to most epoxies [110]. DMSO wet out on almost all of the substrate surfaces in this study, however, even in the systems that produced poor bonds. While lack of a ”DMSO break” would indicate an inadequate surface, wetting by DMSO is not a promise of a strong bond.

Table 5.8: Average contact angle measurements of multiple fluids

Specimen ID #	DIH_2O Avg Angle (St Dev)	Ethylene Glycol Avg Angle (St Dev)	Formamide Avg Angle (St Dev)	DMSO Avg Angle (St Dev)	Glycerol Avg Angle (St Dev)
970/60001	76.9 (4.9)	15.6 (7.5)	38.7 (10.8)	wet out	56.2 (7.4)
970/52006	47.8 (5.3)	20.2 (4.6)	32.8 (4.5)	wet out	51.6 (4.3)
3900/60001	62.9 (2.2)	27.8 (3.6)	NA	7.4 (1.6)	60.4 (5.1)
3900/52006	57.1 (3.9)	20.8 (2.7)	NA	7.6 (1.7)	59.5 (6.1)
3900/SRB	85.8 (4.0)	56 (3.0)	NA	39.2 (4.8)	NA
MxB/60001	54.7 (3.0)	12.3 (4.5)	NA	wet out	NA
MxB/52006	46.1 (3.6)	31.7 (3.0)	NA	wet out	NA

5.3.2 Multiple Measurement Kaelble Plot Technique

To gain a more full picture of the surface energy of the prepared surfaces, and its potential uses for bond quality prediction, a more involved contact angle technique was investigated. Measurements were taken on all surfaces using de-ionized (DI) water, ethylene glycol, DMSO, glycerol, and/or formamide. Diiodomethane and tetrabromoethane were also attempted, but wet out all the surfaces. As mentioned above, most surfaces were wet out by DMSO and those that weren't had very low contact angles. In addition to using more measurements and fluids for higher accuracy, constructing Kaelble plots [110] breaks surface energy into its polar and dispersive components. The known polar and dispersive components of the surface tension (γ_l^p and γ_l^d) of de-ionized (DI) water, ethylene glycol, DMSO, glycerol, and formamide [2] and the measured contact angles (θ) on each surface were used to construct Kaelble plots such as that shown in Figure 5.7 for Toray 3900 laminate prepared with PFG 60001 peel ply. The square of the slope of a linear fit of these plots is the polar com-

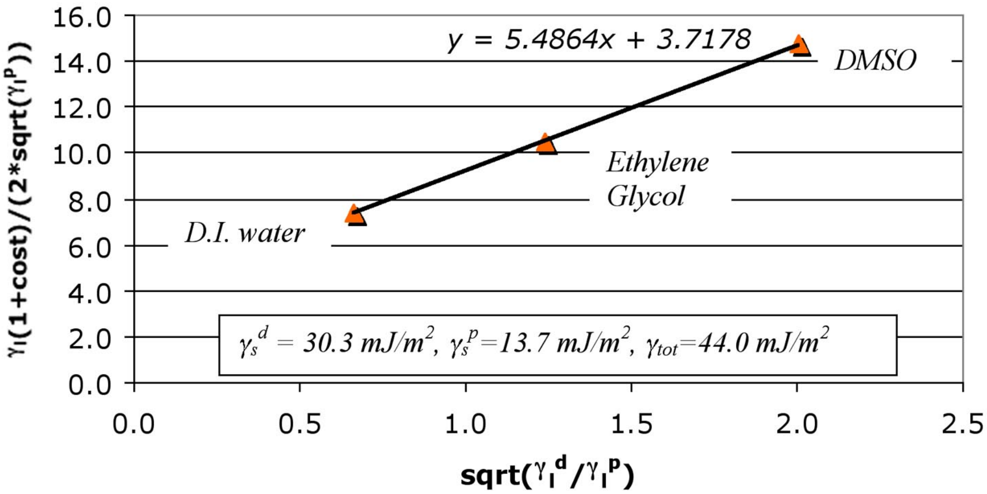


Figure 5.7: Linear Kaelble plot for surface energy measurement from contact angle data on Toray 3900 laminate prepared with PFG 60001 peel ply.

ponent, γ_s^p, and the square of the intercept is the polar component, γ_s^d, of the surface energy of the laminate.

The results of contact angle measurements and calculated surface energies are summarized in Table 5.9. The total surface energy γ_s^{total}, is very similar between the surfaces, however there are significant differences in the dispersive and polar components of the surface energy between the polyester and nylon peel ply prepared surfaces. This technique therefore yields additional information about surface energy in comparison to single contact angle/surface energy measurements. The polyester peel ply prepared surfaces have a greater dispersive component, while the nylons have a larger polar component of surface energy.

Once again a contact angle measurement technique and associated calculated surface

Table 5.9: Surface energy and components of adherend surfaces after peel ply removal, calculated by the Klaeble plot method.

Specimen ID #	γ_s^d	γ_s^p	γ_s^{total}
970/60001	55.5	1.7	57.2
3900/60001	31.9	14.2	46.1
MxB/60001	27.04	20.3	47.3
3900/SRB	32.5	2.6	35.1
970/52006	22.0	25.8	47.8
3900/52006	19.4	26	45.4
MxB/52006	8.41	44.9	53.3

energy could possibly be used to call out a particularly contaminated surface. The 3900 laminate prepared with 60001SRB does have lower surface energy than the rest. The more detailed surface energy measurements still do not correlate to bond quality in the other cases, however, requiring that one ”know the answer” to be sure that the lower surface energy of the 60001SRB is due to contamination that will cause poor bonding. The utility of Kaelble plots therefore lies largely in the creation of wettability envelopes from their determined surface energy components.

5.3.3 Wettibility Envelope Results

Wettability envelopes were calculated using the dispersive and polar components of the surface energy data calculated by the Kaelble plot method above and displayed in Table 5.9. According to the theory, fluids with surface energies that place them inside the envelope of a given surface will spontaneously wet the surface and those outside the envelope will not. It is important for adhesives to wet out the substrate as otherwise there is no hope of the intermolecular contact or mechanical interlocking

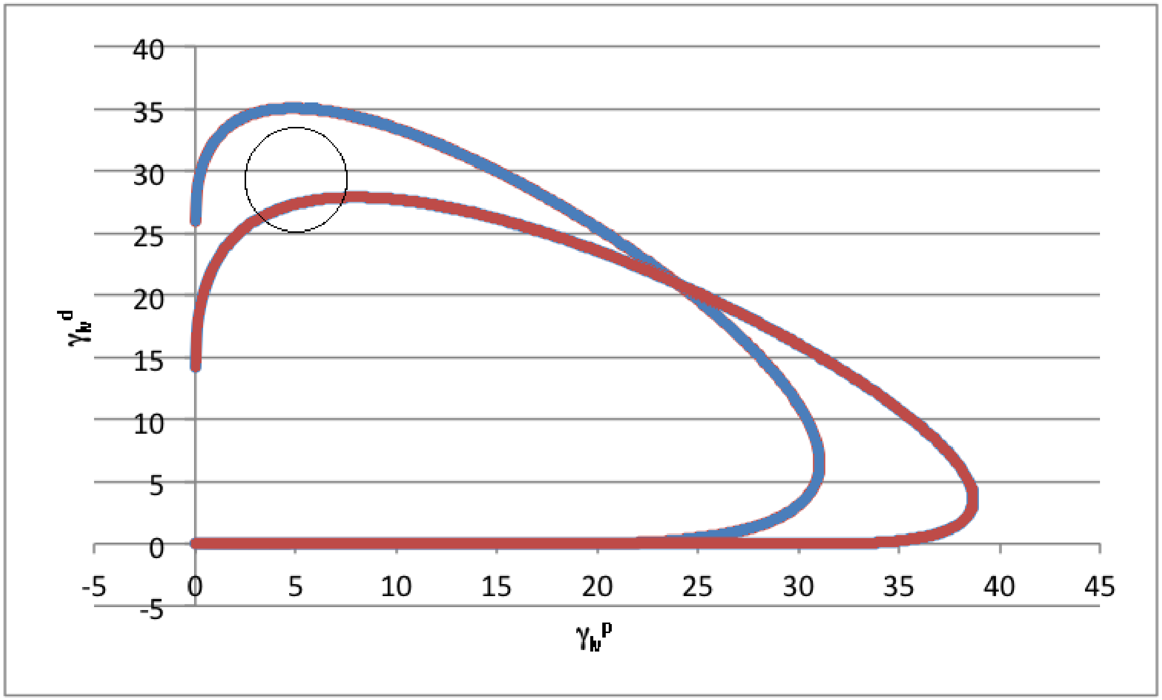


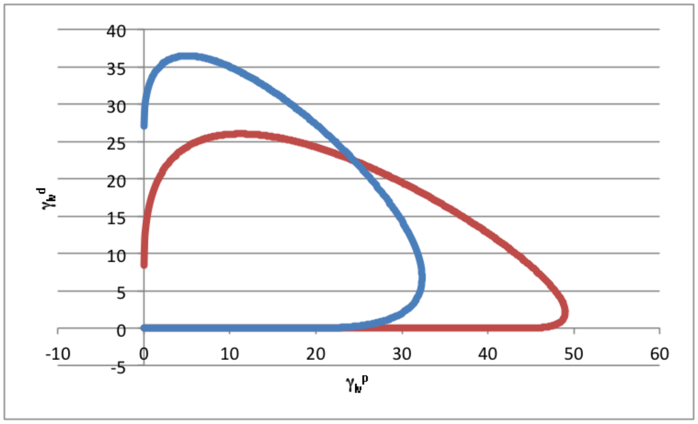
Figure 5.8: Wettability envelopes for Toray 3900 prepared with polyester 60001 (red) and nylon 52006 (blue) peel plies. Circle indicates general region of epoxy adhesives.

required for bonding. Therefore the wettability envelopes are a potential method to determine if a surface is suitable for bonding. The wettability envelopes for all composite systems are shown in Figure 5.9. There are significant differences in the wettability envelopes between nylon and polyester prepared surfaces. For reference, a typical range of values of surface energies for epoxy adhesives are shown by the circle [76] in Figure 5.8. The precise surface energies of the adhesives used in this study were not available from the literature or the manufacturers.

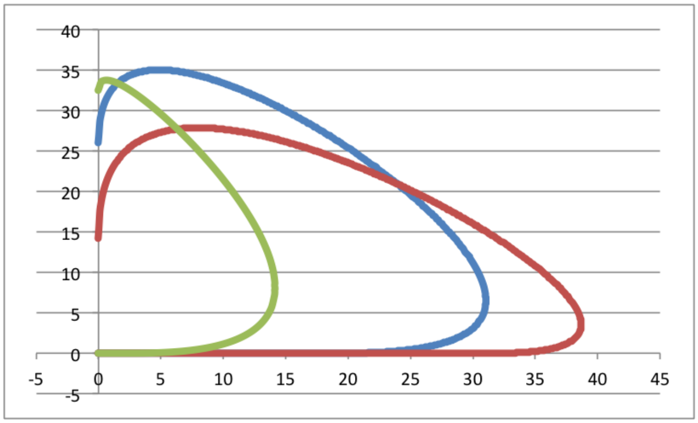
It is important to note that contact angles by themselves were not sufficient to predict poor bonding. Because the bond quality varied between adhesives on surfaces prepared with the same peel ply, it is clear that neither contact angle measurements nor the surface energies derived from them can tell the whole story about the bondability of a surface. Examination of the wettability envelopes could be of some use, however. The shape of the wettability envelope varies substantially between polyester and nylon prepared surfaces, as was shown in Figure 5.9. They therefore show that the surface energetics are indeed changed by the residue left during peel ply removal, something not shown by the contact angles in Table 5.7 or the resulting total surface energy measurements shown in Table 5.9. Therefore their different energy profile (polar vs dispersive) may be much more useful.

Due to the proprietary nature of adhesives the exact value for their surface energies is unknown, but the general range of epoxies are marked on Figure 5.8. Epoxy adhesives fall within the area likely to wet for polyester prepared surfaces, but not all are within the wetting envelope for nylon surfaces. This may offer a possible explanation of the poor bonding with MB 1515-3 on nylon peel ply prepared surfaces in both the Toray 3900 and Cytec 970 composite systems. The surface energy of MB 1515-3 may be slightly outside that wettability envelope of these nylon prepared surfaces. Even this does not, however, explain the fact that polyester prepared surfaces created poor bonds and nylon prepared surfaces created strong bonds on a Cytec MxB laminate. Wetting is therefore a necessary but not sufficient condition for strong bonds.

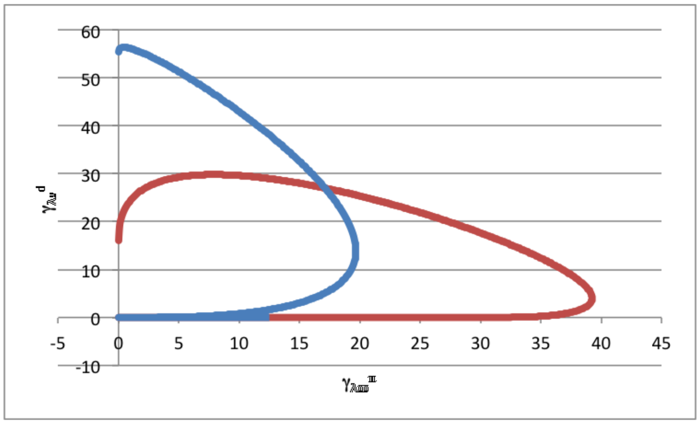
Wettability envelopes can therefore be a useful tool for explaining some failures and possibly a check method for prepared surfaces. Changes in the wettability envelope of a surface known to bond when prepared properly can signal a variation in manufacture. The accidental use of the wrong fabric could be clearly exposed by a wettability envelope due to the substantially different shape, for example, where contact angle or surface energy measurements (currently used as a check in the field) would not show a difference. While projected wetting via the wettability envelope is not enough to confidently predict strong bonding for any given surface, wetting expected on a system that is generally known to bond may be.



(a) Cytec MxB



(b) Toray 3900



(c) Cytec 970

Figure 5.9: Wettability envelopes for polyester 60001 (blue), polyester 60001SRB (green), and nylon 52006 (red) peel ply prepared laminate surfaces.

5.4 Surface Chemistry

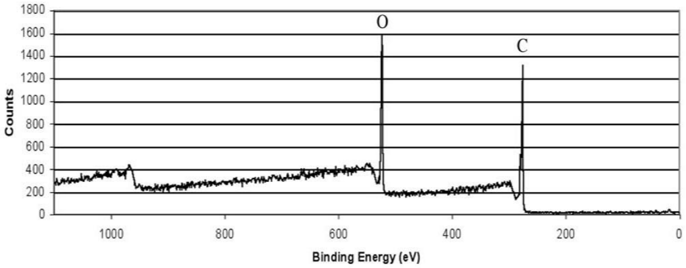
5.4.1 Prepared Surface Chemical Composition Results

The transfer of material from the peel plies was further investigated through XPS analysis of selected samples. Figure 5.10 shows the spectra collected during the survey scan of the Toray 3900 composite surfaces for composition in comparison with a spectrum of an epoxy control. The quantity of nitrogen on the surface of the nylon prepared sample is immediately noticeable, supporting transfer of peel ply to the laminate surface. There is no evidence that the surfaces prepared with nylon (that ultimately failed when bonded with MB 1515-3) were contaminated with something else that could be an alternate explanation for failure.

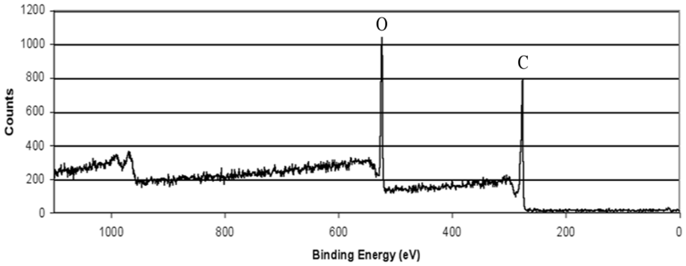
Table 5.10 displays the results of chemical composition scans of the selected prepared surfaces. The nitrogen increase is apparent on all nylon-prepared surfaces, and there is a suggestion of oxygen increase on the surface of the polyester-prepared surfaces which could be the result of polyester transfer to the surface. No extraneous contamination was found.

Table 5.10: Relative concentrations of elements found on laminate surfaces by XPS

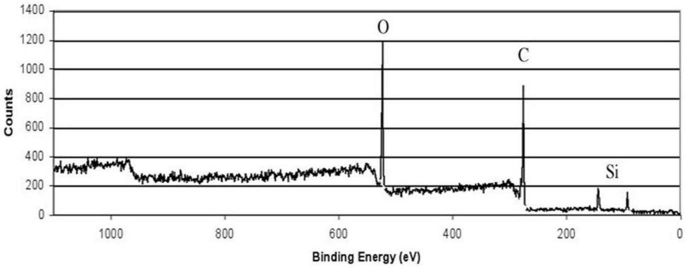
Specimen ID #	C	O	N	Si
3900 laminate	81.1	17.4	1.5	
3900/60001	76.6	22.1	1.3	
3900/52006	73.7	20.3	4.0	
3900/SRB	66.5	15.6	2.6	2.9
MxB/60001	73.8	25.2	1	
MxB/52006	76.1	12.4	11.5	



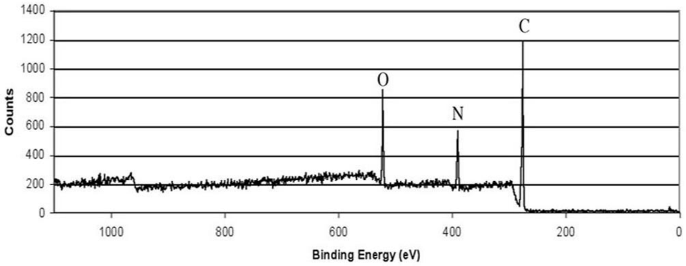
(a) Laminate control



(b) Polyester 60001 prepared



(c) Polyester 60001SRB prepared



(d) Nylon 52006 prepared

Figure 5.10: XPS composition scan spectra of Toray 3900 a) laminate control and laminates after removal of b) Polyester 60001, c) Polyester 60001SRB, or d) Nylon 52006 peel plies.

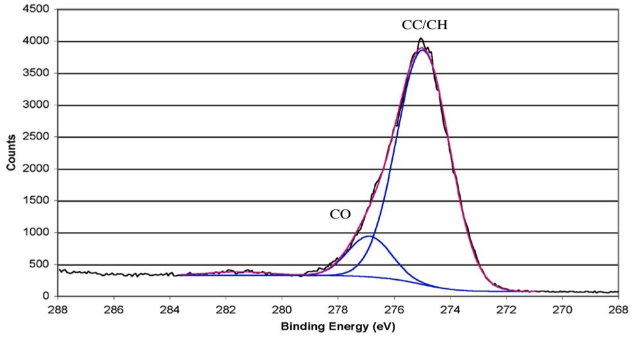
5.4.2 High Resolution Carbon Scan Results

The nitrogen composition and bonding of oxygen were examined more closely through high-resolution scans of the C (1s) region (Figure 5.11). Table 5.11 presents the respective amounts of the carbon species given by these peaks in each composite system.

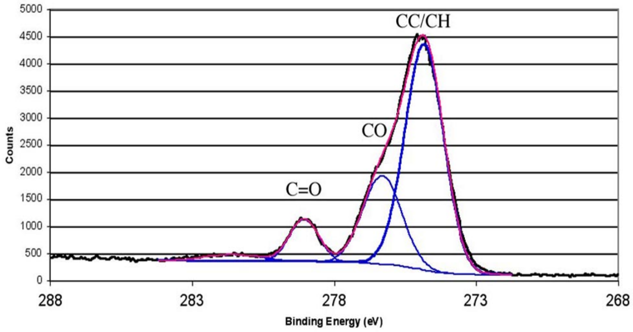
The nitrogen is shown to be part of amide groups, confirming that the nitrogen increase on the surface is the result of nylon transfer. The high-resolution scans also reveal that the polyester-prepared systems show an increase in the C=O bonds characteristic of polyester, reflecting transfer among those systems as well.

Table 5.11: Carbon Bonding in Samples After Peel Ply Removal

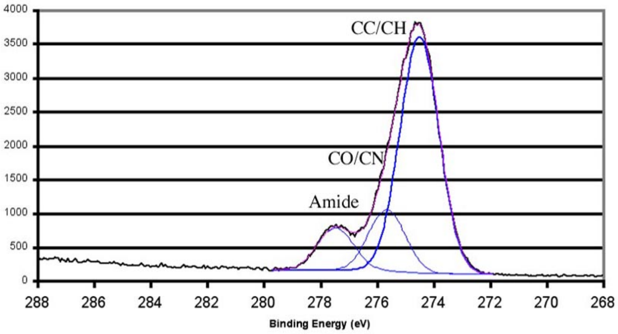
Specimen ID #	Species	%
Epoxy Control	CC/CH	83.8
	CO/CN	16.2
3900/60001	CC/CH	74.9
	CO	15.6
	C=O	9.5
3900/SRB	CC/CH	79.1
	CO	11.4
	C=O	9.4
MxB/60001	CC/CH	75.2
	CO	14.6
	C=O	10.2
3900/52006	CC/CH	71
	CO	17.1
	Amide (NC=O)	11.9
MxB/52006	CC/CH	70.4
	CO	16.5
	Amide (NC=O)	13.1



(a) Laminate control



(b) Polyester 60001 prepared



(c) Nylon 52006 prepared

Figure 5.11: High Resolution C (1s) spectra of Toray 3900 a) epoxy control and after removal of b) polyester 60001, or c) nylon 52006 peel plies.

5.4.3 Failure Surface Chemistry Results

The material transfer from the peel ply fabrics seems to be key in the failure of bonds. This failure could be due to the adhesive not bonding to the remnants, the adhesive bonding to the remnants and then the remnants pulling away from the laminate when under load, or the nylon and polyester peel ply remnants may be breaking and causing bond failure. A failure in adhesion is along the bondline, so one fracture surface will be largely the adhesive and the opposing fracture surface will be left as largely bare matrix epoxy. When considering the surfaces of the current study that have a region including peel ply remnants along the surface, this essentially becomes the three possible types of ”failure in adhesion” seen in Figure 5.12. If the adhesive could not bond to the remnants, they would be left on the laminate side after fracture. If the peel ply fibers were pulling away from the laminate, the characteristic chemical groups would be found only on the adhesive side after fracture. If the peel ply remnants were failing, both sides of the fracture would be left with tell-tale traces. The systems that failed in adhesion were therefore examined with XPS. The chemical species found via high resolution scans of the carbon region are displayed in Table 5.12.

Both fracture surfaces from bonds that had been prepared with nylon 52006 peel ply had a substantial quantity of amide groups that are not a part of the adhesive formulation. XPS of the fracture surfaces from bonds that had surfaces prepared with polyester 60001 peel ply and ultimately failed in adhesion revealed carbon-oxygen double bonds characteristic of the polyester on both sides of the fracture as well. These features indicate that failure is occurring through the fiber remnants. SEM examination of the surfaces of failure in adhesion demonstrated fracture through the

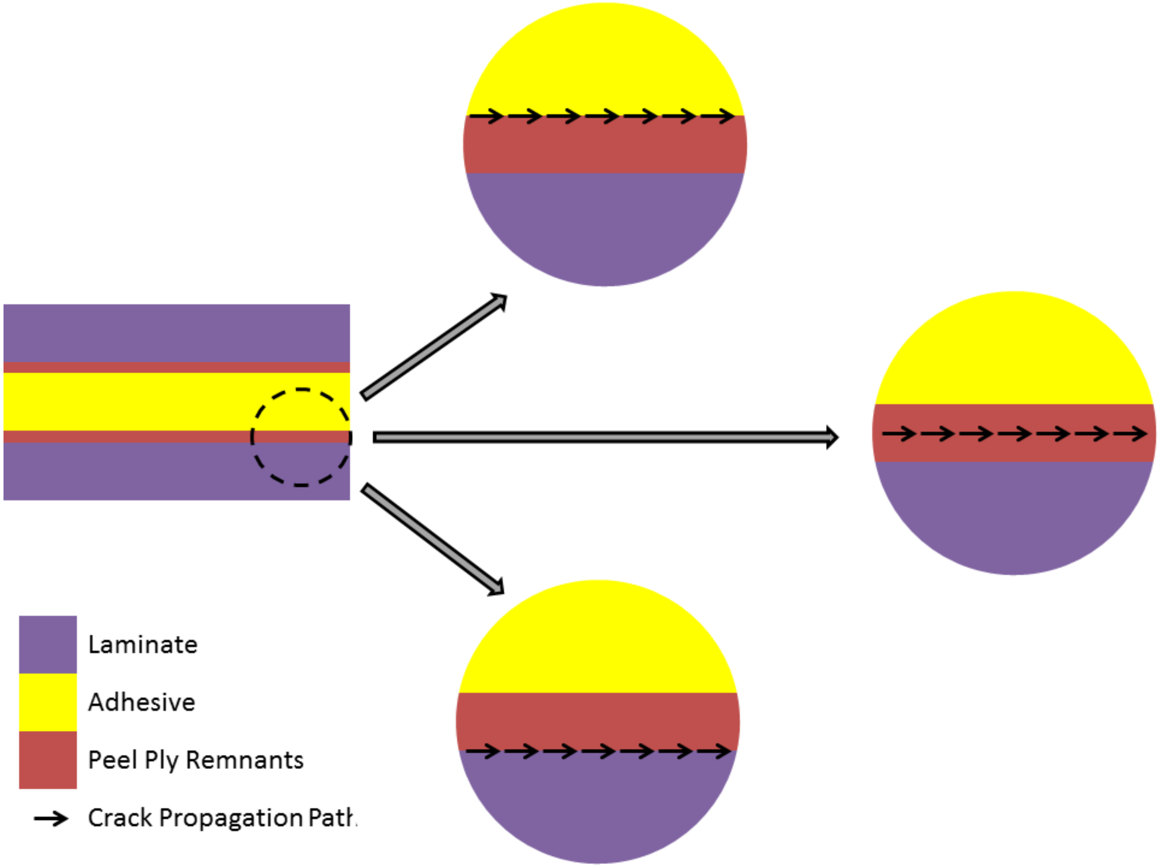
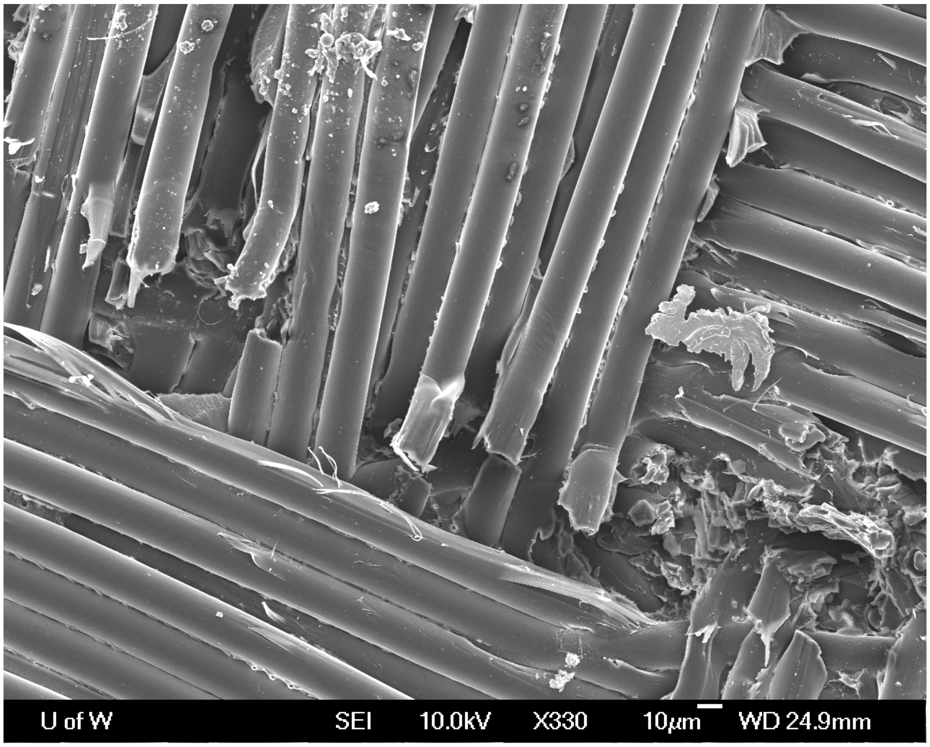


Figure 5.12: Three crack propagation paths with relation to the peel ply remnants that would be classified ”failure in adhesion.”

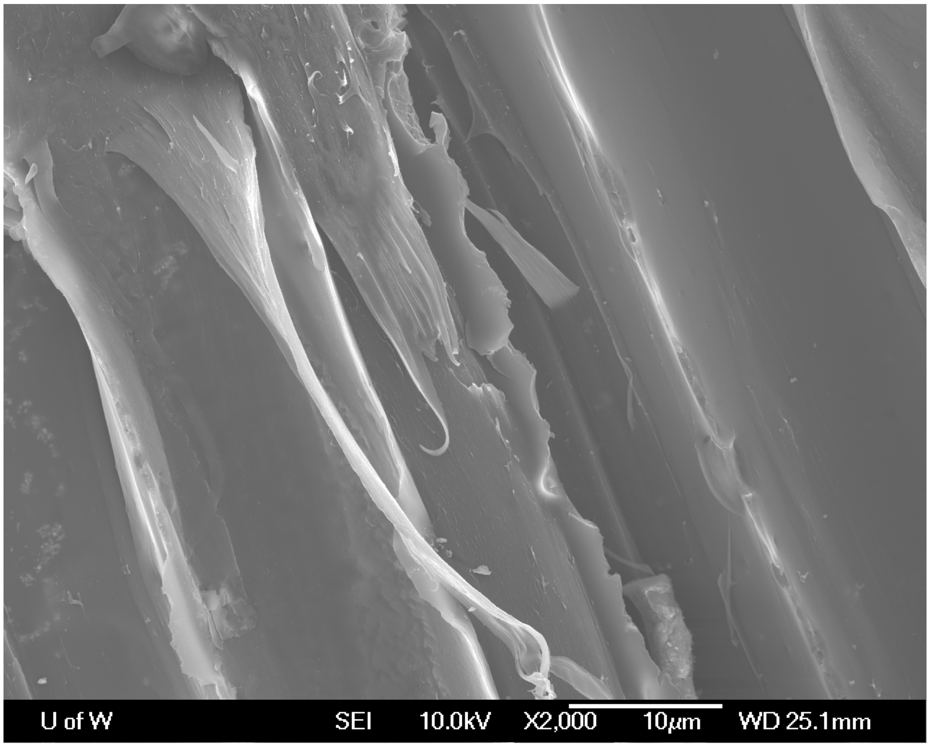
Table 5.12: Carbon Bonding of Adhesive Side After Bond Fracture

Specimen ID #	Species	% Adhesive Side	% Laminate Side
970/MB/60001	CC/CH	71.6	66.5
	CO	22.6	26.8
	C=O	5.9	6.7
MxB/EA/60001	CC/CH	67.6	65.5
	CO	24.9	26.3
	C=O	7.5	8.2
3900/MB/52006	CC/CH	64.4	66.6
	CO	29.8	21.2
	Amide (NC=O)	5.8	12.2
970/MB/52006	CC/CH	65.2	68.5
	CO	27.2	22.8
	Amide (NC=O)	7.6	8.7

remnants as well, as both sides showed the whisps of peel ply fibers as seen in the small areas of ductile fracture in Figure 5.13.



(a) Adhesive Side



(b) Substrate Side

Figure 5.13: SEM of Cytec MxB/60001/EA9696 laminate failure surfaces, illustrating peel ply filaments on both sides of fracture.

Chapter 6

GENERAL DISCUSSION

It was proposed that the inconsistency of peel ply surface preparation bond quality between composite material systems were the result of differing quantities of peel ply debris transferred to the surface and their interactions with the adhesive. The goals of this research were then to identify representative composite systems, compare surface energy measurements and wettability envelopes of the surfaces with resulting bond quality, confirm and characterize peel ply remnants on all surfaces prepared for bonding, and compare the results of peel ply remnant debris to the situation of known chemical surface contamination. This study provided an opportunity to examine the usefulness of prepared surface wettability envelope construction for a prediction of resulting bond quality.

The characteristic systems were chosen to represent materials and techniques currently in use in the aerospace industry. Two 176C cure laminates, Toray 3900 and Cytec 970, were used as well as a 121C cure laminate Cytec MxB. These were all prepared with Polyester 60001 and Nylon 52006 peel ply, and the Toray system was additionally tested with a siloxane-coated polyester 60001SRB. Surface energy values were determined via contact angle measurements, and wettability envelopes were then constructed. 176C cure systems were bonded with MB 1515-3 or AF 555, and 121C cure systems were bonded with EA 9696. The primary assessments of the quality of the resulting bonds were mode of fracture and fracture toughness (G_C) as measured by double cantilever beam (DCB) testing. Failure in adhesion (poor bonding) and in cohesion (strong bonding) were defined as failure in which the crack propagated along the interface between adherend and adhesive, or within the adhesive, respectively. The prepared pre-bond and fractured post-bond surfaces were characterized with SEM and XPS.

All laminates showed regions of fractured epoxy after removal of the peel ply, one of the goals of this surface preparation technique. These were between the fibers and in the corners where warp and weft of the peel ply met. The corners left the largest gaps for the epoxy to seep through and surround the fibers. The peel ply was bonded to the laminate largely through mechanical interlocking during this initial cure, and when the fabric was torn away the epoxy fractured and in those areas left a clean, more chemically active surface.

All tested systems displayed clear imprints of the peel ply texture on the prepared surface. Although there was the aforementioned fracture of the epoxy, the primary mode of fracture during peel ply removal was therefore along the interface between the peel ply filaments and the epoxy matrix. Upon closer inspection with SEM, however, all prepared surfaces showed debris and contained areas of ductile fracture that would not be expected from the epoxy laminate. These areas often had a strand-like appearance, all suggesting that they may be bits of peel ply material that had been transferred to the surface and not removed with the bulk fabric. The removed peel plies showed matching damage to the filaments under the SEM. Strips in the process of peeling away from the outer layers of the aligned polymer chain structure of the peel ply were observed.

XPS composition scans supported the hypothesis of peel ply material transfer as a significant nitrogen increase was apparent on all nylon-prepared surfaces, and there was possible oxygenation of the polyester-prepared surfaces. The high-resolution scans confirmed the transfer, as the nitrogen was largely a part of amide groups (which are not a part of the laminate chemistry), and the polyester-prepared surfaces showed the polyester-characteristic C=O bonds.

The measure of bond strength was G_C as measured by double cantilever beam testing. Tested bonds either measured between 80 and 400 J/m^2 and failed in adhesion (”weak” bonds), or between 600 and 1000 J/m^2 and failed in cohesion (”strong” bonds). Within each laminate system, the difference was clear between G_C values of systems that failed in adhesion and those than failed in cohesion. There was little obvious mixed mode of fracture; samples either failed completely in adhesion, completely in cohesion, or in cohesion with a small fraction of interlaminar (within the laminate) failure. AF555 adhesive worked well in all tested configurations of Toray 3900 and Cytec 970 laminates and Polyester 60001 and Nylon 52006 peel plies, with exception of the intentionally contaminated Polyester 60001SRB. As expected, Polyester 60001SRB created weak bonds that failed in adhesion at the lowest G_C values. MB 1515-3 only created a strong bond in the Toray 3900/60001 system. The Cytec MxB system was much weaker when prepared with the polyester 60001 peel ply rather than the nylon 52006. The Toray 3900/MB 1515-3 system was the opposite, and only the polyester 60001 peel ply preparation created a strong bond.

A comparison of the 970/MB/60001, 970/MB/52006, 3900/MB/52006 and MxB/EA/60001 systems that failed in adhesion showed that 60001 peel ply preparation created stronger (still inadequate) bonds than 52006 peel ply preparation. The failure surfaces of these systems also had the imprint of the peel ply texture, demonstrating that at least superficial wetting is occurring. SEM of the surfaces on both sides of the failure in adhesion showed peel ply fibers, and XPS detected the characteristic chemical signatures of these peel ply remnants (amides and C=O). This is consistent with failure occurring through the fiber remnants.

Within the Cytec MxB systems, bond quality was determined by the quantity of peel ply debris left behind. The Polyester 60001 prepared surfaces were substantially littered with peel ply remnants and failed in adhesion, while the relatively clean Nylon 52006 prepared surfaces failed in cohesion. This may be explained in terms of Robertson's work [51] on critical thickness of a boundary layer to become a weak boundary layer. Nylon contamination was found on the Cytec MxB laminates, but at much higher magnifications and through XPS. The difference in coverage of the surface, therefore, may be one largely of size of the remnants. In terms of Robertson's work, then, the polyester remnants may be beyond the critical thickness for this system to become a weak boundary layer. The existence of SEM-visible polyester fibers and XPS-detected chemical species on both sides of the fracture surfaces that failed in adhesion confirms that the crack was ultimately able to propagate through the boundary layer of nylon remnants. This is consistent with the weak boundary layer of a critical thickness hypothesis. An estimate of the critical thickness of the peel ply remnants based on the work herein might be in the range 1μm-5nm; it is easily detectable by SEM, and larger than the thickness of nylon remnants observed in this study (most on the order of 10nm).

Examination of the adhesive side of the fracture surfaces that failed in adhesion also demonstrated that at least superficial wetting of the laminate by the adhesive is occurring in all samples. The adhesive took on the form of the imprint left by the peel ply, down to some roundness at the top edges of the false "fibers" that lifted out on failure. It is therefore possible that surface texture created by peel ply removal assists some mechanical interlocking mechanism in bonding as suggested by Kieronski [91], especially in the corners where warp and weft had met. This mechanism was not sufficient to overcome the other factors resulting in poor bonding. The adhesive "positive" was still able to lift away.

In the Toray 3900 system bonded with MB1515-3 the peel ply chosen also determined the bond quality, as polyester-prepared surfaces failed in cohesion while nylon-prepared surfaces failed in adhesion. The adhesive used was revealed as a critical factor in this system; Toray 3900 surfaces bonded with AF555 created strong bonds regardless of peel ply choice. In the Cytec 970 systems, adhesive choice dominated bond quality; surfaces bonded with AF555 created strong bonds and surfaces bonded with MB1515-3 failed in adhesion.

If the Toray 3900 and Cytec 970 surfaces prepared with polyester are compared as in Figure 6.1, the importance of peel ply debris quantity becomes clear once again. The Toray 3900 had substantially less debris and failed in cohesion, while the Cytec 970 was substantially cluttered with polyester remnants and failed in adhesion. Comparison of the Toray 3900 and Cytec 970 surfaces prepared with nylon as in Figure 6.2 demonstrates the importance of peel ply debris compatible surface chem-

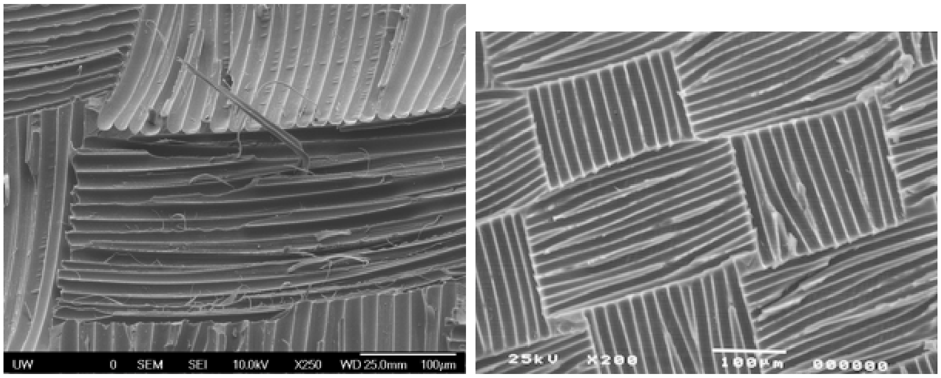


Figure 6.1: Comparison of the Polyester 60001-prepared Cytec 970 (left) and Toray 3900 (right) surfaces. Cytec 970 failed in adhesion and Toray 3900 in cohesion when bonded with AF555.

istry as well as quantity. Both surfaces are only minimally contaminated by peel ply remnants, but both failed in adhesion when bonded with MB1515-3. The hypothesis that bond quality is directly related to quantity of peel ply material transferred to the surface is therefore only part of the story, complicated by adhesive choice. Both the quantity and the chemical compatibility of the peel ply debris determine bond quality. It is possible that AF 555 creates strong enough bonds with the uncontaminated areas of Toray 3900 epoxy that it can compensate for a larger level of fiber debris than MB 1515-3. Due to the proprietary nature of the adhesives used, it can only be guessed that perhaps the AF 555 adhesive utilizes the special techniques (such as incorporating certain side groups along the polymer chain of the adhesive [2]) necessary to allow primary bonding to the matrix epoxy, and the strength of the bond on the areas of clean surface is sufficient to compensate for the weakness of contaminated areas. It is also possible that the AF 555 and MB 1515-3 adhesive formulations result in differing interaction distances for the bonds created between the epoxies of the laminate and

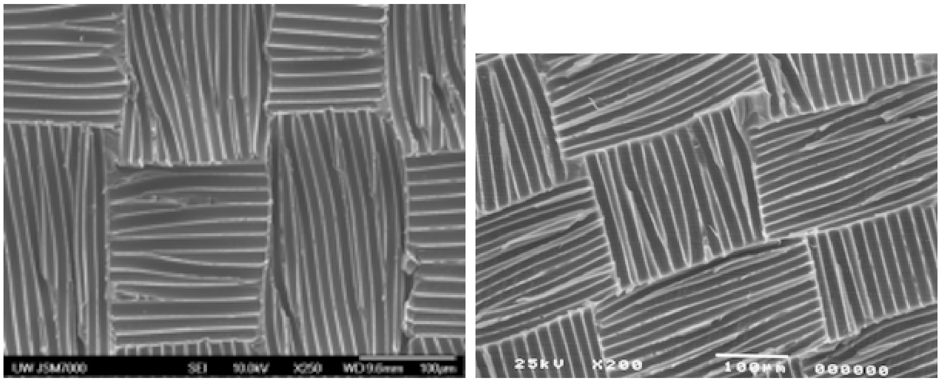


Figure 6.2: Comparison of the Polyester 60001-prepared Cytec 970 (left) and Toray 3900 (right) surfaces. Cytec 970 failed in adhesion and Toray 3900 in cohesion when bonded with AF555.

adhesive. In the cases where the contamination by peel ply remnants is so small as to not be seen through SEM, it is possible that it is a layer thin enough for the AF 555 epoxy to form the necessary secondary bonds for adhesion with the matrix adhesive while the MB 1515-3 formulation does not have sufficient interaction distance. The exact chemistry and mechanism for this greater effectiveness is beyond the scope of the current study, but it can be added to the understanding of the adhesives that AF 555 is tolerant of contamination of the surface by nylon peel ply remnants to a degree MB 1515-3 is not.

In an effort to predict which surfaces have been adequately prepared to bond well, contact angle measurement techniques were investigated. According to theory, high angles mean little wetting and poor bonding, while low angles indicate better wetting behavior and therefore bonding. Single liquid contact angle measurements did find surfaces prepared with Polyester 60001SRB to have the highest angles. Overall, however, the results did not correlate with bond quality. The Toray 3900 and Cytec MxB laminates prepared with Polyester 60001 and Nylon 52006 showed the opposite bond quality from what would be predicted based on their contact angles. Single liquid contact angle measurements/"water break" tests were eliminated as a possible good prediction tool for new composite systems, and were not even a reliable means of judging a known surface fit for bonding (such as revealing a change in manufacture). "DMSO break" tests were not a significant improvement, as DMSO wet out most of the surfaces that failed in adhesion in this study, and are advised against as well. DMSO could be used to reject a surface, as lack of wetting by DMSO assures a poor bond, but not to approve one.

The more detailed technique of using multiple liquid measurements to construct Kaelble plots and then wettability envelopes revealed that despite very similar total surface energies, nylon- and polyester-prepared surfaces have significant differences in the dispersive and polar components of the surface energy. The polyester peel ply prepared surfaces have a greater dispersive component, while the nylons have a larger polar component of surface energy. They therefore show that the surface energetics are indeed changed by the residue left during peel ply removal, something not shown by contact angles or the resulting total surface energy measurements. Not all important contaminations, perhaps, significantly change the total surface energy as is seen with something like a siloxane contamination from the SRB coated peel ply, or more dramatically in the contamination by oils of metal parts that historically were the domain of the water break test. The polymer peel ply fibers are simply not that different from the matrix in terms of total surface energy, but their affect on bonding is still clear. Therefore their different energy profile (polar vs dispersive) may be much more useful.

Epoxy adhesives fall within the area of the wettability envelopes most likely to wet for polyester prepared surfaces, but only some of the range overlaps with the wettability envelope of nylon prepared surfaces. This possibly explains the poor bonding with MB 1515-3 on nylon peel ply prepared Toray 3900 surfaces. It still cannot explain the contradiction that polyester prepared surfaces created poor bonds and nylon prepared surfaces created strong bonds on a Cytec MxB laminate. Wettability envelopes therefore cannot predict bonding for any given surface, but are more useful in explaining some failures and possibly as a check method for prepared surfaces than the currently used water break tests. Changes in the wettability envelope of a surface known to bond when prepared properly could expose the accidental use of the wrong fabric, for example.

This study has shown that the surface left behind after peel ply preparation is a determining factor for creating a high quality bond, and the situation is complex. Both the quantity and the chemical compatibility with the system adhesive are critical. Wetting, as shown via contact angle measurements, is a necessary but not sufficient condition for creating a high quality bond. The wettability envelope of a surface can expose changes in a known system that might preclude wetting and strong bonding, but even its additional information is not enough to guarantee an adequate bond in an unknown system. Single fluid contact angle measurements, water break tests, and DMSO break tests were all found to be insufficient for judging a surface adequately prepared for bonding. SEM is not always enough to demonstrate a poor surface, though SEM images with substantial debris are almost assured to fail. XPS can expose smaller quantities of peel ply transfer in apparently clean surfaces, and these quantities can be enough to cause premature bond failure. Such trace debris was found on all surfaces studied.

Chapter 7

FUTURE WORK

Many questions remain within peel ply surface preparation of composites for bonding. Some possible areas include

Critical thickness Development of a test and measurement method either to directly measure the thickness of the peel ply debris left on the surfaces, or for determining whether the strips coming off the peel ply fibers are planar. If they are, or nearly enough to be relevant, measure the widths of the remnants and determine thicknesses taking into consideration stretching and twisting that may have occurred during peel ply removal.

Adhesive bond type and interaction distance The differing results between adhesives on the visibly clean surfaces that show contamination via XPS suggest that perhaps the critical thickness of peel ply contamination affects bond quality based on the chemical bonding characteristics of the peel ply. Study of the adhesives could reveal whether adhesives such as AF 555 are successful even in the presence of small peel ply debris because of, for example, an interaction distance that allows bonding through the interphase or the strength of primary bonds formed in the areas without contamination.

ToF-SIMS Imaging and FTIR While in this study SEM gave excellent information on surface morphology and peel ply transfer, and XPS gave some quantification, further investigation may be well served by a technique that allows mapping of chemical species on the surface such as time of flight secondary ion mass spectrometry or Fourier transform infrared spectroscopy. Mapping the chemical species on the surface could help discover the extent to which peel ply species are transferring to the surface as a thin boundary layer, beyond larger fragments. SIMS could also be used to create a depth profile of the areas of contamination unseen by the SEM to determine the depth of such a coating.

Time in place studies In addition to being used to actually treat the surface, peel ply is used simply as a protective layer as a part is moved around and stored before being bonded. The amount of time and conditions of storage, such as UV exposure, that might weaken the peel ply may be relevant to the amount of peel ply transferred to the laminate surface.

Wet peel plies New peel plies are entering the market that are preimpregnated with their own epoxies. These should be thoroughly evaluated for debris left on the surfaces.

Manufacturer variation The final stages of peel ply manufacturing (heat setting, solvent baths, etc) are proprietary processes that vary by manufacturer. With the clear importance of the outermost layer of the peel plies shown in the current study, plies even of the same basic materials from other manufacturers may have very different results.

Chapter 8

SUMMARY

The goal of this research was to examine the prepared composite surfaces of key representative systems in order to examine how the surface created by peel ply affects bonding, taking special note of peel ply remnants, and to examine the usefulness of prepared surface wettability envelope construction for a prediction of resulting bond quality. The results contributed to the fundamental understanding of the role surface energy and the interphase thickness play in resulting bond quality. The following were demonstrated:

- The division was clear between strong bonds (G_C of 600-1000J/m^2 and failure in cohesion) and weak bonds (G_C of 80-400J/m^2 and failure in adhesion).
- 970/AF/60001, 970/AF/52006, 3900/AF/52006, 3900/AF/60001, 3900/MB/60001, and MxB/EA/60001 created strong bonds.
- 970/MB/60001, 970/MB/52006, 3900/MB/52006, 3900/AF/SRB, 3900/MB/SRB and MxB/EA/60001 systems created weak bonds.
- Within the systems that bonded weakly, 60001 created stronger bonds than 52006.
- Siloxane coated Polyester 60001SRB peel ply prepared surfaces bonded weakly

regardless of adhesive.

- The choice of peel ply determined bond quality within a consistent laminate/adhesive system.
- All laminates showed the imprint of the peel ply and evidence of epoxy fracture between where the fibers had been (especially at the joining of warp and weft) after the fabric was removed. The mode of fracture upon peel ply removal was therefore mixed; partially through the matrix epoxy and partially at the interface between the peel ply and the laminate.
- All prepared laminates showed evidence of peel ply remnants after fabric removal, and the fabrics showed matching damage.
- XPS confirmed transfer of peel ply material to all laminate surfaces.
- Within an adhesive system, large amounts of SEM visible peel ply material transfer correlated with poor bond quality and cleaner surfaces with higher bond quality.
- The thickness of the remnants is an important factor in determining bond quality. The SEM visibility of remnants in systems that failed in adhesion suggests a critical thickness of peel ply fiber remnant in the range of 1μm-5nm.
- AF 555 adhesive is more tolerant of nylon peel ply contamination than MB 1515-3, and created strong bonds with all but the intentionally siloxane contaminated surfaces.
- The critical thickness of the peel ply remnants may vary by adhesive, possi-

bly based on the interaction distance for the epoxy bonds or the formation of substantially stronger primary bonds in uncontaminated areas.

- The adhesive side of failed weak bonds showed evidence of peel ply remnants under SEM and XPS, showing that at least some failure is occurring through the remnants.
- Single fluid contact angle measurements/water break tests are not predictive of bond quality, and are recommended against.
- DMSO break tests may be used to eliminate surfaces for bonding, but not to approve them.
- The total surface energies of all prepared surfaces were very similar, but they had very different polar/dispersive component profiles.

Chapter 9

CONCLUSIONS

- Peel ply was shown to be system specific; there is no one peel ply for all laminates and adhesives.
- Both peel ply and adhesive choice are critical to resulting bond quality.
- All peel plies transfer debris to the surface; the quantity and compatibility with the adhesive determine bond quality. Small amounts of peel ply transfer can be overcome by a good adhesive, or can be enough to ruin bond quality for an incompatible adhesive.
- Single fluid contact angle measurements/water break tests are not predictive of bond quality, and are recommended against.
- Wettability envelopes are not valid for predicting bond quality in new systems, but may be used to detect changes or errors in surface preparations of known systems.
- Wetting is a necessary but not sufficient condition for strong bonding.

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