

DEVELOPMENT OF BONDING METHODS FOR THERMOPLASTIC
ADVANCED COMPOSITES

by

Jared W. Nelson

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Chair: Daniel O. Adams









K. L. DeVries

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Date

Daniel O. Adams
Chair: Supervisory Committee

Approved for the Major Department

Kent S. Udell
Chair

Approved for the Graduate Council

David S. Chapman
Dean of The Graduate School

ABSTRACT

Given high strength-to-weight and stiffness-to-weight ratios, sandwich composite materials are continually being considered for automotive applications. Thermoplastic materials, while difficult to bond, have an increased ease of manufacture and are recyclable making them even more attractive than thermoset composites. This investigation evaluates the adhesion of 13 adhesives with 8 surface treatments on both nylon and polypropylene thermoplastic adherends made from Towflex® pre-impregnated fabric. A method of manufacture of these plates without contaminating the bonding surface while establishing an acceptable surface finish was developed. Adhesives and surface treatments were investigated and the candidates with the greatest likelihood of success without overlap were chosen. Initial testing was performed using the qualitative spot adhesion test (ASTM D3808) to identify the most likely adhesive and surface treatment parameter groups with each thermoplastic. From these results, 10 parameter groups were identified and tested quantitatively using the lap shear test (ASTM D 3163). Comparative bond strengths are calculated from the peak load and bonded area of each specimen. The results for the nylon were similar between the two tests, but the polypropylene was generally inconsistent. The results indicate that further testing to completely develop joining methods with nylon thermoplastic treated at least with an acid wash and bonded with Lord 320/322 could result in a method of adhesively joining thermoplastic sandwich composites.

TABLE OF CONTENTS

ABSTRACT	iv
LIST OF TABLES.....	vii
ACKNOWLEDGMENTS	viii
1 INTRODUCTION	1
2 LITERATURE REVIEW	5
3 THERMOPLASTIC FACE SHEETS AND MANUFACTURING	17
3.1 Fiber Reinforced Thermoplastic Material	17
3.1.1 Polypropylene.....	18
3.1.2 Nylon	18
3.2 Manufacturing	19
3.2.1 Thermoplastic Plate Consolidation.....	20
3.2.2 Contamination Issues.....	27
4 ADHESIVES AND SURFACE TREATMENTS.....	30
4.1 Introduction	30
4.2 Overview of Adhesives	31
4.3 Surface Treatments.....	32
4.3.1 As-Molded	34
4.3.2 Acid Washing	34
4.3.3 Hand Sanding	35
4.3.4 Grit Blasting	36
4.3.5 Openair® Plasma.....	36
4.3.6 ATmaP® Flame.....	38
4.3.7 Corona	39
4.3.8 Surface Activation (Sulfonation).....	39
4.4 Summary of All Parameters	40
5 QUALITATIVE TESTING.....	42
5.1 Introduction	42

5.2	Spot Adhesion Test Background	43
5.3	Methods	45
5.4	Results and Discussion	46
5.4.1	Adhesives.....	50
5.4.2	Surface Treatments	53
5.5	Summary.....	60
6	QUANTITATIVE TESTING.....	62
6.1	Introduction	62
6.2	Lap Shear Test Background	62
6.3	Methods	64
6.4	Results and Discussion	66
6.4.1	Acid Washed Nylon/Lord 320/322.....	71
6.4.2	Acid Washed Nylon/3M 8239.....	71
6.4.3	ATmaP® Nylon/Lord 320/322.....	73
6.4.4	Openair® Plasma Nylon/Lord 320/322.....	73
6.4.5	Surface Activation Nylon/Lord 320/322	75
6.4.6	Openair® Plasma Nylon/3M 8239	75
6.4.7	Surface Activation Polypropylene/Lord 7542.....	77
6.4.8	Surface Activation Polypropylene/Lord 320/322.....	78
6.4.9	Openair® Plasma Nylon/Bondmaster M1315.....	78
6.4.10	Openair® Plasma Polypropylene/3M 8239.....	78
6.5	Summary.....	80
7	CONCLUSIONS AND RECOMMENDATIONS	82
	REFERENCES	86

LIST OF TABLES

Table 3-1: Data from initial XPS testing.....	28
Table 3-2: XPS results utilizing new tooling and zinc stearate mold release.....	29
Table 4-1: List of adhesives, adhesive type and comments regarding application of those used in this investigation.....	33
Table 4-2: Parameters used for qualitative testing matrix.....	41
Table 5-1: Averaged scores from all initial spot adhesion tests. Parameter groups with no scores were not tested.....	48
Table 5-2: Spot adhesion test scores for the three epoxies tested.	51
Table 5-3: Spot adhesion test scores for the three acrylics tested.	52
Table 5-4: Spot adhesion test scores for the three urethanes tested with the addition of an adhesion promoter.....	53
Table 5-5: Spot adhesion test scores for as-molded and acid wash treatments.....	54
Table 5-6: Spot adhesion test scores for hand sanded and grit blasted treatments.....	55
Table 5-7: Spot adhesion test scores for ATmaP® surface treatment.....	57
Table 5-8: Spot adhesion test scores for Openair® plasma surface treatment.	58
Table 5-9: Additional spot adhesion scores for polypropylene samples treated at 5 different Openair® plasma treatment levels.....	58
Table 5-10: Spot adhesion test scores for Surface Activation surface treatment.	59
Table 5-11: Additional spot adhesion scores for polypropylene and nylon samples treated at different Surface Activation treatment levels.	60
Table 5-12: Highest scoring parameter groups that warrant quantitative testing.....	61
Table 6-1: Comprehensive data collected and calculated from lap shear testing.....	67

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1 INTRODUCTION

The use of advanced composites materials in automobiles is on the rise. For example, the Chevrolet Corvette has been focusing on using lighter materials to increase vehicle performance with the use of sheet molding compound (SMC) reinforced with random chopped fiberglass. Although this is still the primary use on the Corvette, monolithic and sandwich composites utilizing continuous fibers are increasingly being incorporated. The benefit of incorporating these structural materials is to reduce weight thereby improving efficiency and performance. Such applications have focused primarily on thermoset composites. However, thermoplastic composites offer reduced cycle-times, improved ease-of-manufacturing and are recyclable. The greatest difficulty, however, is bonding them to other structures. Previous research at the University of Utah, focused on characterizing candidate sandwich composites for use in automotive floor applications, indicated that thermoplastic composite facesheets were difficult to bond to core materials [1]. Based on this previous research, this current study focused on developing and evaluating joining methods between thermoplastic composite facesheets and candidate core materials in sandwich composites.

Sandwich composites are comprised of a core material that is sandwiched between two laminated facesheets. The core material is much thicker than the facesheets, is generally low density and is intended to carry shear stresses from transverse loading. The facesheets are thin, resin/fiber reinforced sheets with high

specific stiffness and strength to resist tensile and compressive loadings in bending. Overall, sandwich structures offer increased strength-to-weight and stiffness-to-weight ratios.

When bonding thermoplastics, the removal of surface contamination due to low molecular weight molecules can improve bonding and is commonly achieved by mechanical abrasion and solvent cleaning. Mechanical abrasion includes sanding, grinding, and grit blasting all of which mechanically alter the surface to increase wet-out and surface energy. Solvent cleaning relies on the fact that low molecular weight molecules go into solution more readily than the larger molecules. Since there are no known low-temperature solvents to remove contaminants from nylon or polypropylene, solvent cleaning is not a viable option for removing contamination as it is with thermoset epoxies. However, using an acidic solution for surface etching can improve adhesion of thermoplastics.

Increasing the surface energy of unmelted thermoplastics to improve wetting and increase bond strength can be achieved by a number of methods. Even though it requires handling of hazardous materials, oxidation by strong chemicals can improve bondability. The use of flame, sulfonation and plasma treatments not only can clean the surface, but also can introduce polar chemical groups through oxidation. These procedures are currently practiced in industry and can result in good adhesion with common adhesives. A downside is that the benefits of these surface treatments are prone to fade over time or under elevated temperature, requiring them to be a process step just prior to bonding.

The thermoplastic facesheets used in this study featured both polypropylene and nylon matrices reinforced with continuous carbon fiber. The investigation has focused on identifying promising bonding methodologies for joining thermoplastic substrates. A follow-up investigation will focus on developing and evaluating joining methods for thermoplastic sandwich composites utilizing the most promising bonding methodologies identified in this investigation. Additionally, research in this later investigation will focus on evaluating the structural and energy absorption properties of thermoplastic sandwich composites. Ultimately, the core materials to be investigated will include balsa wood, structural foams and honeycombs. In short, this initial investigation will focus on identification of bonding methods of the thermoplastic face sheets that will be incorporated into a later investigation utilizing these findings for bonding of sandwich composites.

A consolidation method was developed yielding contaminant-free plates using a heated press with aluminum tooling surfaces and zinc stearate mold release. The manufacturing process was also adapted to improve surface finish and ensure plates were manufactured flat and free of warping. This process is comprehensively outlined and a summary of the removal of contaminants is given.

This investigation focused on identifying promising adhesives, surface preparation methods, surface treatments, and procedures for use in bonding thermoplastic substrates. Materials and processes were identified that held promise in achieving suitable strength bonds between selected thermoplastic composites and adhesives, independent of the core material. Candidate adhesives were also determined with 11 adhesives representing all of the major chemistries including

epoxy, toughened epoxy, urethane, acrylic and cyanoacrylate. In addition, seven surface treatments were used with both thermoplastic composite materials including as-molded, acid washed, hand sanded, grit blasted, ATmaP® flame, Openair® plasma and Surface Activation treatments.

A two-round experimental evaluation was used to investigate a wide range of materials and processes. An initial qualitative round used a simple spot adhesion test (ASTM D 3808) to qualitatively determine adhesion. This test was used because it allowed for many different parameter groups to be tested quickly, effectively, and inexpensively. A tester qualitatively determined the level of adhesion by comparing the difficulty of prying cured adhesive spots from a plate. In total, over 150 parameter groups were tested by two testers. Further tests were performed emphasizing the most promising adhesives while changing surface treatment parameters such as exposure time and intensity. Results are presented and discussed.

The quantitative round of testing consisted of lap shear (ASTM D 3163) testing to quantitatively identify bond strength of the most promising adhesive and surface treatment parameter groups identified in the qualitative testing. Results are presented and discussed.

2 LITERATURE REVIEW

The use of composite materials in the automotive industry continues to grow though affordability, energy absorption, surface finish quality, and recyclability are difficult and necessary issues. Although a majority of the focus to date has been on monolithic composite laminates, composite sandwich structures are being considered for selected automotive applications to provide even greater strength-to-weight and stiffness-to-weight ratios. Composite sandwich structures consist of an inner, low-density core encased by and bonded to a pair of thin, outer composite facesheets. Currently, the primary interest for these sandwich composites appears to be in roof and floor applications, where the improved bending properties of sandwich structures are a major consideration [2].

Thermoplastic materials are plastic materials that can repeatedly melt when heated and freeze at ambient temperatures. In general, thermoplastics are polymers that can be melted and re-frozen unlike thermosetting materials. Combining this with the decreased cycle time compared to thermosets and thermoplastics become quite attractive for manufacture. However, the end use must be considered because as the glass transition temperature of the thermoplastic is reached, the Young's modulus decreases [3]. Thus, the use of thermoplastics in higher temperature environments such as in engines could cause softening and loss of structural integrity. Details on the specific thermoplastics used in this investigation are given later.

Thermoplastics are typically insoluble in each other so that the adhesive and the adherent must be the same polymer for melt bonding. Since they do not mix chemically, polyethylene will not adhere to polypropylene when melted together. Welding of adherends of like material has become an accepted method of joining; however this can be difficult with complex shaped parts [4]. Adhesives tend to have difficulty wetting out or spread on thermoplastics because of a low surface energy and thus require elevated temperatures to develop strong bonds. Due to a smooth, impermeable surface and low molecular weight molecules interfering with the bond, mechanical interlocking directly onto the surface can be difficult [5].

Often the surface is contaminated due to low molecular weight molecules migrating to the surface during consolidation. Removal can improve bonding and is commonly achieved with mechanical abrasion or solvent cleaning. Mechanical abrasion includes sanding, grinding, grit blasting or any other process mechanically changing the surface. Mechanical abrasion (sanding or grit blasting) of the thermoplastic surface was found to improve bond strength in the previous University of Utah research [1]. Solvent cleaning relies on the fact that low molecular weight molecules go into solution more readily than the larger molecules. While solvent cleaning has been shown to be successful in removing such material from thermoset epoxies, it is much more difficult for polypropylene and nylon thermoplastics, since there are few if any reasonable low-temperature solvents for these materials [5, 6].

Increasing the surface energy of unmelted thermoplastics to improve wetting and increase bond strength can be achieved by a number of methods. Even though it requires handling of hazardous materials, oxidation by strong chemicals can greatly

improve bondability. The use of flame, sulfonation and plasma treatments not only cleans the surface, but also introduces polar chemical groups through oxidation. These procedures are practiced in industry and can be successful when combined with the proper adhesive materials. These surface treatments do tend to fade under elevated temperature conditions or over time and processing should be done just prior to bonding [5, 6].

Primers are often used to enhance the bonding of an adhesive to a substrate. In some cases where the adhesive will not bond strongly directly to a substrate, a substance may be used as an “intermediary” between the adherend and the adhesive. If a very thin layer of this substance is applied to the substrate, it may form a primer to which the adhesive will develop a strong bond [5, 6].

Internal additives can be incorporated into nonpolar polymers that provide bonding if the polymer is in a molten form. For example, maleic anhydride of acrylic acid can be grafted to the polypropylene backbone. When the polypropylene is molten, the polar group will migrate to the bond line and greatly improve adhesion [5, 6].

Similarly, coupling agents are typically “bi-functional” molecules; on one end of the molecule they contain a function that can chemically interact with the adhesive while the other interacts with the adherend. In effect, these coupling agents build chemical bridges of substantial strength between the two materials. The most commonly used coupling agents today are silanes though to a lesser extent, titanates and zirconates are also used [7]. In general, the development of coupling agents

remains as an active research area. Literally hundreds of different end groups have been designed to interact with different materials.

Primer, additives and coupling agents theoretically have potential, but they are not commonly investigated. To date, most studies investigate only several parameter groups of adhesives, surface treatments, and/or thermoplastics. Lap shear testing is the most common as it provides quantitative analysis of the different parameter groups. Given the time required for the setup and testing, only a few parameters are investigated leaving many other potential parameter groups out of the study.

The aerospace industry has provided much of the research of joining thermoplastic composites to date because joining is critical to the manufacture of aerospace structures. Much of this research took place in the late 1980s and early 1990s in an attempt to move the use of thermoplastics into mainstream aerospace use. The joining methods commonly tested can be grouped into two categories; standard thermoset joining methods adapted for thermoplastics and methods specific for thermoplastics. The standard thermoset joining methods are co-consolidation, adhesives and fasteners. However, co-consolidation of thermoplastics is actually a melt fusion process as opposed to co-curing for thermosets. Joining methods specific for thermoplastics include resistance welding, induction bonding, ultrasonic welding and microwave bonding [8].

Previous research performed at the University of Utah focused on the characterization of candidate sandwich composites for the use of automotive floor applications [1]. Six sandwich configurations utilizing thermoplastic materials—carbon/nylon, carbon/polypropylene and glass/polypropylene with polyurethane and

balsa wood cores—were tested. Candidate adhesives were identified and flatwise tensile testing was used to identify the best suited adhesives to bond the facesheets to the core: Lord 320/322 toughened epoxy and Loctite 907 epoxy. Preliminary results also showed that surface preparation of the composite—specifically abrasion—increased the bond strength.

Further flatwise tensile and core shear testing identified that these thermoplastic sandwiches predominantly failed between the adhesive and the facesheet as shown in Figure 2-1. As noted in these previous studies, the bond strength between the facesheet and the adhesive was lower than the strength of the core itself which is undesirable (Figure 2-2). Based on the poor bond strength of the parameter groups used, only thermoset facesheets were used for future sandwich composite evaluation. However, this previous testing [1] identified the need for further research to develop and evaluate joining methods between thermoplastic composite facesheets and candidate core materials as is undertaken in this study.

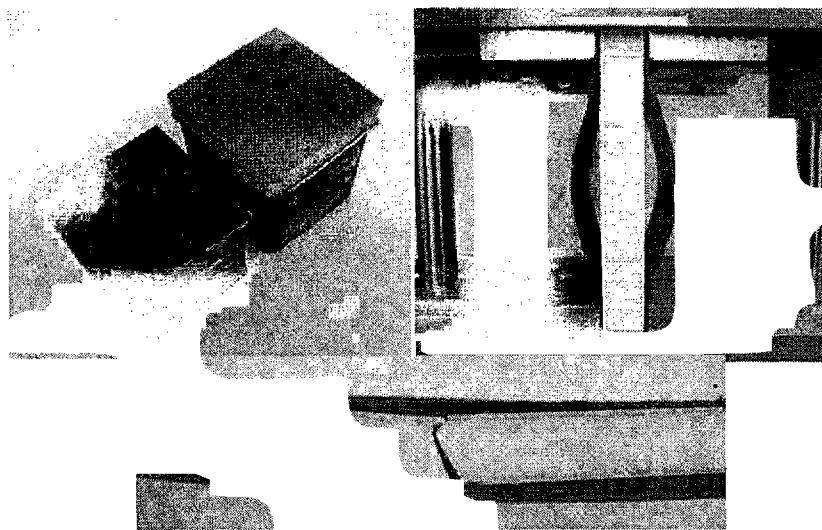


Figure 2-1: Previous testing at the University of Utah involving bonding of thermoplastic composites resulted in adhesive or interface failure.

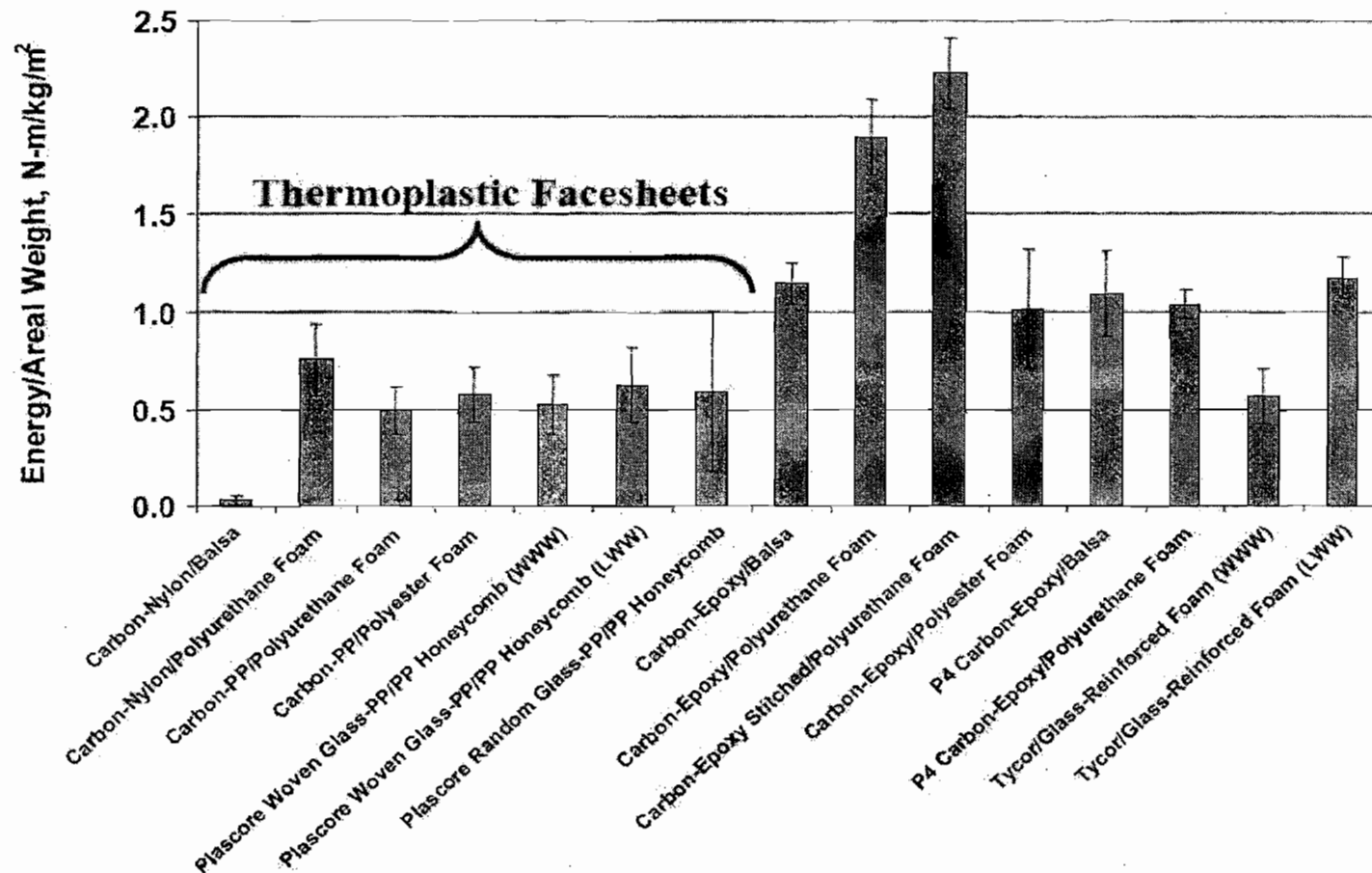


Figure 2-2: Three point flexure testing results from previous University of Utah research with lower bond strength thermoplastic composite facesheets indicated.

In other research, Ageorges and Ye reaffirm the statement that joining composite materials is an issue because traditional joining technologies are not directly transferable to composite structures. As noted above, fusion bonding and the use of thermoplastic films as hot melt adhesives offer an alternative to mechanical fastening and thermosetting adhesive bonding. Fusion bonding technology which originated from the thermoplastic polymer industry has gained a new interest with the introduction of thermoplastic matrix composites which are currently regarded as candidates for primary structures. Building on Todd's and Wingfield's research [8,9], Ageorges and Ye's findings reveals the state of the art of fusion bonding technology and focuses particularly on the three most promising fusion bonding techniques: ultrasonic welding, induction welding and resistance welding. They concluded that fusion bonding, although presenting great promise, is not without flaws. Thus, particular applications need to be studied to determine the best method for joining [10].

Davies et al. [11] investigated the joining of thermoplastic composites using a conventional epoxy adhesive with four surface treatments—no treatment, sand blasting, chromic acid etch and plasma treatment. Lap shear testing was performed and acid etching and plasma treatment were most successful. In addition, fusion bonding was investigated and lap shear results were compared to the adhesive bonded samples. Adhesive and fusion bonding were then compared in terms of static strength, the influence of moisture, fracture toughness and fatigue behavior. It was concluded that both can be problematic. Adhesive bonding requires a prebonding surface treatment, whereas fusion bonding requires temperatures that can easily compromise

surround structures. It is also noted that significant scatter exists within the results of both methods.

In a similar study, using a thermal fusion technique, thermoplastic composite materials were bonded with an amorphous resin as a bonding agent at a temperature substantially below the composite processing temperature. Two composite materials, Graphite/PEEK, based on polyetheretherketone matrix and Graphite/HTA, based on polyarylsulfone matrix, were bonded with neat resins polyetherimide and polyethersulfone. Lap shear tests were used to evaluate the bond strength at room temperature and elevated temperature after environmental exposure. The lap shear strength again was comparable to that of co-consolidated and exhibited superior hot/wet properties [12].

In a study focusing on newly developed adhesives in the late 1980s, Powers and Trzaskos [13] investigated fastening techniques for the use of advanced thermoplastic composites for structural applications. Lap shear testing was performed with two structural epoxy film adhesives and two structural curing epoxy adhesives. Grit blasting, grit blasting followed by a solvent wipe and plasma treatments were used as surface treatments. They concluded that each of these treatments was effective with these adhesives and sufficient strengths were achieved in all cases. It is also interesting to note that a correlation was performed between the strength of the bonded joint and the number of plies and orientation used. Shear strength was shown to increase as laminate thickness increased to a nominal thickness of 0.25 cm (0.10 in). In addition, laminates with surface plies having fibers oriented parallel to the shear load had at least 15% improved shear strength.

Prior to the above studies, Kodokian and Kinloch [14, 15] determined that use of light abrasion/solvent wipe treatment with structural epoxy adhesives was inadequate. The resulting joints were relatively weak and the data had significant scatter. Adhesive or interfacial failure was observed. They determined a more comprehensive study was on order, which led to these later studies of more specific areas. Two composite materials were used—carbon fiber reinforced PEEK thermoplastic and epoxy thermoset. Two toughened epoxies and PEEK hot-melt were used in conjunction with simple abrasion, molding next to clean aluminum foil followed by an acid wash, acid etch and corona discharge. A double cantilever beam test was used with a crack initiated at one end.

All four treatments were successful with the use of the epoxies in bonding the thermosets, but the simple abrasion was not successful. In addition, the use of the aluminum foil and acid etch did not increase bond strength significantly, indicating that surface contamination from mold release is not the essence of the problem. This was confirmed with the use of XPS to determine that silicone and fluorine levels were very low. Parker [16] similarly determined that initial bond strength is related to presence of contaminants on the adherend surface. Thus, confirmation of a clean surface after adherend manufacture is necessary.

Kodokian and Kinloch [14, 15] also found that the use of the hot-melt did increase bond strength with the PEEK samples, but had little adhesion with the thermoset adherends. Corona discharge did improve fracture energy (G_c) values and cohesive failures were noted with both materials.

Finally, it is important to note that surface angle measurements were also taken. This measure of the contact angle of a liquid placed onto a surface of a material indicating the wettability or surface tension of a surface. This testing can also be performed using a series of different liquids of differing viscosity, which is called a Dyne test. As surface energy increases, liquids wet-out a surface more completely and effectively. Surface energy is often correlated to increased bondability and thus bond strength. Kodokain and Kinloch determined that the contact angle decreased most significantly with the use of corona treatment on the PEEK thermoplastic [14, 15].

Another factor that can influence bond strength is the bondline thickness. McKnight et al. [17] investigated the effects of adhesive cure cycle and final bondline thickness on bond strength. Using adherends of S-2 glass/polyphenylene sulfide, thermoplastic composites with a co-molded polysulfone surface layer were bonded using a high performance epoxy film adhesive and an epoxy paste adhesive. Results indicated that bondline thickness reaches an optimum level before resulting in decreasing strength values.

Silverman [18] chose a slightly different approach using six different joining concepts to achieve strengths approaching 93.0 MPa (13,500 psi). The concepts included adhesive bonding using a commercially available epoxy system, mechanical fasteners plus adhesive bonding, resistance heating, focused infrared heating, ultrasonic welding, and a novel technique employing an amorphous thermoplastic film. Advanced thermoplastic composites specimens were made using PEEK reinforced with AS-4 graphite pre-preg tapes. Tensile lap shear coupons were used for screening the alternative joining methods and measuring the bond strengths. Surface

preparation methods examined included grit blasting, acid etching, and cold gas plasma etch treatment. The fusion bonding methods of resistance heating, focused infrared heating, and ultrasonic welding used a thin film of the neat thermoplastic PEEK in the joint prior to fusion. Even though none of the methods achieved the intended strength, epoxy with plasma treatment had the highest joint strength at 41.6 MPa (6037 psi) with cohesive and adhesive failure occurring equally. The strengths of the other methods dropped significantly.

More recently, Loven [19] investigated the use of adhesives for structural bonding for the automotive and marine industry. It is quite common that composites research for these industries follows several years behind the use in the aerospace industry. Ford has illustrated the benefits of properly defining the durability requirements of structurally-bonded assemblies at the beginning of the process by successfully bonding over four billion bumpers with zero failures. Even though this study does not investigate scientifically beyond a case study, it does point out that thermoplastics and composites can be structurally bonded in application.

Little research has been performed particularly with nylon thermoplastic composites. Wade et al. [20] did investigate the surface modification and adhesive bonding of a nylon 6,6 reinforced with unidirectional glass fiber. Wettability studies of plasma-treated specimens showed a significant reduction of contact angles in water, relative to untreated material. The most effective treatment used oxygen plasma. The increases in wettability observed were determined to be the result of two effects. First, the treatment resulted in an increase in the concentration of oxygen and nitrogen containing functional groups on the surface of the polymer. Second, the plasma

treatment removed fluorine contamination, the source of which was identified as the PTFE mold release agent. The surface modification resulted in significantly improved adhesion between the composite and an applied toughened epoxy adhesive. Thus, a considerable increase in the Mode II critical strain energy release rate, G_{IIc} , was observed following plasma treatment. Specimens treated in oxygen plasma showed the greatest improvement in G_{IIc} and resulted in a cohesive failure. Without plasma treatment, the specimens failed in an adhesive mode at very low values of G_{IIc} . Adhesion was further optimized by molding the nylon-6,6 plates directly against steel plates instead of PTFE thereby removing any chance of fluorine contamination.

As noted, previous significant previous research has focused on determining methods to successfully join thermoplastic composites. These investigations have largely used different surface treatment methods that include abrasion, acid etching and plasma treatment. However, other surface treatments exist such as flame, corona and sulfur exposure. Development of these treatments and advances in the others result in the need for further investigation and testing of a wider variety of surface treatments as is taken on in this study. Details of the surface treatments investigated and used are found below.

3 THERMOPLASTIC FACE SHEETS AND MANUFACTURING

3.1 Fiber Reinforced Thermoplastic Material

Two thermoplastic matrix materials reinforced with carbon fiber were used in all testing: polypropylene and nylon. The material, TowFlex® woven fabric reinforced thermoplastic, was produced by and purchased from Hexcel Composites [21, 22]. TowFlex® laminates are manufactured using a compression molding process, where the material is heated to a specified melt temperature, pressure is applied for consolidation, and the resulting part is cooled while maintaining pressure. Details of this manufacturing process are outlined below.

The two thermoplastic materials used are very common and their use is widespread in the plastics industry. Use in the composites industry has been hindered by not only the ability to bond to other structures, but also the ability to adhere the thermoplastic matrix to the fiber reinforcement. Hexcel has successfully accomplished this bonding by spreading and powder coating continuous carbon and glass fibers with thermoplastic particles. The thermoplastic particles are subsequently melt-fused to the reinforcement fibers, producing a flexible material. Similar to a pre-impregnated material, TowFlex® is then ready for consolidation off of the roll [21, 22].

3.1.1 Polypropylene

Polypropylene has a wide variety of uses from reusable storage to clothing. It is highly resistant to chemicals and has higher softening and melting temperatures than other common plastics. The Young's (elastic) modulus is midrange, allowing for use where stiffness is needed, but has some resistance to brittle failure [3]. Polypropylene is an addition polymer meaning it is synthesized from propylene. The propylene monomers are added together without the loss of any atoms or molecules to create the polypropylene chain seen in Figure 3-1.

3.1.2 Nylon

Nylon is a family of synthetic polymers created by Dow Chemical in the 1930s. It was originally used in women's stockings, parachutes and more recently has been used in ropes, guitar strings and mechanical parts. Like polypropylene, the Young's modulus is favorable to provide stiffness without likely brittle failure. Unlike polypropylene the monomers used donate carbon to the polymer to create chains of six-sided carbon groups as seen in Figure 3-2. This process defines the two most common types of nylon: nylon 6 and nylon 6,6. Nylon 6,6 has an additional 6 carbon molecules repeated in the polymer chain that give extra strength and the resilience compared to nylon 6 [3]. The TowFlex® material in this study utilizes nylon 6.

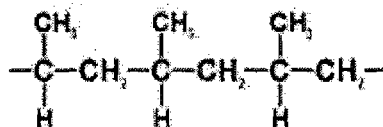


Figure 3-1: A general polypropylene chain.

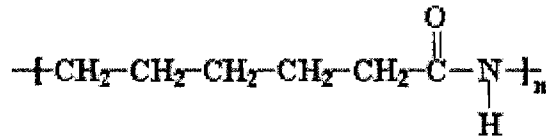


Figure 3-2: A general nylon 6 chain.

3.2 Manufacturing

The thermoplastic adherends used were fabricated at the University of Utah using a heated press to consolidate the TowFlex® woven fabric reinforced thermoplastic. Material orientation was not considered beyond use in the 0/90° orientation due to the findings of Powers and Trzaskos [13] noted above. Aluminum tooling surfaces were used to enhance surface finish. The consolidation cycle for the nylon-based TowFlex® was 1.0 MPa (~150 psi) at approximately 260°C (500°F) for approximately five minutes. The consolidation cycle used for the polypropylene-based TowFlex® was 1.0 MPa (~150 psi) at approximately 190°C (375°F) also for approximately 5 minutes. A forced convection cooling method was used to increase the cooling rate of the mold and the platens while the mold remained under pressure.

Details of the manufacturing process for the thermoplastic plates are outlined below. Images, where useful, follow the specific process step. This detail includes discoveries made for improved surface finished and consolidation while minimizing warping. Following the process is a summary of the contamination issues faced in using mold release and film barriers, justifying the contamination-free method that has been used.

3.2.1 Thermoplastic Plate Consolidation

Below is a detailed process instruction discovered and used for the manufacture of the thermoplastic plates used in this investigation.

1. Put on sterile gloves to prevent contamination during all steps of the process (Figure 3-3).
2. Cutting Material
 - a. Wipe table and tools with acetone and paper towel to prevent contamination.
 - b. Using two squares and a straight edge for alignment a 25.4 cm (10 in.) piece of Towflex® is cut off at the width of the roll (Figure 3-4).
 - c. Noting the orientation, this piece is cut into 3 pieces 25.4 cm (10 in.) square; ensuring the selvage edge of the roll is not used (Figure 3-5).
 - d. Extra material is stored for potential later use.

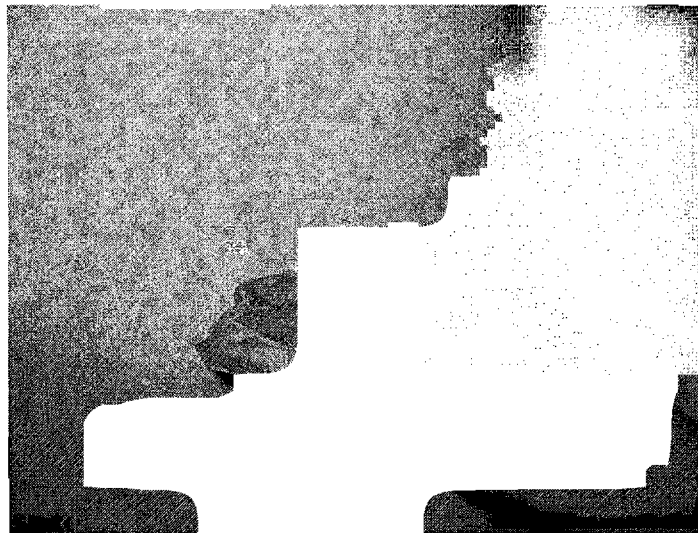


Figure 3-3: Sterile gloves are worn through out the process to reduce contamination.

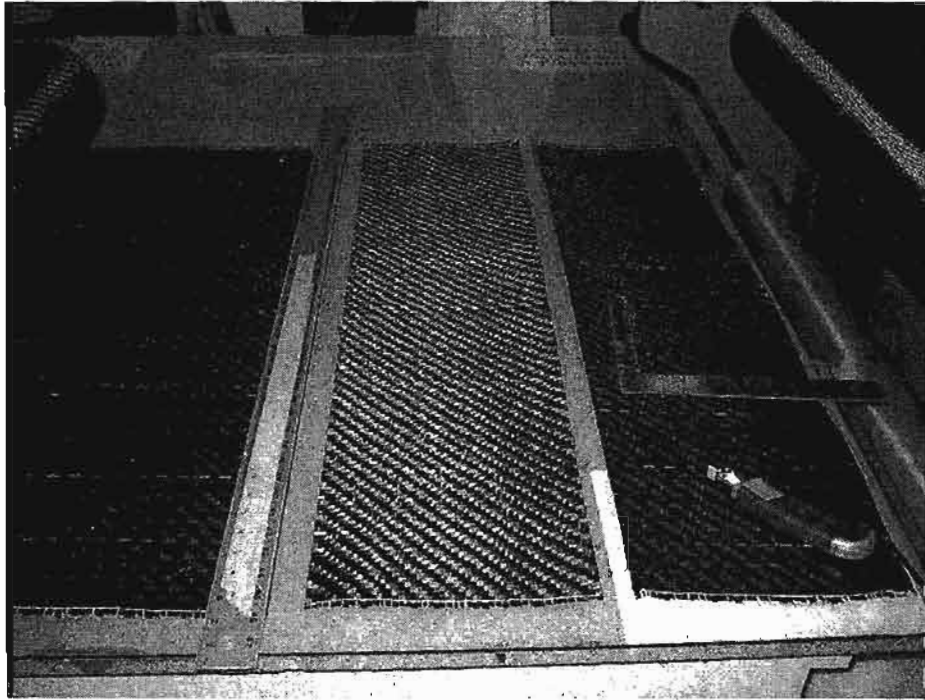


Figure 3-4: 10" strips of material are cut from the roll of thermoplastic material.

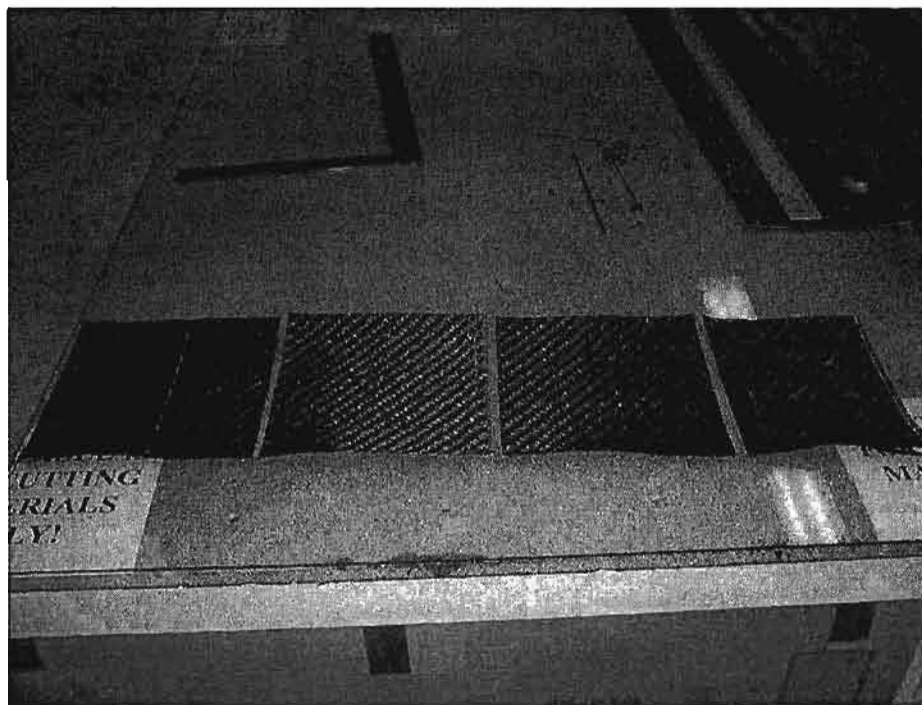


Figure 3-5: The 10" strips are then cut into pieces making 10" by 10" squares.

3. Tool Preparation

- a. Aluminum plate 30 cm by 30 cm by 6.5 mm (12in x 12in x 1/4in) is used as a tooling surface.
- b. Aluminum foil is placed over the surface and folded around the edges. This provides a smooth repeatable surface with an adequate release so no initial or additional polishing must be done with the aluminum sheet stock (Figure 3-6).
- c. Aluminum plate with foil is taken away from all thermoplastic materials and zinc stearate is applied with a side-to-side motion as a mold release. This is to prevent contamination from the spraying of the mold release in the laboratory.
- d. The released aluminum plate is brought back into the laboratory.

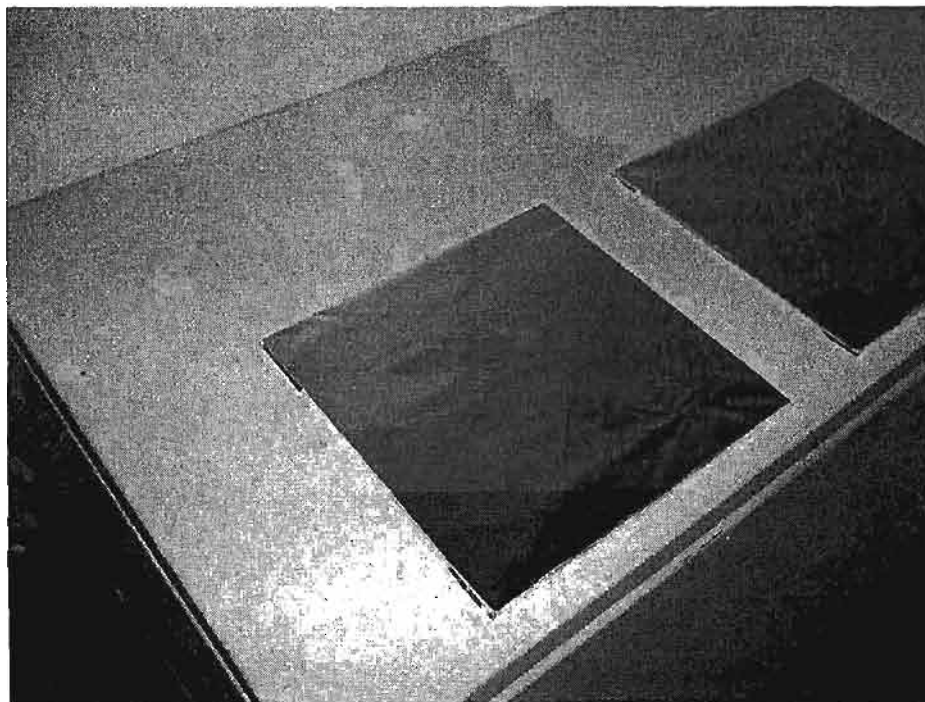


Figure 3-6: Aluminum foil is applied to the mold surface.

4. Material Layup

- a. Four plies of the material Towflex® are used.
- b. Material is oriented in the 0/90 direction only.
- c. The curl of the material is placed onto the prepared tooling surface in the same direction so the edges curl up. This was found to give the smallest amount of warping of a finished plate (Figure 3-7).

5. Shim Placement

- a. Shim thickness is 1.5 mm (0.060 in).
- b. Four shims are placed just inside the tool edge to ensure thermoplastic plate thickness.
- c. The shims must be placed in such a fashion so that when the curl of the material is flattened they do not interfere with the layup (Figure 3-8).

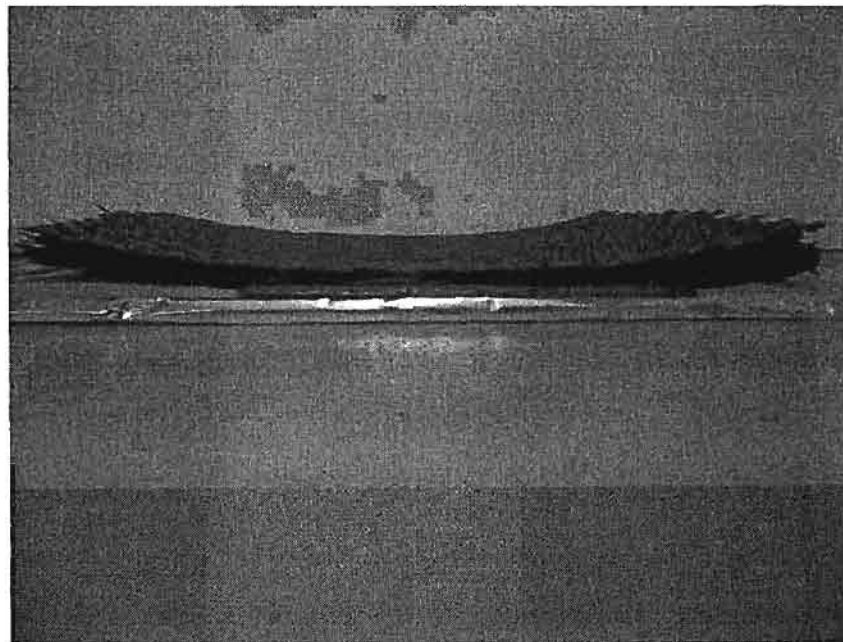


Figure 3-7: Material is placed onto the tooling surface.

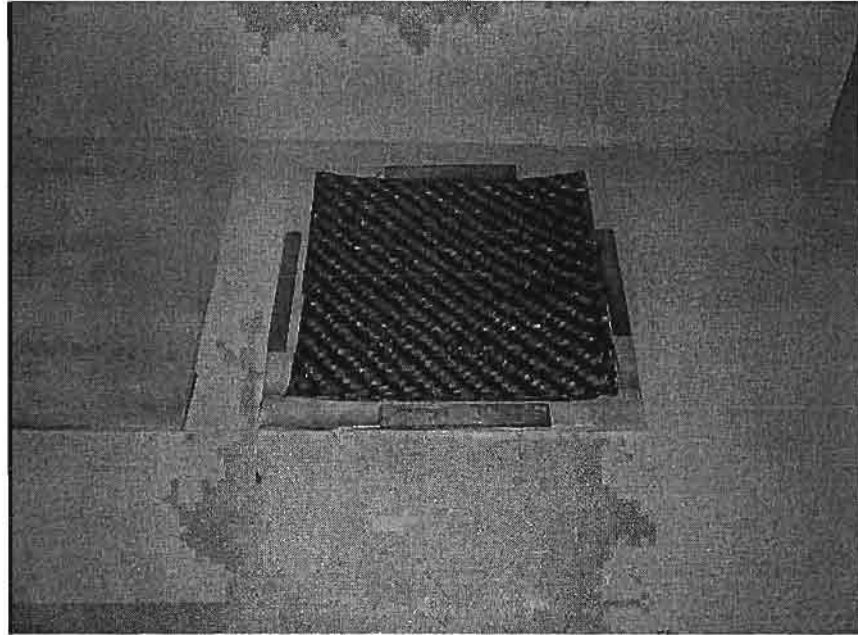


Figure 3-8: Shims are placed onto the tooling surface clear of interaction with thermoplastic material.

6. Pressing

- a. Press is preheated to 260°C (500°F) for the nylon and 190°C (375°F) for the polypropylene (Figure 3-9).
- b. The tool with the layup is placed into the press making sure that none of the shims shift inside.
- c. Press the tool with the hydraulic ram to achieve 1.0 MPa (~150 psi).
- d. Allow the press to come back up to 260°C (500°F) for the nylon and 190°C (375°F) for polypropylene, and allow to consolidate at least 5 minutes at these temperatures.
- e. Ensure pressure remains constant at 1.0 MPa (~150 psi) for the entire consolidation.
- f. Turn the heaters off on the press, but leave the pressure on the tool. Use a fan on the press to speed the cooling.



Figure 3-9: The mold is pressed to consolidate the thermoplastic material.

- g. After the temperature has been reduced to 95°C (200°F), for both materials, the tool can be removed from the press. This temperature was found to provide the least amount of warping for the nylon and is well below the glass transition temperature for polypropylene. If the tool is cooled to room temperature, however, a better release can be obtained.

7. Removal of the Panel from the Tool

- a. Use a scraper or large screw driver to pry the two halves of the tool apart (Figure 3-10).
- b. Aluminum foil that is still attached to the plate can be removed by hand or with a razor blade (Figure 3-11).
- c. In one corner of the panel write: Date, Type of Material (PP or N6), and Number.
- d. Place the panel in the storage bag
- e. Record the process in lab book and all deviations from the procedure.



Figure 3-10: The mold is opened.

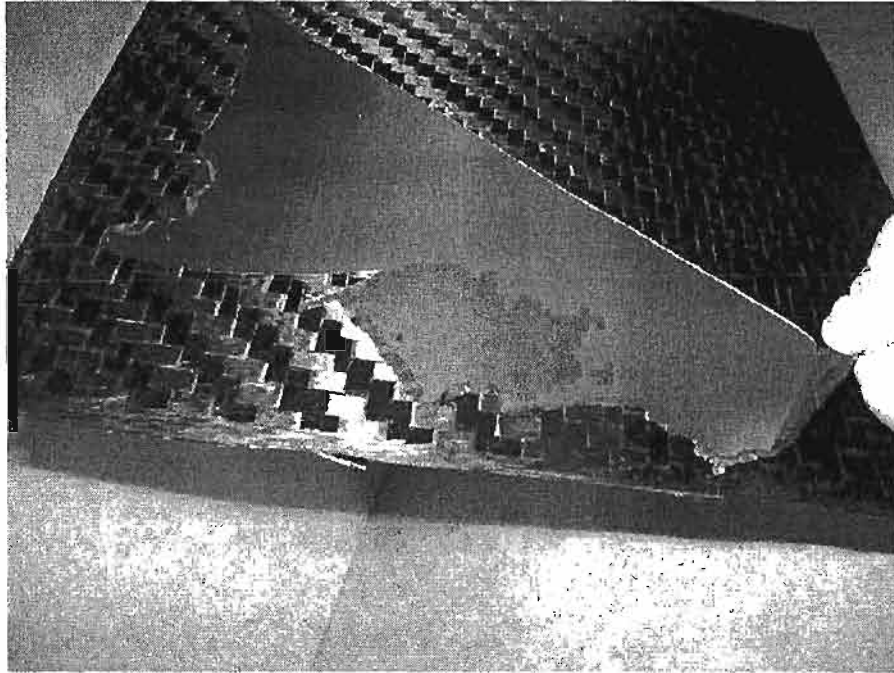


Figure 3-11: Excess aluminum foil is removed.

3.2.2 Contamination Issues

Imperative to bonding plates successfully is ensuring the plates are free of contaminants. Contamination of the surface can result in a barrier between the adhesive and the adherend, resulting in decreased bond strength. Contaminants of great concern are the same materials that are often used in mold releases and include fluorine and silicone based materials. These particular materials reduce friction and surface energy when they are included on the surface of the adherends, which is of benefit when de-molding and a hindrance when bonding. The manufacture of clean, contaminant-free adherends requires measures be taken to ensure a clean environment around the material and that only certain mold releases be used.

Initially, a tool was used that was well seasoned with PTFE mold release. This led to contamination of the bonding surface as was confirmed by poor bonding and X-

ray Photoelectron Spectroscopy (XPS) performed at Ford Research Center. Based on these results, additional samples were made using a new aluminum plate as a tooling surface. A TFE film was used as a barrier and as a release layer. However, XPS analysis confirmed that high levels of fluorine (up to 7.9%) were still found on the plate surface as shown in Table 3-1. It was assumed that transfer of fluorine was occurring from the TFE film to the thermoplastic adherend.

Given the level of fluorine on the surface, a series of plates were made utilizing new aluminum tooling surfaces and zinc stearate as a mold release. Plates were manufactured with no mold release; however the thermoplastic bonded to the aluminum plates necessitating some level of mold release. XPS analysis was performed in the University of Utah Nanofabrication Laboratory. Results indicated (Table 3-2) that while the use of new aluminum tooling surface and zinc stearate eliminated dubious contaminants, the addition of aluminum foil improved surface finish. Thus, the processing of plates in this investigation, as noted above, utilized this method.

Table 3-1: Data from initial XPS testing.

Sample	Elemental Composition--Atomic %									
	C	O	N	F	S	Si	K	Na	Cl	Al
PP-2	89.3	5.9	-	3	0.79	-	-	1	-	-
PP-3	87.6	9.2	1.2	1.7	0.13	-	-	0.27	-	-
PP-4	74.8	17.7	-	-	-	5.1	-	0.4	0.47	1.5
PP-Bulk	97.9	2.1	-	-	-	-	-	-	-	-
N6-2	69.1	13.2	7.3	7.9	0.74	0.31	0.66	0.88	-	-

Table 3-2: XPS results utilizing new tooling and zinc stearate mold release.

Peak	Position	FWHM	Raw	Area	RSF	Atomic	Atomic	Mass
BE	(eV)	(eV)	(CPS)	Mass	Conc	%	Conc	%
Zn	2p	1022	3.982	39896.2	5.589	65.387	0.45	2.27
F	1s	689	1.822	17.5	1	18.998	0	0
O	1s	532	3.648	144893.8	0.78	15.999	10.64	13.07
Ca	2p	348	3.667	19175	1.833	40.078	0.62	1.92
C	1s	285	3.197	394655.9	0.278	12.011	86.18	79.51
Si	2s	153	3.206	4605	0.324	28.086	0.89	1.91
N	1s	401	2.82	9843.3	0.477	14.007	1.22	1.31

4 ADHESIVES AND SURFACE TREATMENTS

4.1 Introduction

In a bonded joint, the adhesive joins two surfaces often called adherends or substrates. An adhesive is generally considered a material that bonds or unites two adherends together such that they act as a unit and load is transferred through the joint. Most structural adhesives are thermosetting, meaning that they cross-link and thus increase the number of primary bonds when curing [5, 6]. Epoxies have historically been the most commonly used adhesive with composites, new chemistries have improved acrylics, cyanocrylates and urethanes for use in this industry.

However, using the proper adhesive is only part of the solution when bonding composites and particularly thermoplastic composites. Surface treatments to increase surface tension can increase wet-out of adhesives increasing bond strength. In addition, surface treatments can remove contaminants that can result in a barrier between the adherend and adhesive causing low bond strength.

There are four common theories used to explain how adherends and adhesives stay bonded together. Mechanical interlocking is the simplest and suggests that the adhesive fills into voids in the surface of the adherend and cures. Once it is cured, it cannot be pulled out of the voids unless the adhesive or the adherend fails. Surface treatments can remove contamination and open up these voids for this bonding to take

place. In addition, treatments that mechanically change the surface also increase the surface area of interaction between the adherend and adhesive [5, 6].

Covalent bonding is a second theory that suggests that primary bonds occur between the adhesive and adherend during curing. For this to occur, chemical groups must cause a reaction at the interface of the materials. Electrostatic attraction is a third theory and suggests that the materials bonded together have an ionic attraction. Finally, acid-base interactions result in an interaction where one material gives up a hydrogen atom and the other accepts it [5, 6].

It is important to note that these theories are not completely established and much debate continues to surround them. No attempt is made to understand which type of bonding has occurred in this investigation. Instead, an understanding of failure type is deemed more important. Thus, failures are judged to be adhesive or cohesive. Adhesive failures occur between the adhesive/adherend interfaces and are considered unfavorable as the interface is the weakest point of the joint. Cohesive failures occur within adhesive itself. In addition, failure within the adherend can occur. These are considered favorable because the bond strength is greater than the adhesive strength [3].

Below are a summary of the adhesives and surface treatments investigated and an outline of the decision process used in the selection process.

4.2 Overview of Adhesives

The different types of adhesives available are too extensive to list. For this investigation, only thermosetting structural adhesives were considered. This resulted in the identification of four types of adhesives: epoxies, acrylics, cyanoacrylates, and

urethanes. In recent years, structural adhesive manufacturers have developed chemistries that include aids to bonding and have improved the strength of all of these adhesive types.

Adhesive suppliers were contacted [23-28] and the purpose of the investigation was explained. These suppliers were asked to offer any advice on which of their products would be most likely to have acceptable bond strengths with thermoplastic composites. Data sheets along with curing instructions and recommendations for use were acquired, and are available at each supplier's website.

The process for determining which adhesives to include was such that no adhesives recommended for use were left out. This was largely due to the simplicity of the qualitative test method used for initial evaluation. Thus, adhesives from each of the major chemical families were included and are listed in Table 4-1.

4.3 Surface Treatments

Surface treatments were divided into two groups: in-house and specialty treatments. The in-house treatments are those that do not require highly-specialized processing equipment. In-house treatments investigated included as-molded, acid washing, hand sanding and grit blasting. The specialty treatments require highly-specialized equipment which in each case investigated requires significant capital investment. Specialty treatments investigated include ATmaP® flame, Openair® plasma, Sulfonation, and Corona treatments. Each surface treatment method is summarized below.

Table 4-1: List of adhesives, adhesive type and comments regarding application of those used in this investigation.

Supplier/Adhesive	Adhesive Type	Comments
Bondmaster E04	toughened epoxy	More difficult to use and spread.
Bondmaster M1314	acrylic	Easy to use and spread. Noxious odor.
Lord 7542	urethane	Easy to use and spread. Slight noxious odor.
Lord 320/322	toughened epoxy	Difficult to use and spread. High viscosity.
Loctite 907	epoxy	Easy to use and spread.
Loctite 401	cyanocrylate	Very low viscosity. Single part. Very easy to use.
Huntsman Ardalite 2041	acrylic	Easy to use and spread. Slight noxious odor.
Huntsman Ardalite 2043	urethane	Easy to use and spread. Slight noxious odor.
3M DP-8010	acrylic	Easy to use and spread. Slight noxious odor.
3M 8239 TPO Repair	urethane	Easy to use and spread. Noxious odor.
3M 8239 TPO Repair w/ 3M 5907 adhesion promoter	urethane	Easy to use and spread. Noxious odor.
Dow LESA	acrylic	Easy to use and spread. Noxious odor.
Dow LESA w/ Dow 5404A adhesion promoter	acrylic	Easy to use and spread. Noxious odor.

4.3.1 As-Molded

Included as a baseline treatment, the as-molded adherends were tested with no surface treatment. Thermoplastic plates were manufactured as described above and no modification or cleaning of the surface was performed prior to bonding. A clean, soft towel was used to remove any dust just prior to bonding to ensure no outside contamination occurred.

4.3.2 Acid Washing

The acid wash treatment was a simple cleaning with a 3% phosphoric acid solution to potentially remove contaminants. This is a commonly used method for removing small amounts of zinc stearate left on the surface after manufacture. Adherends were completely submerged (Figure 4-1) in the 3% phosphoric acid solution for approximately 5 minutes before being rinsed clean with distilled water. Adherends were bonded within 24 hours of treatment.

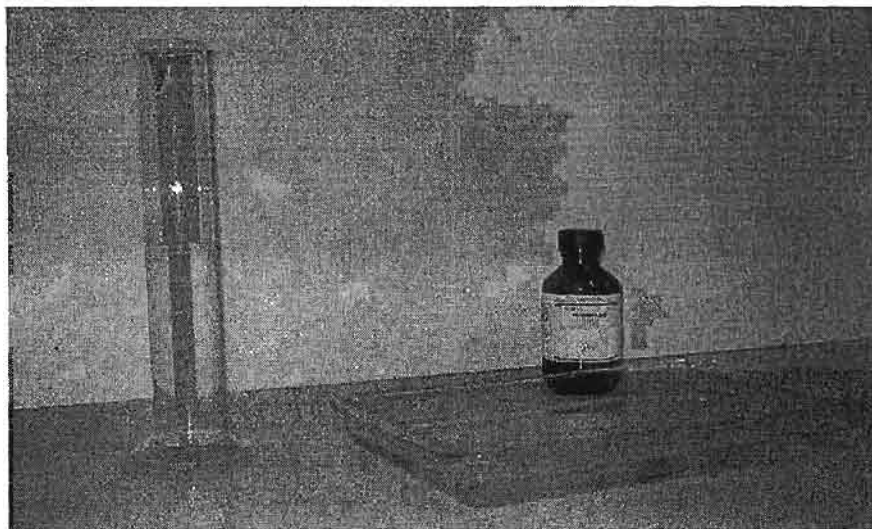


Figure 4-1: Acid washing comprised of submersion in a 3% phosphoric acid solution for approximately 5 minutes.

4.3.3 Hand Sanding

Hand sanding is a very common method of increasing surface energy of composites prior to bonding. The water-break test is often used to establish a sand protocol and readily shows the increase in surface energy from sanding. The abrasion of the sand paper results in the adherend surface becoming rough and increasing the likelihood of a mechanical interlocking bond. Common practice is to use several grits of sand paper or abrasive pads working from coarse to fine grit. For this investigation, dry 220 grit, wet 320 grit, and green Scotch-Brite® (Figure 4-2) were followed with an acetone wipe to clean the surface of debris. All sanding was performed in an overlapping circular motion until the surface visually appeared consistent before moving to the next grit. Adherends were bonded within 24 hours of treatment to remove fade as an unwanted potential parameter.

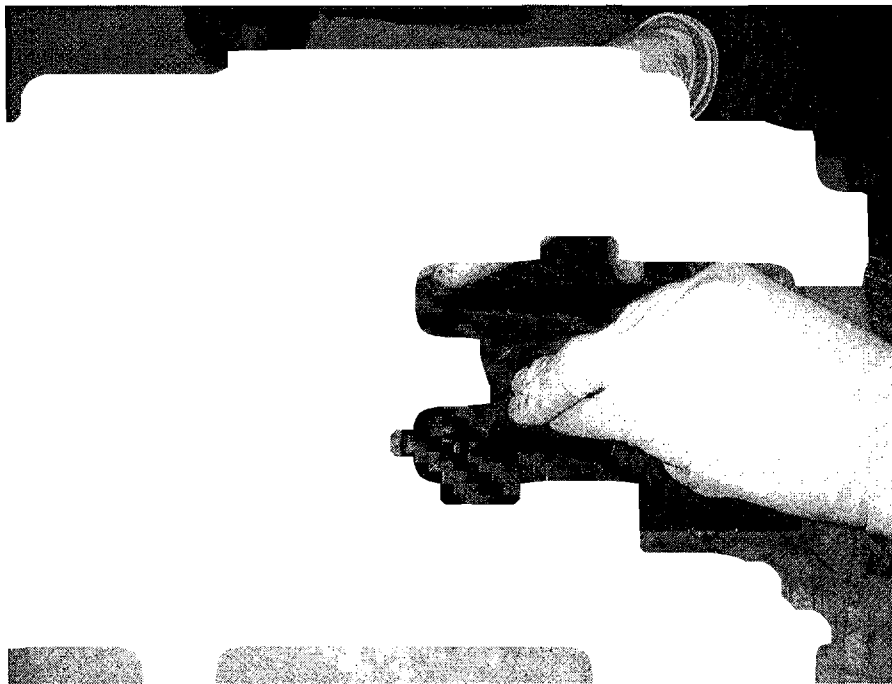


Figure 4-2: Hand sanding consisted of dry 220 grit, wet 320 grit and Scotch-Brite® sanding.

4.3.4 Grit Blasting

Grit blasting commonly uses pressurized air mixed with an abrasive media to abrade a surface. The operation is often performed inside of a chamber to keep the airborne media contained. Aluminum oxide was used in this investigation and overlapping passes performed. A rhythm was used to establish as consistent exposure as possible and a visual inspection was performed. New aluminum oxide was used to reduce the likelihood of embedding contaminants from previous uses of the blasting chamber. Adherends were bonded within 24 hours of treatment to remove fade as an unwanted potential parameter.

4.3.5 Openair® Plasma

Plasma is simply a higher energy state of matter composed of charged particles. It is what comprises the sun, stars and other objects seen outside of our solar system. Here on Earth, it can be found in neon lights, flames and electric discharges. While these sources are often associated with heat, the temperature of plasma is often below the temperature of the same material in a gaseous phase. Thus, a plasma treatment can be performed at a lower temperature thereby reducing potentially negative effects of heat.

Openair® is a trademarked name owned by Plasmatreat North American Inc. Previously, plasma treatment had existed but it had to be contained within a chamber, making treatment difficult for large or complexly shaped parts. The Openair® method uses electricity to excite molecules in the air, thereby generating plasma. This plasma removes contaminants, static electricity and dust by oxidizing these compounds. The exposed polymer chains of the thermoplastic are also affected and the ends are broken

off and replaced with highly reactive $-OH$ and $-NH$ groups. This increases the wettability and surface energy which potentially increases the bond strength of the treated adherend. The Openair® system utilizes a robot arm to move the nozzle that projects the plasma (Figure 4-3), allowing for varying speed and hence time of exposure of the surface being treated. In addition, the amount of plasma, or intensity, can be varied [29].

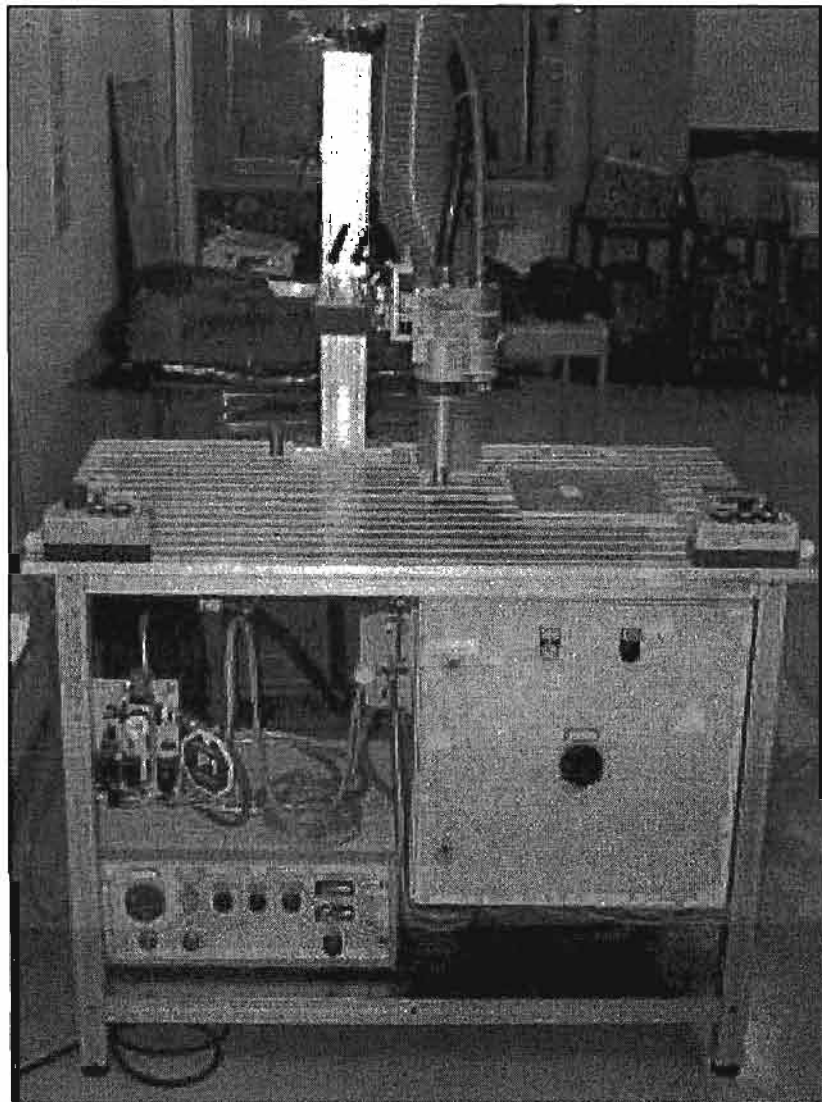


Figure 4-3: The Openair® plasma machine used by Ford RIC to treat adherends.

Adherends were treated courtesy of Ford RIC of Dearborn, MI. Five different parameter sets were used where speed and intensity of the plasma beam were varied. In all cases, adherends were bonded within 24 hours of treatment to remove fade as an unwanted potential parameter.

4.3.6 ATmaP® Flame

Flame treatment utilizes combustion to burn contaminants, increase surface energy and improve wettability. Historically, flames of most all types have been used though significant advances have been made in the past decade. The ATmaP® flame Technology is a trademarked process by FTS Technologies of Flint, MI. The ATmaP® delivers a highly controlled flame that burns with an oxygen content of 0.2-1.2% oxygen. A water-borne diimine solution is evaporated into the flame and interacts with the surface to replace lower energy molecules that are removed from the plasma contained in the flame. Nitrogen is used to encompass the flame which results in the surface becoming polarized. The system allows for each of these parameters to be controlled in addition to flame dwell time through the use of a computer-controlled robot arm.

Adherends were treated courtesy of FTS Technologies. FTS performed a series of tests to determine the ideal treatment parameters based on contact angle measurements. Contact angle measures the angle of various fluids dropped onto a surface. As the angle between the droplet and surface decreases, the surface is considered to have higher wettability and therefore have higher bond strength. Even though contact angle is not a direct correlation to bond strength, it is assumed that smaller angles result in better bond strength. Even though previous research by FTS

has shown that fade does not occur, the treated adherends were bonded within 24 hours of treatment to remove fade as an unwanted potential parameter [30].

4.3.7 Corona

Corona treatment utilizes a high voltage electric discharge where oxygen molecules are separated from the air and become free to bond to the material surface. This increase in oxygen on the surface increases surface energy and wettability. Traditionally, corona treatment has been performed on plastic films that are to be bonded. A plastic film is stretched and passed over a series of rollers to expose it to the treatment. However, a useful method for this investigation was not found and thus corona treatment was not considered further [5].

4.3.8 Surface Activation (Sulfonation)

Surface Activation is a modification of traditional sulfonation. It is the exposure to specific concentrations of sulfur trioxide gas, thus attaching sulfur and oxygen atoms to the surface of the adherend. Next, the sulfonate is made chemically inert by treating the surface with a neutralizing agent. The result is a chemically modified polar surface layer that is up to 25 microns thick. The exposure takes place inside of the chamber filled with sulfur trioxide where most of the sulfur trioxide is recaptured, filtered and reused.

The Surface Activation was performed by Surface Activation Technologies of Troy, MI. Exposure time was varied from 3 to over 10 minutes. Given the depth of the treatment, fade was not considered to be an issue [31]. However, adherends were bonded within 24 hours of treatment.

4.4 Summary of All Parameters

In summary, 2 thermoplastic materials were tested with 13 adhesive and 7 surface treatments parameter groups. Of the 13 adhesive parameter groups, there were 11 adhesives and 2 adhesion promoters. Table 4-2 lists all of the individual parameters that were used for qualitative testing.

Table 4-2: Parameters used for qualitative testing matrix.

		Material/Treatment	Type
Adherends	1	Nylon 6, AS4 Carbon Fiber	Prepreg Thermoplastic
	2	Polypropylene, AS4 Carbon Fiber	Prepreg Thermoplastic
Adhesives	1	Bondmaster E04	toughened epoxy
	2	Bondmaster M1314	acrylic
	3	Lord 7542	urethane
	4	Lord 320/322	toughened epoxy
	5	Loctite 907	epoxy
	6	Loctite 401	cyanocrylate
	7	Huntsman Ardalite 2041	acrylic
	8	Huntsman Ardalite 2043	urethane
	9	3M DP-8010	acrylic
	10	3M 8239 TPO Repair	urethane
	11	3M 8239 TPO Repair w/ 3M 5907 adhesion pro	urethane
	12	Dow LESA	acrylic
	13	Dow LESA w/ Dow 5404A adhesion promoter	acrylic
Treatments	1	As Molded	No treatment
	2	Acid Wash	3% Phosphoric Acid Bath
	3	Hand Sand	220 dry, 320 wet
	4	Grit Blast	Al Oxide media
	5	ATmaP Flame Treatment	Flame exposure in N2 environment
	6	Openair Plasma	Plasma exposure
	7	Sulfonation	SO3 exposure

5 QUALITATIVE TESTING

5.1 Introduction

As noted, thermoplastics are notoriously difficult to bond because of their low surface tension. The purpose of this study was to determine viable methods to adhere thermoplastic composites together. The proper preparation of the surface was deemed equally important to the selection of the adhesives in achieving good bonding. Surface treatments and adhesives were investigated, identified and chosen to be used based on potential effectiveness and to make the scope of the testing as wide as possible. Adhesives from all the major chemistries were chosen with minimal overlapping to keep the scope reasonable. Two versions of TowFlex® woven carbon fiber fabric reinforced thermoplastic, produced by Hexcel Composites Inc., were used in testing: polypropylene and nylon [21, 22]. Given these three parameter sets, a total test matrix was identified and is shown above in Figure 4-2.

A qualitative test outlined in American Society for Testing and Materials (ASTM) designation ASTM D 3808 gave each tester an idea of how each of the over 150 different parameter groups performed quickly and inexpensively. Each spot was considered a test and given a numerical score to allow for quantitative analysis based on the difficulty prying the adhesive dots off thermoplastic composites. The results were analyzed first by looking at the different adhesive groups. Several adhesives showed good adhesion and were deemed suitable candidates for further testing. The

next analysis was within each of the surface treatments. The results of this analysis indicate that adhesion was improved with several of the surface treatments and could be improved further by adjusting the parameters of the treatment.

5.2 Spot Adhesion Test Background

Outlined in designation ASTM D 3808 is the standard practice for *Qualitative Determination of Adhesion of Adhesives to Substrates by Spot Adhesion Test Method* [32]. The test outlines “a simple qualitative procedure for quickly screening whether an adhesive will, under recommended application conditions, bond to a given substrate without actually making bonded assemblies.” Since the test is qualitative, it is “a quick, simple and inexpensive practice” that allows for performance assessment without having to actually make bonded assemblies. This test is intended to be a gateway standard to other quantitative standards that can be used to obtain measurements of the performance of adhesive/adherend parameter groups.

This standard is under the jurisdiction of the ASTM committee D-14 on adhesives that has standardized a variety of tests for determining the strength of adhesive joints. These test methods are useful for comparing the relative strength of different adhesive/adherend parameter groups and the bonding geometry of the joint must be considered when determining a test method. Since joint strength is a combined property of both the adhesive and adherends, subtle geometric differences can result in vastly different strengths. Even though geometries visually appear similar with different surface treatments, the surface geometry is quite different. Thus, a much more complex stress state exists in adhesive joints. Using a simple and quick test is

then easily justifiable to test not only many different surface treatments/geometries, but also many different adhesives.

The ASTM D 3808 standard [32] dictates that spots of adhesive are applied and cured onto the adherend as recommended and acceptable by both the adhesive supplier and user. A specific spot size is not given and can vary, but is generalized as about 6 mm (1/4 in). It is specified that adherend preparation and exposure of the spot can be varied as desired. The actual testing of the spots is performed by simply trying to pry the spot of adhesive from the adherend. This test is to be performed with a thin stainless steel spatula or similar probe as a prying lever as shown in Figure 5-1.

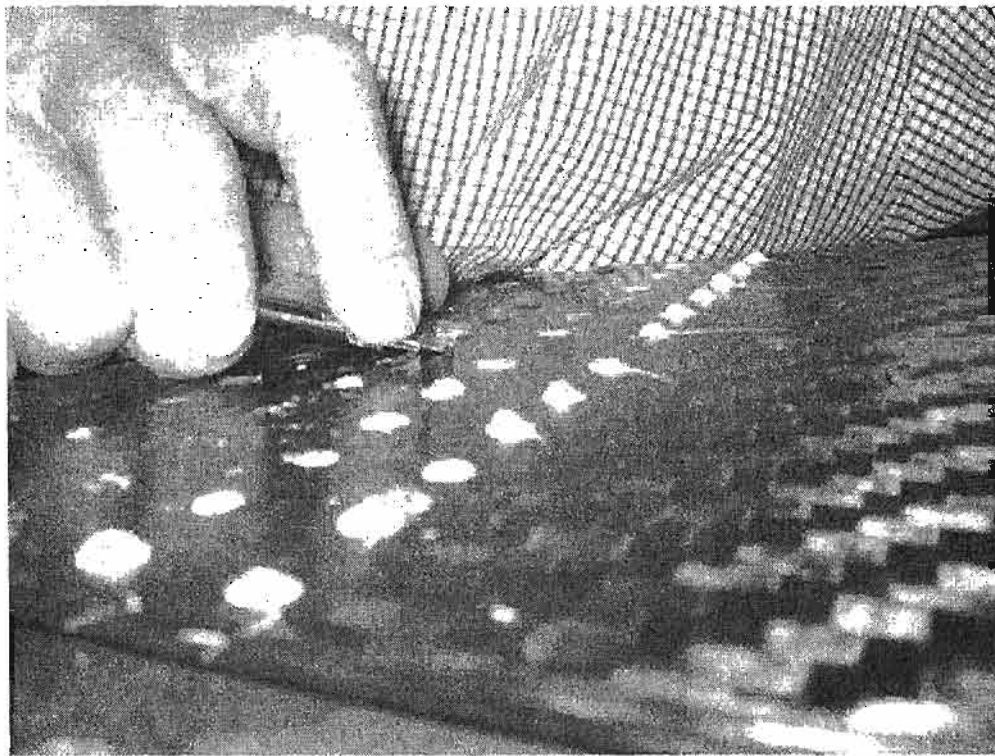


Figure 5-1: An adhesive spot is pried from the adherend as described in ASTM D 3808.

5.3 Methods

The spot adhesion tests were conducted by applying and curing a small spot of an adhesive on the prepared surface of each panel (Figure 5-2). A 1 mm (0.040 in) of TFE with rows of 6 mm (1/4 in) holes was used as a guide for applying uniform and consistent spots. The sheet was used for each row and then lifted before the adhesive cured. The two-part adhesives were thoroughly mixed using 50, 200 or 400 ml mixing guns with supplier specified static mixers. The only exception to this was the Loctite 907 adhesive which was mixed by hand following the supplier recommendations. Uniform color was observed to ensure consistent mixing with all two-part adhesives. One-part adhesives were applied directly to the adherends.

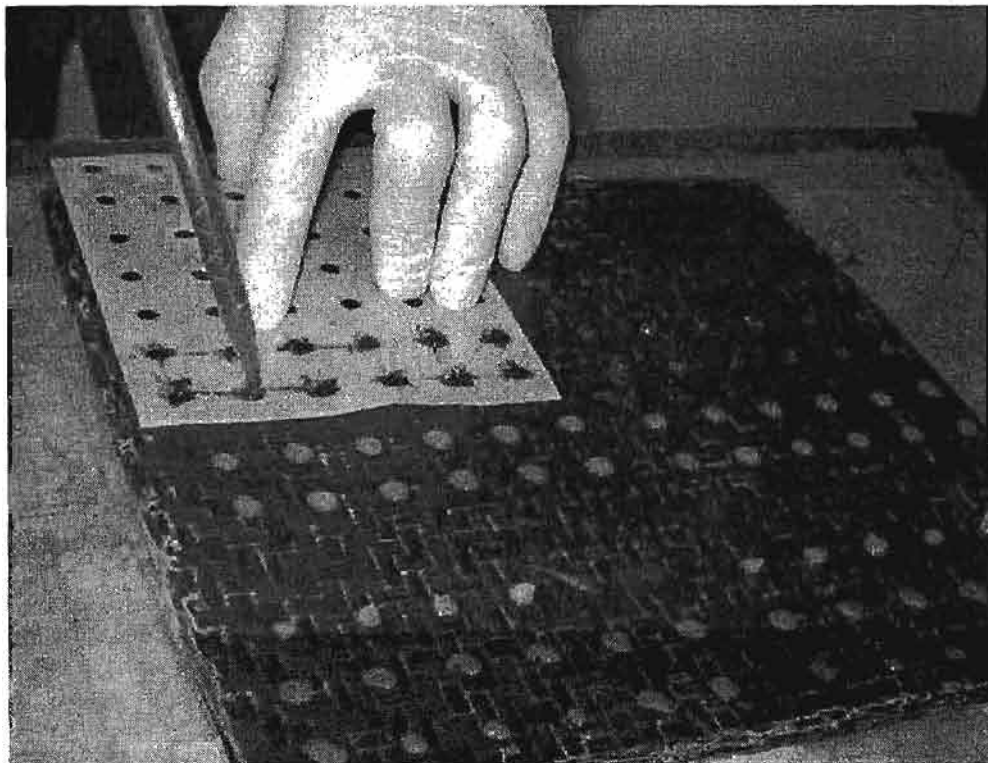


Figure 5-2: As recommended in ASTM D 3808 spots of adhesive are applied to each treated laminate and cured per each manufacturer's specifications.

Since each of the adhesives used was a room-temperature cure, curing time of 48-72 hours was allowed. This exceeded all suppliers' recommendations, the longest of which was a cure time of 24 hours. However, this ensured that all adhesives had sufficient time to cure ensuring the validity of each test.

To test the adhesion of the adhesive spot, a window scraper was used to pry the spot from the substrate. The sharp edge of the scraper allowed for the edge to slightly cut into the adhesive and then be pried up from the surface. This ensured that the adhesive could be pried up consistently.

The difficulty of debonding this spot from the thermoplastic substrate provided a qualitative measure of the potential strength of a joint formed with the particular adhesive and surface treatment applied to the specifically treated thermoplastic composite. Although the spot adhesion test is qualitative in nature, a four-level bond strength determination can be made. After each test a rating of 1-4 (1=poor, 2=fair, 3=good, 4=excellent) was given corresponding to the bond strength using only whole numbers. To prevent potential bias, two test conductors performed the spot adhesion tests on all adhesive/surface treatment parameter groups independently. A minimum of six adhesive spots were tested for each parameter group. Several rounds of spot adhesion testing were performed and low scoring and redundant parameter groups were removed from further testing.

5.4 Results and Discussion

With three parameter sets and two different testers, the data shown in Figure 5-3 were very difficult to analyze. While peaks can be chosen, these were not necessarily the highest scoring parameter groups for both testers. In some cases, one tester had a

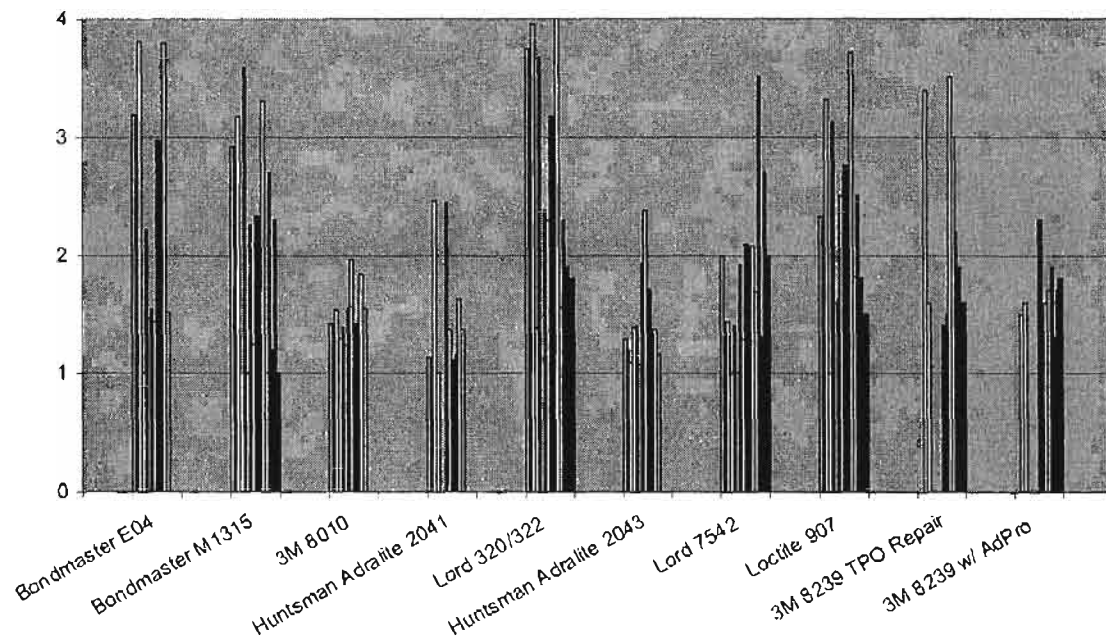


Figure 5-3: Comprehensive results of initial spot adhesion test (ASTM D 3808).

higher score for a particular parameter group than the other tester had. Thus, the scores were averaged not only for each parameter group, but also for both testers. This procedure was validated by listing the top 10 scoring parameter groups for each tester. Seven of the ten parameter groups from each tester were common to both. In addition, the top seven combined scores were the same seven parameter groups from both testers top ten, thus confirming that the averaging was validated. The averaged results are shown below in Table 5-1 with the highest scoring parameter groups for each material. Parameter groups that with low spot adhesion scores were eliminated between rounds of testing resulting in approximately 150 groups tested of a possible maximum of 182 parameter groups.

Table 5-1: Averaged scores from all initial spot adhesion tests. Parameter groups with no scores were not tested.

	As Molded		Acid Wash		Hand Sand		Grit Blast		AtmaP® Flame		Openair® Plasma		Surface Act. (5 min)		Surface Act. (3 min)	
	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP
Bondmaster E04	3.2	1.0	3.8	1.0	2.2	1.5	1.5	1.4	3.0	1.1	3.8	1.5	-	-	-	-
Bondmaster M1315	2.9	1.0	3.2	1.0	3.6	1.0	2.3	1.3	2.3	1.0	3.3	1.0	2.7	1.2	2.3	1.0
3M 8010	1.4	1.2	1.5	1.3	1.4	1.3	1.5	2.0	1.4	1.1	1.8	1.5	-	-	-	-
Huntsman Adralite 2041	1.1	1.0	2.5	1.0	-	-	2.4	1.4	1.1	1.2	1.6	1.4	-	-	-	-
Lord 320/322	3.7	1.4	4.0	1.4	3.7	1.1	2.4	2.3	3.2	1.7	4.0	1.6	2.3	1.9	1.3	1.8
Huntsman Adralite 2043	1.3	1.2	1.1	1.4	1.4	1.1	1.9	2.4	1.7	1.2	1.4	1.2	-	-	-	-
Lord 7542	2.0	1.0	1.4	1.0	1.4	1.0	1.9	1.3	2.1	1.5	2.1	1.7	3.5	1.3	2.7	2.0
Loctite 907	2.3	1.0	3.3	1.0	3.1	1.6	1.6	2.5	2.8	1.2	3.7	1.8	2.5	1.8	1.2	1.5
3M 8239 TPO Repair	-	-	3.4	1.6	-	-	-	-	1.4	1.5	3.5	3.0	2.2	1.9	1.2	1.6
3M 8239 w/ AdPro	-	-	1.5	1.6	-	-	-	-	2.3	1.6	1.6	1.7	1.9	1.3	1.7	1.8

The results in Table 5-1 indicate that nylon adherends had better adhesion than polypropylene particularly with acid wash and Openair® plasma treatments using toughened epoxies. Polypropylene adherends had only one score above a 2.5 indicating poor to fair adhesion. Given the ease of prying a spot scoring below a 3, parameter groups were required to have an average score of 3 or greater to be considered for further testing.

Several observations were made from by the testers and confirmed by the results. First, it appeared that the surface treatment were more variable than the adhesive for each material. The results for each individual adhesive compared with all of the surface treatments shows less variability of spot adhesion test scores. Whereas, for each surface treatment compared with all of the adhesives have more variability. In short, the scores of the adhesive rows are less variable than the surface treatment columns in Table 5-1.

The spot adhesion test, in addition to a wide range of test scores, also had each type of failure. Adhesive, cohesive, and laminate failures were noted as seen in Figure 5-4. The testers noted that adhesive, or interface, failures occurred with low scoring parameter groups while high scoring groups failed cohesively.

Each specific result group is summarized and evaluated within the two categories: adhesive chemistries and surface treatments. The results in Table 5-1 were used to identify the highest scoring parameter groups which were then investigated more closely to determine if additional improvement could be made through optimization of the surface treatment.

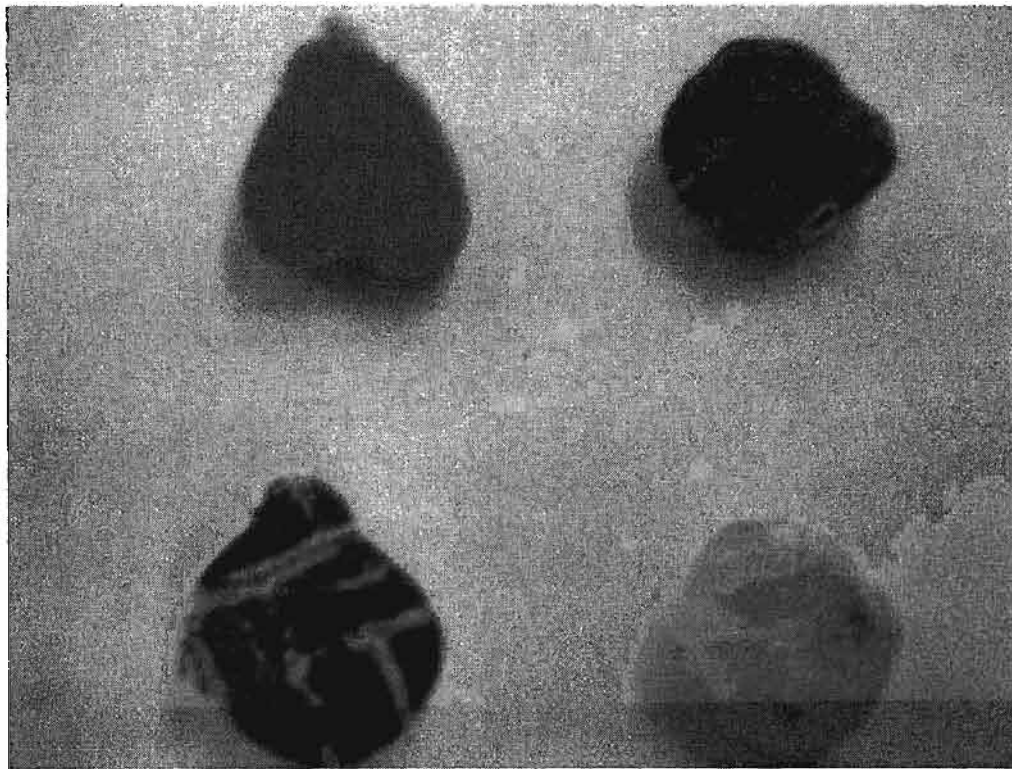


Figure 5-4: Adhesive, cohesive and laminate failures were observed (clockwise from top left: adhesive, adhesive/interface, cohesive, and laminate).

5.4.1 Adhesives

Upon completion of initial testing, the spot adhesion scores of adhesive groups were reviewed and compared. Two of the adhesives were found to not be testable and a summary of the findings of each adhesive group is outlined.

5.4.1.1 Untestable Adhesives: Loctite 401 and Dow LESA

Two of the adhesives, Loctite 401 and Dow LESA, were not testable and thus results are missing from Table 5-1. The Loctite 401 was not able to be tested because of its low viscosity. Spots were not able to be formed and in some cases it ran into other adhesives, contaminating them as seen in Figure 5-5. As expected, this was the case where surface treatments lowered the surface energy thereby allowing the low viscosity material to run out over the surface more easily. Therefore, these spots were not tested.

A standard gun with static mixers was used to dispense the Dow LESA. However, the adhesive leaked past the plunger back onto the gun, potentially throwing off the mix ratio. Further, the two parts did not mix and a “zebra” stripe was noted in the adhesive instead of the normal uniform color. Thus, no spot adhesive testing was performed using the Dow LESA with or without the 5404A adhesion promoter.

5.4.1.2 Epoxies

Several epoxies were tested and consistently scored among the highest of any adhesive tested (Table 5-2). The Lord 320/322 and Bondmaster E04 epoxies tested were toughened epoxies, while the Loctite 907 was as standard epoxy. The Lord

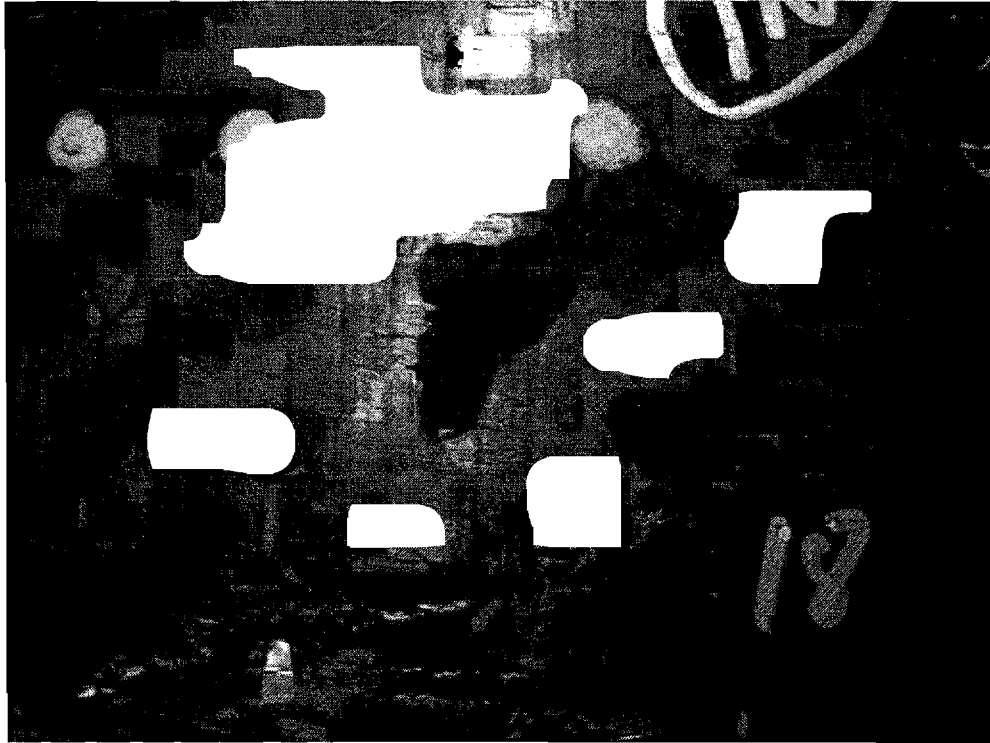


Figure 5-5: The Loctite 401 had a very low viscosity and could not be tested.

Table 5-2: Spot adhesion test scores for the three epoxies tested.

	As Molded		Acid Wash		Hand Sand		Grit Blast		AtmaP® Flame		Openair® Plasma		Surface Act. (5 min)		Surface Act. (3 min)	
	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP
Lord 320/322	3.7	1.4	4.0	1.4	3.7	1.1	2.4	2.3	3.2	1.7	4.0	1.6	2.3	1.9	1.3	1.8
Loctite 907	2.3	1.0	3.3	1.0	3.1	1.6	1.6	2.5	2.8	1.2	3.7	1.8	2.5	1.8	1.2	1.5
Bondmaster E04	3.2	1.0	3.8	1.0	2.2	1.5	1.5	1.4	3.0	1.1	3.8	1.5	-	-	-	-

320/322 on the nylon thermoplastic scored above 3 with all surface treatments except grit blasting and was the highest scoring adhesive observed. Both the Bondmaster E04 and Loctite 907 epoxies on the nylon thermoplastic had many scores of 3 or above. Since the latter epoxies did not score as high as the Lord 320/322 and continuing with several epoxies was deemed redundant, the Bondmaster E04 adhesive was not considered for further testing. However, the Loctite 907 was used as a reference to ensure consistency for preliminary Surface Activation testing. These

scores were not considered when evaluating the performance and are listed as a reference only.

5.4.1.3 Acrylics

Three different acrylics were tested from three different manufacturers. Of the three, only the Bondmaster M1315 scored above a 3 and only when used on the nylon thermoplastic as seen in Table 5-3. The other two acrylic adhesives, Huntsman Adralite 2041 and 3M 8010, scored significantly lower than 3 in all parameter groups as did the Bondmaster M1315 when used with the polypropylene thermoplastic. Thus, only the Bondmaster M1315 used with nylon was considered for further testing.

5.4.1.4 Urethanes

While only three different urethanes were used, the 3M 8239 TPO Repair came with a recommended adhesion promoter. Thus, four different adhesive parameter groups were tested within the urethane group. Within this group, the Lord 7542 was initially thought to score high enough with the polypropylene and was reviewed further (Table 5-4). However, the only score above the minimum of 3 was with the Surface Activation and further testing was performed with this parameter group.

Table 5-3: Spot adhesion test scores for the three acrylics tested.

	As Molded		Acid Wash		Hand Sand		Grit Blast		AtmaP® Flame		Openair® Plasma		Surface Act. (5 min)		Surface Act. (3 min)	
	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP
Bondmaster M1315	2.9	1.0	3.2	1.0	3.6	1.0	2.3	1.3	2.3	1.0	3.3	1.0	2.7	1.2	2.3	1.0
Huntsman Adralite 2041	1.1	1.0	2.5	1.0	-	-	2.4	1.4	1.1	1.2	1.6	1.4	-	-	-	-
3M 8010	1.4	1.2	1.5	1.3	1.4	1.3	1.5	2.0	1.4	1.1	1.8	1.5	-	-	-	-

Table 5-4: Spot adhesion test scores for the three urethanes tested with the addition of an adhesion promoter.

	As Molded		Acid Wash		Hand Sand		Grit Blast		AtmaP® Flame		Openair® Plasma		Surface Act. (5 min)		Surface Act. (3 min)	
	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP	N6	PP
Lord 7542	2.0	1.0	1.4	1.0	1.4	1.0	1.9	1.3	2.1	1.5	2.1	1.7	3.5	1.3	2.7	2.0
Huntsman Adralite 2043	1.3	1.2	1.1	1.4	1.4	1.1	1.9	2.4	1.7	1.2	1.4	1.2	-	-	-	-
3M 8239 TPO Repair	-	-	3.4	1.6	-	-	-	-	1.4	1.5	3.5	3.0	2.2	1.9	1.2	1.6
3M 8239 w/ AdPro	-	-	1.5	1.6	-	-	-	-	2.3	1.6	1.6	1.7	1.9	1.3	1.7	1.8

Otherwise, all other parameter groups with the Lord 7542 and all parameter groups with the Huntsman Adralite 2043 were eliminated from further testing.

The 3M 8239 TPO Repair and 5404A Adhesion Promoter were added after the first round of testing and were only tested with the most promising surface treatments. In all cases, use of the adhesion promoter hindered the bond and resulted in lower scores. This is likely due to the adhesion promoter not bonding to the adherend as well as the adhesive itself would have. It could be the case that the adhesion promoter would improve the performance when used on an as-molded adherend, but this parameter group was not tested, and given the low scores was deemed unnecessary. However, the 3M 8239 without the adhesion promoter performed well, especially with plasma treated polypropylene. Thus, it was considered for further testing in several parameter groups.

5.4.2 Surface Treatments

After reviewing the results of the different adhesive groups, a review of the surface treatments was performed. Surface treatments were either eliminated or

considered for further testing. The specialized surface treatments considered were tested further to optimize the treatment parameters before quantitative testing began.

5.4.2.1 As Molded and Acid Washed

The as-molded and acid washed samples performed very consistently with each adhesive. In most all cases, the acid washed performed slightly better than the as-molded. The cases where it did not had scores that were significantly below 3 and were not considered further as seen in Table 5-5. Since the two treatments were very similar, it was decided to make the acid wash the baseline of the quantitative portion of this investigation. Further, to ensure consistency and try to improve all surface treatments a process step was added whereby all adherends were acid washed prior to any additional treatment.

Table 5-5: Spot adhesion test scores for as-molded and acid wash treatments.

	As Molded		Acid Wash	
	N6	PP	N6	PP
Bondmaster E04	3.2	1.0	3.8	1.0
Bondmaster M1315	2.9	1.0	3.2	1.0
3M 8010	1.4	1.2	1.5	1.3
Huntsman Adralite 2041	1.1	1.0	2.5	1.0
Lord 320/322	3.7	1.4	4.0	1.4
Huntsman Adralite 2043	1.3	1.2	1.1	1.4
Lord 7542	2.0	1.0	1.4	1.0
Loctite 907	2.3	1.0	3.3	1.0
3M 8239 TPO Repair	-	-	3.4	1.6
3M 8239 w/ AdPro	-	-	1.5	1.6

The highest scores for the acid washed adherends were seen with all of the epoxies and the 3M 8239 urethane. Since the Lord 320/322 toughened epoxy was chosen as a representative epoxy as noted above, two parameter groups were chosen for quantitative testing: Lord 320/322 and 3M 8239 with acid washed nylon thermoplastic. There were no parameter groups utilizing as-molded or acid washed treatments with the polypropylene thermoplastic that warranted further investigation.

5.4.2.2 Hand Sanded and Grit Blasted

The results of both the hand sanded and grit blasted appear dubious. Even though several high scores existed when these treatments were used with the nylon thermoplastic, the scores were more inconsistent than the other surface treatments (Table 5-6). In addition, the grit blast is the only surface treatment where the

Table 5-6: Spot adhesion test scores for hand sanded and grit blasted treatments.

	Hand Sand		Grit Blast	
	N6	PP	N6	PP
Bondmaster E04	2.2	1.5	1.5	1.4
Bondmaster M1315	3.6	1.0	2.3	1.3
3M 8010	1.4	1.3	1.5	2.0
Huntsman Adralite 2041	-	-	2.4	1.4
Lord 320/322	3.7	1.1	2.4	2.3
Huntsman Adralite 2043	1.4	1.1	1.9	2.4
Lord 7542	1.4	1.0	1.9	1.3
Loctite 907	3.1	1.6	1.6	2.5
3M 8239 TPO Repair	-	-	-	-
3M 8239 w/ AdPro	-	-	-	-

polypropylene outscored the nylon. The inconsistencies are likely the result of inconsistent treatment across the surface. Some areas were treated effectively, and other areas had too much or too little treatment. In addition to the questionable data, the automotive industry was unwilling to use either of these processes resulting in their removal from any further testing.

5.4.2.3 ATmaP® Flame

Several nylon thermoplastic adherends treated with the ATmaP® process performed well enough to suggest that further testing could be beneficial (Table 5-7). The scores were just above the minimum of 3 and measures were taken to improve by FTS Technologies. Several samples of nylon thermoplastic underwent a variety of treatment parameters using contact angle measurements to determine surface energy. Improvements were noted and FTS treated the nylon plates for quantitative testing with Lord 320/322 adhesive.

A similar approach was taken with the polypropylene though it was deemed that significant improvement was unlikely given the low scores from the spot adhesion testing. FTS followed the same test pattern attempting to increase the surface energy. However, the ATmaP® process does not seem to favor the polypropylene thermoplastic used and even though contact angles could be increased, they faded back to the lower levels within several hours. Thus, no further testing was performed with the polypropylene using the ATmaP® process.

Table 5-7: Spot adhesion test scores for ATmaP® surface treatment.

	AtmaP® Flame	
	N6	PP
Bondmaster E04	3.0	1.1
Bondmaster M1315	2.3	1.0
3M 8010	1.4	1.1
Huntsman Adralite 2041	1.1	1.2
Lord 320/322	3.2	1.7
Huntsman Adralite 2043	1.7	1.2
Lord 7542	2.1	1.5
Loctite 907	2.8	1.2
3M 8239 TPO Repair	1.4	1.5
3M 8239 w/ AdPro	2.3	1.6

5.4.2.4 Openair® Plasma

The Openair® plasma process scored above 3 with several adhesives with nylon adherends (Table 5-8). Similar to the acid wash, it scored well with all of the epoxies, especially the Lord 320/322. In addition, the Bondmaster M1315 acrylic and 3M 8239 both scored highly. Thus, quantitative testing of all three of these adhesives with Openair® treated nylon adherends was warranted.

Further testing of the polypropylene was deemed necessary given the low scores with one acceptable score using the 3M 8239 urethane. This lone acceptable score indicated that perhaps changing the treatment parameters could result in higher scores with other adhesives. Ford RIC treated five different polypropylene plates at varying treatment parameters and further spot adhesion testing was performed with Lord

Table 5-8: Spot adhesion test scores for Openair® plasma surface treatment.

	Openair® Plasma	
	N6	PP
Bondmaster E04	3.8	1.5
Bondmaster M1315	3.3	1.0
3M 8010	1.8	1.5
Huntsman Adralite 2041	1.6	1.4
Lord 320/322	4.0	1.6
Huntsman Adralite 2043	1.4	1.2
Lord 7542	2.1	1.7
Loctite 907	3.7	1.8
3M 8239 TPO Repair	3.5	3.0
3M 8239 w/ AdPro	1.6	1.7

320/322, 7542 and 3M 8239. As shown in Table 5-9, no significant improvement was noted. Plasma #4 in this table is the same as the original parameters and this level of treatment still scored the highest. Thus, the original Openair® plasma treatment was used with the polypropylene adherends and 3M 8239 adhesive for quantitative testing.

Table 5-9: Additional spot adhesion scores for polypropylene samples treated at 5 different Openair® plasma treatment levels.

	Plasma #1	Plasma #2	Plasma #3	Plasma #4	Plasma #5
	PP	PP	PP	PP	PP
Lord 320/322	2.5	2.4	2.2	1.6	2.0
Lord 7542	2.0	2.6	1.4	2.4	2.3
3M 8239	1.7	1.8	1.5	3.1	1.6

5.4.2.5 Surface Activation

Since the Surface Activation surface treatment was added after the initial testing, only the best candidates from each adhesive group were tested (Table 5-10). Initially, two exposure levels were used: 3 and 5 minutes. Of these only the nylon treated for 5 minutes with the Lord 7542 scored above the minimum of 3 and was used in quantitative testing. Further testing to optimize the surface treatment was deemed necessary.

Table 5-10: Spot adhesion test scores for Surface Activation surface treatment.

	Surface Act. (5 min)		Surface Act. (3 min)	
	N6	PP	N6	PP
Bondmaster E04	-	-	-	-
Bondmaster M1315	2.7	1.2	2.3	1.0
3M 8010	-	-	-	-
Huntsman Adralite 2041	-	-	-	-
Lord 320/322	2.3	1.9	1.3	1.8
Huntsman Adralite 2043	-	-	-	-
Lord 7542	3.5	1.3	2.7	2.0
Loctite 907	2.5	1.8	1.2	1.5
3M 8239 TPO Repair	2.2	1.9	1.2	1.6
3M 8239 w/ AdPro	1.9	1.3	1.7	1.8

Surface Activation Technologies then exposed several more plates both of polypropylene and nylon. Treatment levels of the polypropylene were increased such that the exposure time was increased as was the concentration level of sulfur trioxide in the chamber. While both of these parameters were increased for all of the polypropylene plates, negative returns were quickly seen. As shown in Table 5-11, the plate identified as SAT 243 had a level higher than the initial tests, but lower than the other tests. This treatment level was deemed optimal and the nylon was treated similarly. In both cases, improvements were made such that the treated polypropylene and nylon were both tested quantitatively with the Lord 320/322 and 7542.

5.5 Summary

As noted, adjusting the surface energy can greatly improve adhesion. From the results, it is quite apparent that with toughened epoxies very good adhesion is possible directly out of the mold with nylon thermoplastics. This can be improved by one of the several surface treatments noted. Even though the polypropylene scored poorly in most all situations, several parameter groups did have good adhesion.

Table 5-11: Additional spot adhesion scores for polypropylene and nylon samples treated at different Surface Activation treatment levels.

	SAT 243	SAT 244	SAT 245	SAT 265
	PP	PP	PP	N6
Lord 320/322	3.0	2.4	1.3	3.1
Lord 7542	3.6	2.4	2.2	3.8
3M 8239	2.3	1.4	1.8	2.7

These results fall in with previous research. It has been shown that glass reinforced nylon thermoplastic composites have significantly improved adhesion with toughened epoxies when plasma treated [20]. Even though this previous study did not investigate the use of carbon fibers, polypropylene or the other surface treatments investigated, this comparison with the nylon does offer validation of the use of the spot adhesion test and the results. Thus, the parameters specified above which are summarized in Table 5-12 were studied further utilizing quantitative tests.

Table 5-12: Highest scoring parameter groups that warrant quantitative testing.

	Acid Wash		AtmaP® Flame		Openair® Plasma		Surface Act.	
	N6	PP	N6	PP	N6	PP	N6	PP
Lord 320/322	X		X		X		X	X
Lord 7542								X
Bondmaster M1315					X			
3M 8239	X				X	X		

6 QUANTITATIVE TESTING

6.1 Introduction

Selected adhesives and surface treatments were used for follow-on quantitative testing to determine adhesive bond performance with two continuous fiber thermoplastic composite materials: nylon and polypropylene. A simple quantitative test, the single lap shear test, was used to quickly and inexpensively identify the adhesive and surface treatment combinations with the best adhesion.

As noted in the review of previous studies, quantitative measures of bond strength are commonplace. In many such tests, the test specimens are relatively easy to construct and testing requires only a tensile testing apparatus. In this investigation, lap joints are tested in tension at room temperature following procedure ASTM D 3163 [33]. Load versus displacement curves were generated for each test and compared to determine consistency of the bond strength between replicate specimens. The peak load was determined and the bonded area was measured for each parameter group to be used to calculate the comparative bond strength.

6.2 Lap Shear Test Background

The lap shear joint test is a commonly used adhesive test, specimens are simple to build, test, and readily resemble the geometry of many practical joints. Even though different configurations can be used, the most common for rigid plastic adherends is the single lap test outlined the ASTM designation D 3163 shown in Figure 6-1. This

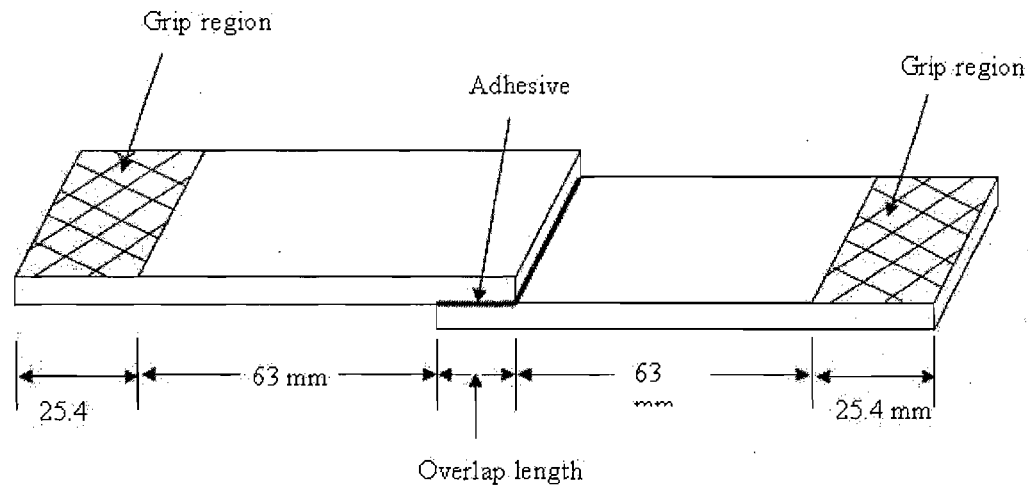


Figure 6-1: The single lap shear test configuration outlined in ASTM D 3163.

test method is titled *Determining the Strength of Adhesively Bonded Rigid Plastic Lap Shear Joints in Shear by Tension Loading* [33].

It must be noted that although the test is called lap shear the failure is usually related to the tensile stresses rather than strictly the shear stresses. Typically, the apparent adhesive strength or lap shear strength is reported as the ratio of the load at failure to the area of overlap. This value is often reported in adhesive handbooks and on data sheets supplied by adhesive manufacturers even though the value is often different from the maximum stress. This has led to use of overly simplified design rules such as average stress criteria that can lead to inaccurate assumed bond strength. Often left out are effects resulting from adherend thickness, adhesive bond thickness and overlap length which Powers and Trzaskos determined affected bond strength significantly [13]. This test can be useful for comparison of the parameter groups in this investigation but, the results must be interpreted with caution. Thus, the term comparative bond strength is used to imply that this value should be used only for comparison within this investigation. For more information regarding the known

issues associated with the single lap shear joint test, the reader is referred to ASTM D 4896 [34].

6.3 Methods

For lap shear testing, the test specimen geometry was selected in accordance with ASTM D 3163. The manufacturing procedure of the thermoplastic plates outlined in Chapter 3 was again followed. An acid wash was performed prior to all surface treatments, in an attempt to remove additional contaminants. The specimens were 4 plies thick and 25.4 mm (1.0 in) wide. Each specimen was approximately 101.6 mm (4.0 in) long and a bond length, L , was chosen to be 12.3 mm (0.5 in). Bond thickness was controlled by placing 0.51 mm (0.020 in) thick wires in the bond area. Fixtures were machined to hold the specimen plates at the proper places with respect to each other and pins were used to ensure proper placement. Plates at least 127 mm (5 in) wide bonded for each parameter group and all samples tested were cut from the same larger plate. The plates were held in the fixtures (Figure 6-2) for at least 12 hours which at least doubled the hardening time for each adhesive. After removal from the fixtures, the specimens were cured at room temperature for at least 48 hours before they were cut ensuring that at complete and consistent cure was achieved.

A minimum of three specimens were tested for each test parameter group resulting in at over 30 tests. In several cases, additional specimens were tested if one of the other specimens was damaged when handled or loaded into the test frame. Specimens were loaded into an Instron 4303 tensile testing frame with a 5 kip load cell as seen in Figure 6-3. A constant displacement rate of 1.27 mm/min (0.050 in/min) was used. Load versus displacement curves, bond area, peak load, and failure type

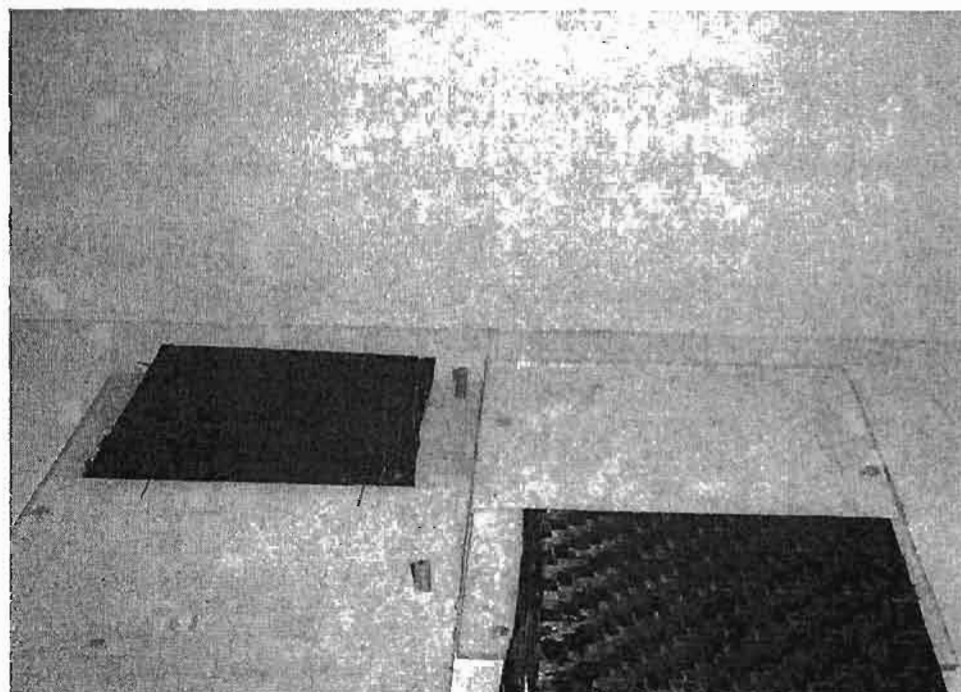


Figure 6-2: Fixtured lap shear test specimens just prior to bonding.

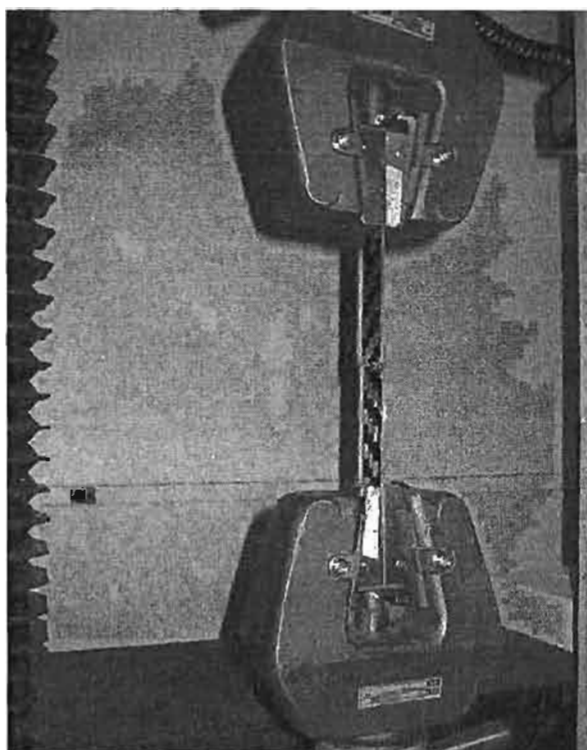


Figure 6-3: A lap shear specimen being tested using an Instron 4303 load frame.

were noted for each specimen tested. The bond area and peak load were used to calculate comparative bond strength for each specimen and average stress for each parameter group. These bond strengths were then used to compare the different parameter groups and assess which parameter group achieved highest bond strength. The calculated strengths are not intended for use in design, but only as a reference to compare the different parameter groups within this investigation.

6.4 Results and Discussion

Compared to the amount of data from the qualitative testing, the results from the quantitative testing were easier to analyze largely due to the reduced number of parameter groups tested. Results are summarized in Table 6-1.

The data from Table 6-1 was viewed graphically to compare individual comparative bond strength (Figure 6-4) and average comparative bond strength (Figure 6-5) for each group. As seen in both Figures 6-4 and 6-5, the parameter groups involving nylon achieved the highest comparative bond strength. The average strengths of the polypropylene parameter groups were significantly lower than the nylon. In addition, the higher strength parameter groups also had a smaller normalized variation. It is interesting to note that the highest strength was achieved with a simple acid wash, even though all of the samples were acid washed prior to any surface treatment suggesting further analysis would be useful.

The Lord 320/322 epoxy had the highest comparative bond strengths with a small change in strength with the different surface treatments. Four of the five highest strength groups were bonded using this Lord epoxy and the average strengths all these

Table 6-1: Comprehensive data collected and calculated from lap shear testing.

Combination	Sample	Bonded Area (m ²)	Peak Force (N)	Bond Strength (Mpa)	Ave. Bond Strength (Mpa)	Failure Type
Acid Wash Nylon/Lord 320/322	1	2.68E-04	7513	28.0	26.9	cohesive
	2	2.77E-04	7561	27.3		
	3	2.78E-04	7016	25.3		
Acid Wash Nylon/3M 8239	1	2.68E-04	7016	26.2	25.7	fiber pull and cohesive
	2	2.83E-04	7234	25.5		
	3	2.78E-04	7055	25.3		
ATmaP® Nylon/Lord 320/322	1	3.04E-04	7571	24.9	25.7	cohesive
	2	2.84E-04	7371	25.9		
	3	2.82E-04	7371	26.2		
Openair® Nylon/Lord 320/322	1	2.53E-04	6344	25.1	25.0	cohesive
	2	2.46E-04	6897	28.0		
	3	2.57E-04	5644	21.9		
Surface Act Nylon/Lord 320/322	1	2.87E-04	6874	24.0	22.6	fiber pull and cohesive
	2	2.86E-04	6533	22.8		
	3	2.88E-04	6025	20.9		
Openair® Nylon/3M 8239	1	2.79E-04	1351	4.8	13.8	mixed
	2	2.81E-04	5254	18.7		
	3	2.76E-04	5301	19.2		
	4	2.82E-04	3538	12.6		
Surface Act Polypro/Lord 7542	1	3.04E-04	1544	5.1	6.1	fiber pull and cohesive
	2	2.99E-04	1557	5.2		
	3	3.03E-04	2408	7.9		
Surface Act Polypro/Lord 320/322	1	2.61E-04	1745	6.7	5.5	fiber pull and cohesive
	2	2.68E-04	1131	4.2		
	3	2.78E-04	n/a	n/a		
Openair® Nylon/Bond master	1	2.84E-04	944	3.3	5.4	adhesive
	2	2.82E-04	1367	4.8		
	3	2.80E-04	2209	7.9		
Openair® Polypro/3M 8239	1	2.93E-04	898	3.1	4.9	adhesive
	2	3.11E-04	2007	6.5		
	3	3.00E-04	1749	5.8		
	4	3.18E-04	1351	4.2		

groups were less than 15% below the highest average strength. Thus, further analysis of these groups should be performed including feasibility and cost analyses.

The results from the lap shear test also match the results from the spot adhesion test. In addition to the average comparative bond strength, Figure 6-5 has the spot adhesion scores for each group tested. While the general trend of the two test methods is similar, a strong correlation does not appear to exist. The variation between the highest scoring spot adhesion scores and comparative bond strengths seen upon examination of Figure 6-5 suggests that spot adhesion test is limited. The spot adhesion test can give a general idea of strength, but to compare combinations that score similarly a quantitative method is needed.

Beyond these general observations, specific observations are made for each of the specimen groups tested.

Figure 6-4: Comparative bond strength of each specimen tested using the lap shear test.

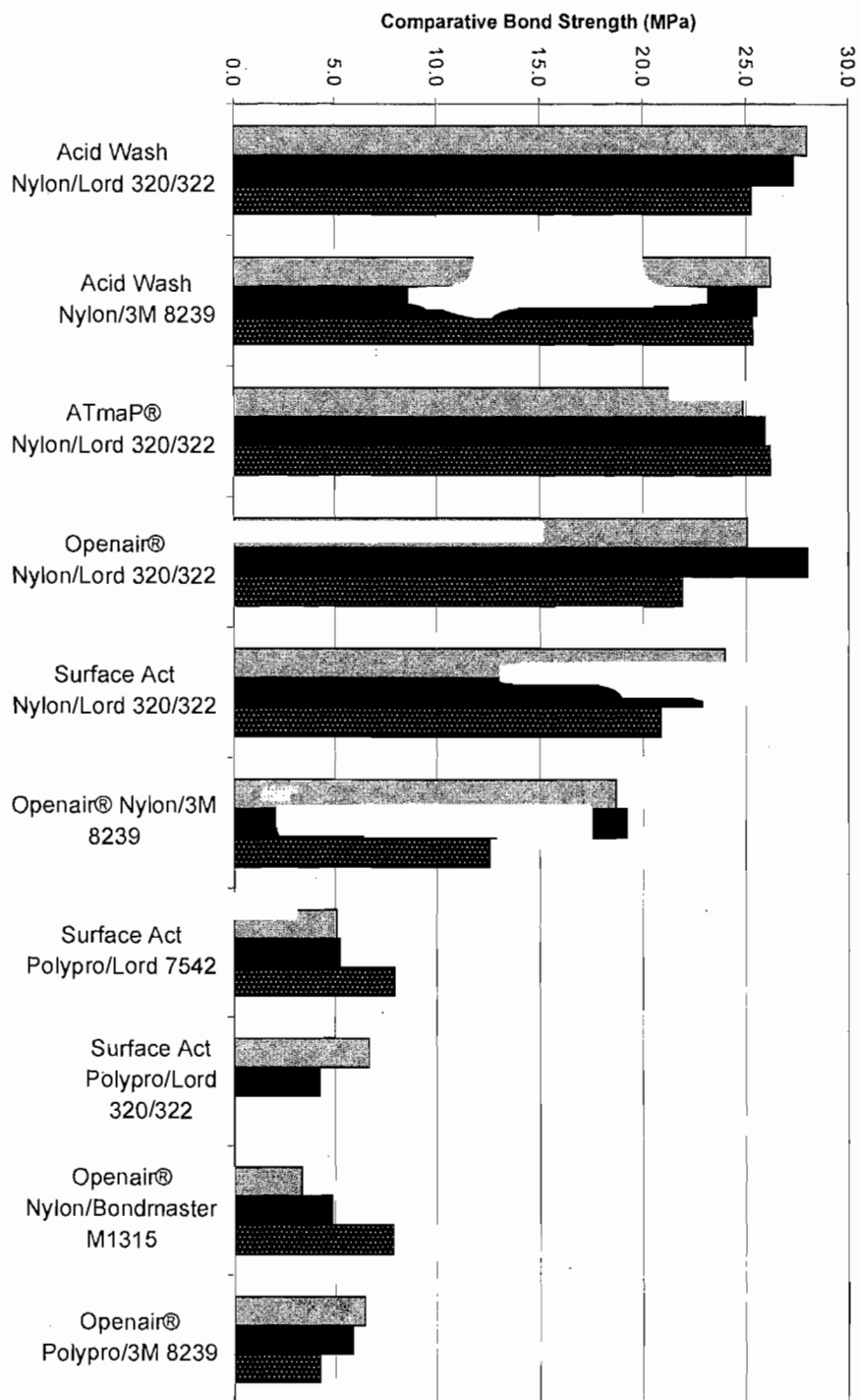
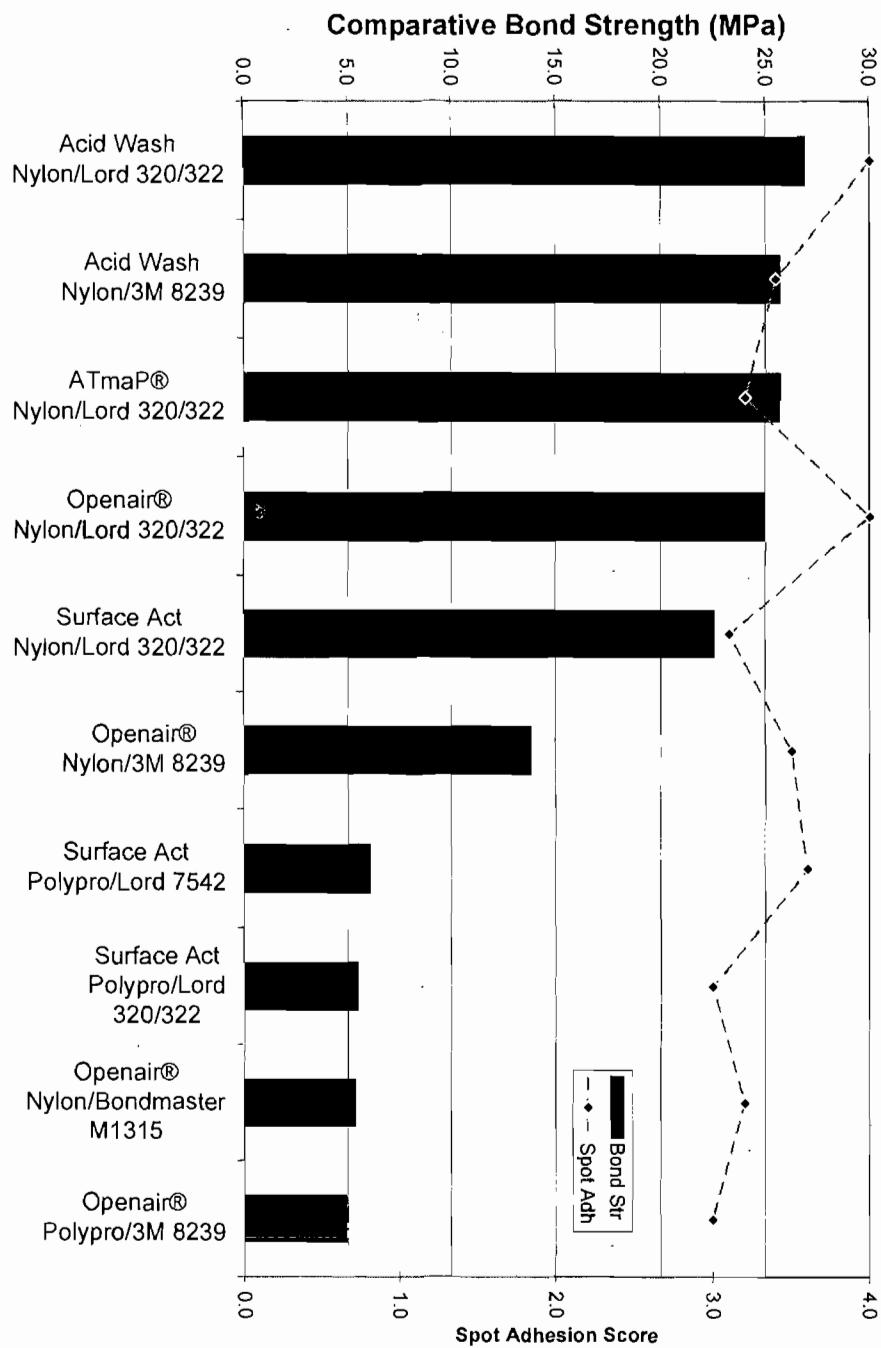


Figure 6-5: Average comparative bond strength of each of the parameter groups tested using the lap shear test.



6.4.1 Acid Washed Nylon/Lord 320/322

The highest comparative bond strength of 26.9 MPa (3.9 ksi) was obtained with Acid Washed nylon thermoplastic adherends bonded with Lord 320/322 adhesive. The load versus displacement curves for the three samples (Figure 6-6) indicates that while there was some subtle variation between the three specimens, the load versus displacement behavior was consistent. All three samples also consistently failed cohesively, which is the preferred failure mode. These results are consistent with the results from the earlier spot adhesion test where this parameter group was only one of two to score a 4.0—the highest possible score.

6.4.2 Acid Washed Nylon/3M 8239

The parameter group of Acid Washed nylon thermoplastic adherends with the 3M 8239 adhesive tied for the second average highest comparative bond strength of 25.7 MPa (3.7 ksi). The load versus displacement curves for the three samples were very consistent as observed by the difficulty in distinguishing the three tests in Figure 6-7. In addition, all three samples failed cohesively. Comparing these quantitative results with the average score of 3.4 from the spot adhesion test, the comparative bond strength appeared to be higher than anticipated. However, this parameter group performed similarly to several other parameter groups with the Lord 320/322 adhesive all of which score between 3.1 and 4.0 in the spot adhesion test.

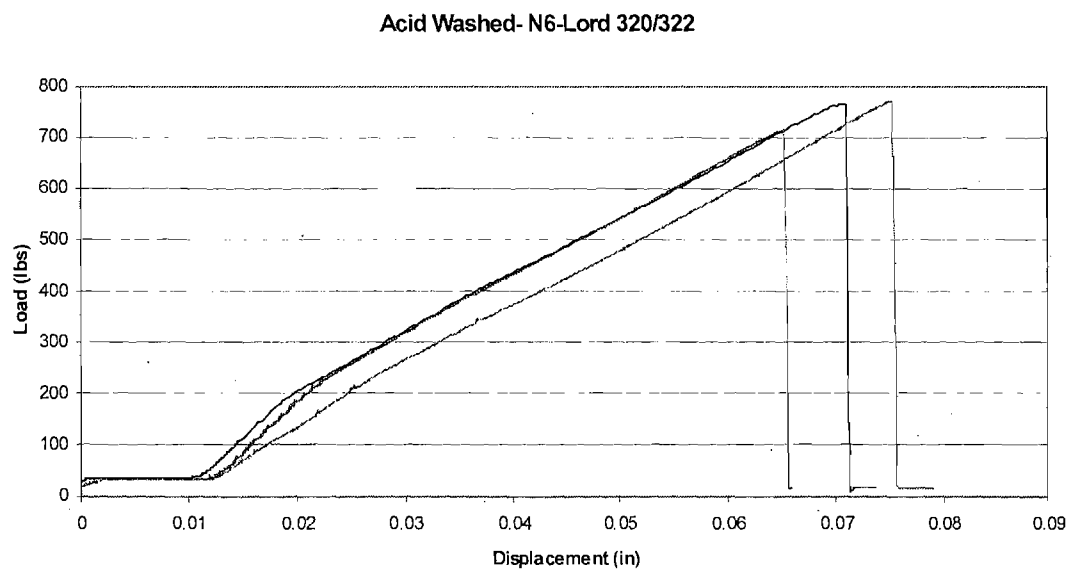


Figure 6-6: Load vs. displacement curves for acid washed nylon bonded with Lord 320/322 adhesive.

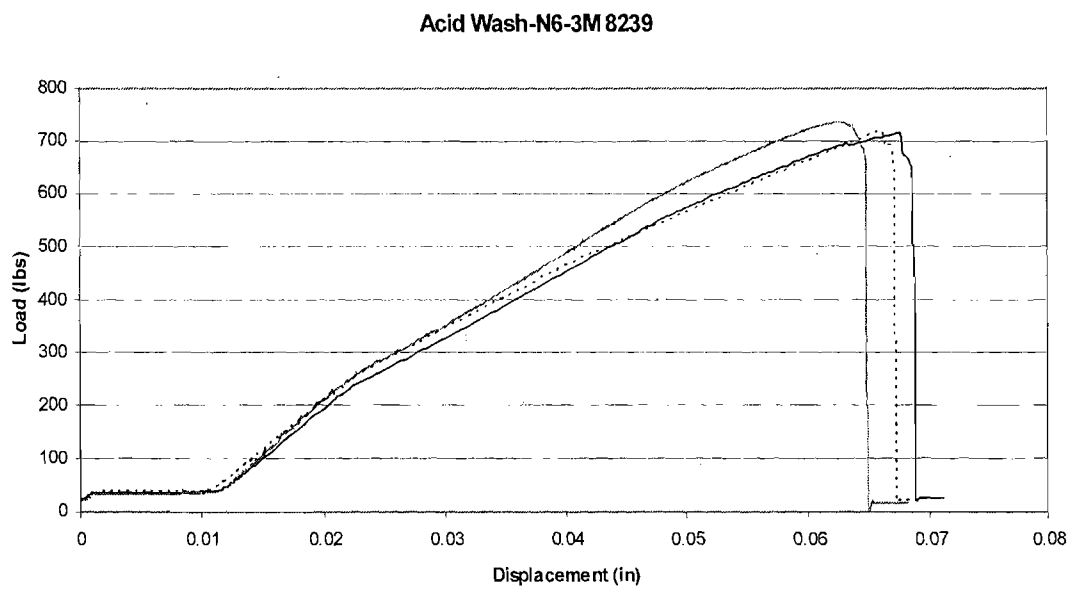


Figure 6-7: Load vs. displacement curves for acid washed nylon bonded with 3M 8239 adhesive.

6.4.3 ATmaP® Nylon/Lord 320/322

The parameter group of ATmaP® treated nylon thermoplastic adherends with the Lord 320/322 adhesive had identical average comparative bond strength to the acid washed nylon/3M 8239 parameter group of 25.7 MPa (3.7 ksi). The load versus displacement curves for the three samples were very consistent as seen in Figure 6-8. It should be noted that the third specimen slipped in the grips a small amount explaining the difference in displacement. Again, all three samples failed cohesively. Similar to the acid washed parameter group, the average spot adhesion score was 3.4 suggesting that the additional work to optimize the treatment parameters was effective.

6.4.4 Openair® Plasma Nylon/Lord 320/322

The parameter group of Openair® plasma treated nylon thermoplastic adherends with the Lord 320/322 adhesive had similar average comparative bond strength to the previous two parameter groups of 25.0 MPa (3.6 ksi). The load versus displacement curves for the three samples were consistent as seen in Figure 6-9, though the peak load of the third sample dropped from the first two specimens. This is likely due to premature crack growth or a small amount of surface contamination on that particular specimen. Once again, all three samples failed cohesively. Differing from the previous two samples, the spot adhesion test score observed was a 4.0. It appears that the inconsistent peak loads resulted in more variation and perhaps lower comparative bond strength.

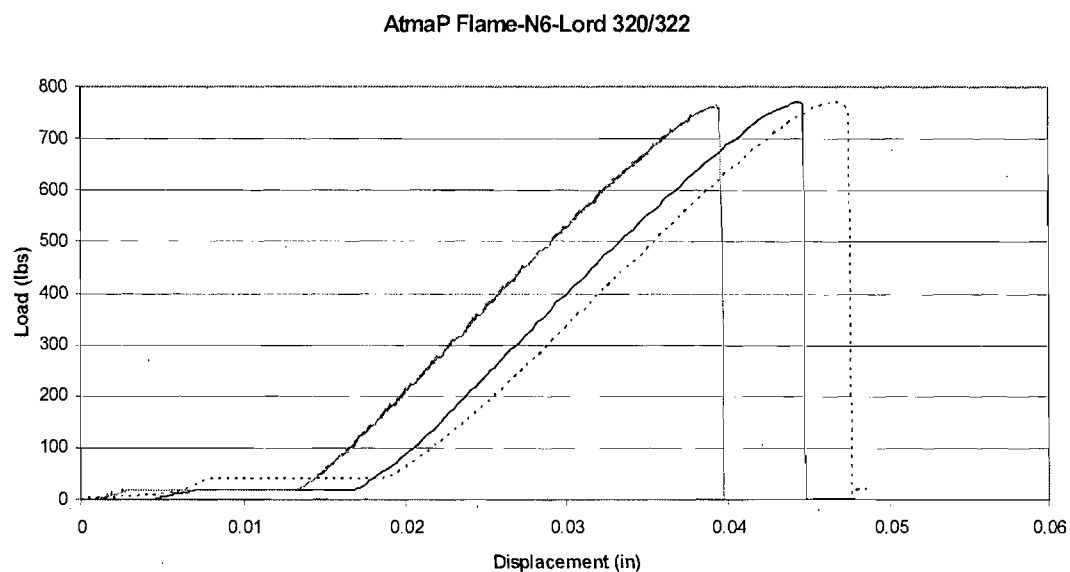


Figure 6-8: Load vs. displacement curves for ATmaP® treated nylon bonded with Lord 320/322 adhesive.

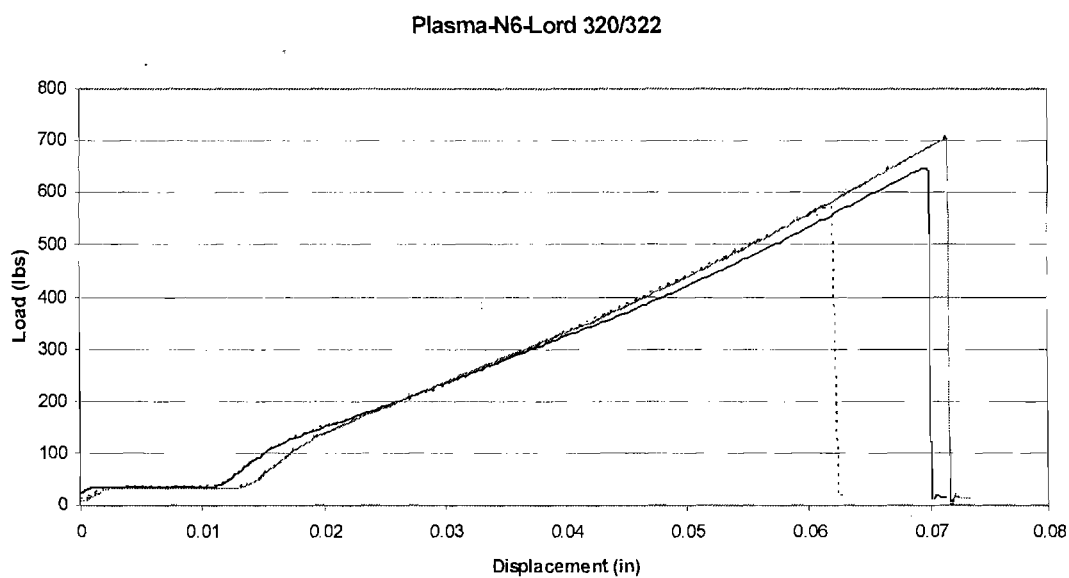


Figure 6-9: Load vs. displacement curves for Openair® plasma treated nylon bonded with Lord 320/322 adhesive.

6.4.5 Surface Activation Nylon/Lord 320/322

The parameter group of Surface Activation treated nylon thermoplastic adherends with the Lord 320/322 adhesive had average comparative bond strength of 22.6 MPa (3.3 ksi). This strength was almost 15% reduction in strength from the highest strength group, acid washed Nylon bonded with Lord 320/322 epoxy. The load versus displacement curves for the three samples were consistent (Figure 6-10), though some variation did exist in the displacement possibly due to a small amount of slipping in the grips. Once again, all three samples failed cohesively. Similar to the ATmaP® parameter group, the average spot adhesion score was 3.1 suggesting that the additional work to optimize the treatment parameters was effective.

6.4.6 Openair® Plasma Nylon/3M 8239

The parameter group of Openair® plasma treated nylon thermoplastic adherends with the 3M 8239 adhesive was the first parameter group that resulted in a significant drop in average comparative bond strength. The strength of this group was 13.8 MPa (2.0 ksi) which is approximately 50% of the highest strength group. While the first two load versus displacement curves were consistent (Figure 6-11), the third had a much lower peak load. Even though the peak load for all three specimens was significantly lower, the difference in the peak load of the third specimen affected the average. Failure was observed to be mixed between cohesive and adhesive with all three samples. Since the spot adhesion score from this parameter group was 3.5, the strengths are lower than anticipated. The lower strength could be due to contamination or a more rapid effect of fade than previously thought existed.

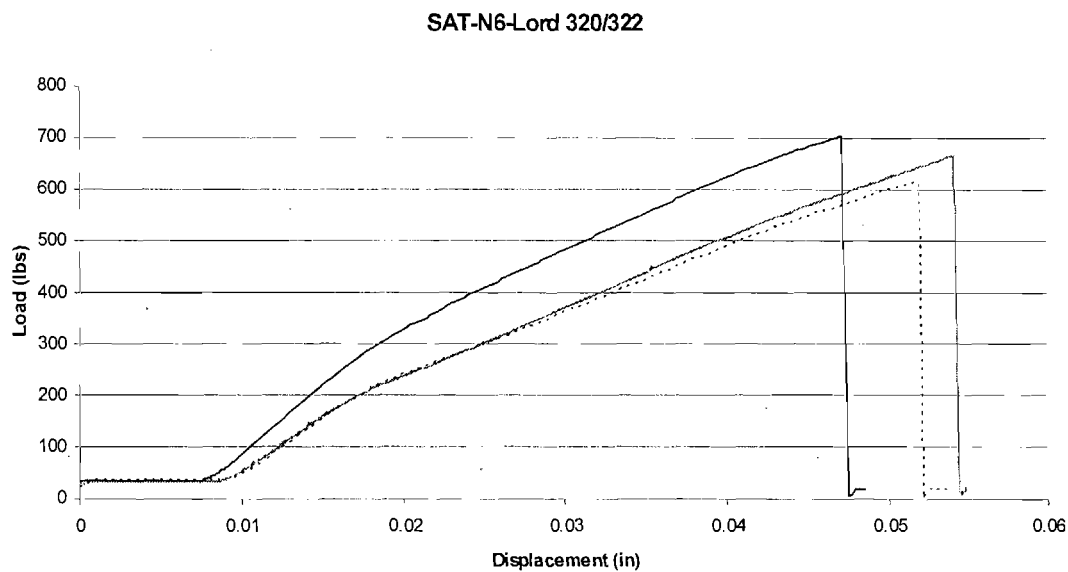


Figure 6-10: Load vs. displacement curves for Surface Activation treated nylon bonded with Lord 320/322 adhesive.

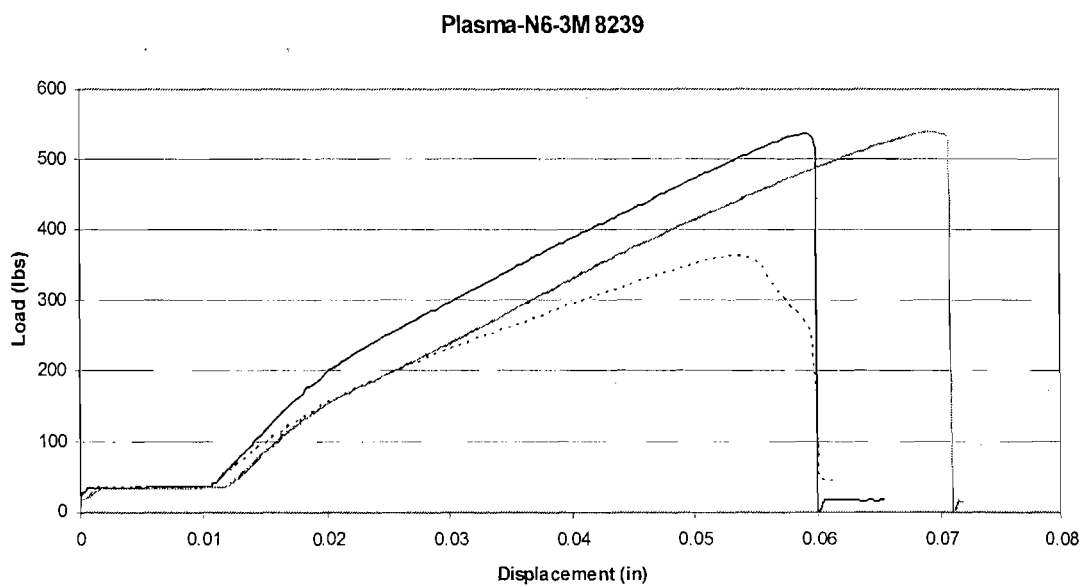


Figure 6-11: Load vs. displacement curves for Openair® plasma treated nylon bonded with 3M 8239 adhesive.

6.4.7 Surface Activation Polypropylene/Lord 7542

The parameter group of Surface Activation treated polypropylene thermoplastic adherends with the Lord 7542 adhesive was the highest strength polypropylene with comparative bond strength of 6.1 MPa (885 psi). The load versus displacement curves for the three specimens show significant inconsistency in the peak load (Figure 6-12). A portion of the inconsistency may have been produced by damage to the specimens prior to testing that was not discovered until after the testing was completed. While removing excess adhesive squeeze-out, some of the fibers on the adherend surface appeared to have been cut. Thus, the adherend was not able to transfer load effectively and failed prematurely. However, since both laminate and cohesive failures were observed, this was likely not the only contributing factor to the inconsistency in strength. Even though the spot adhesion score was a 3.6, there was considerable variation with the individual scores.

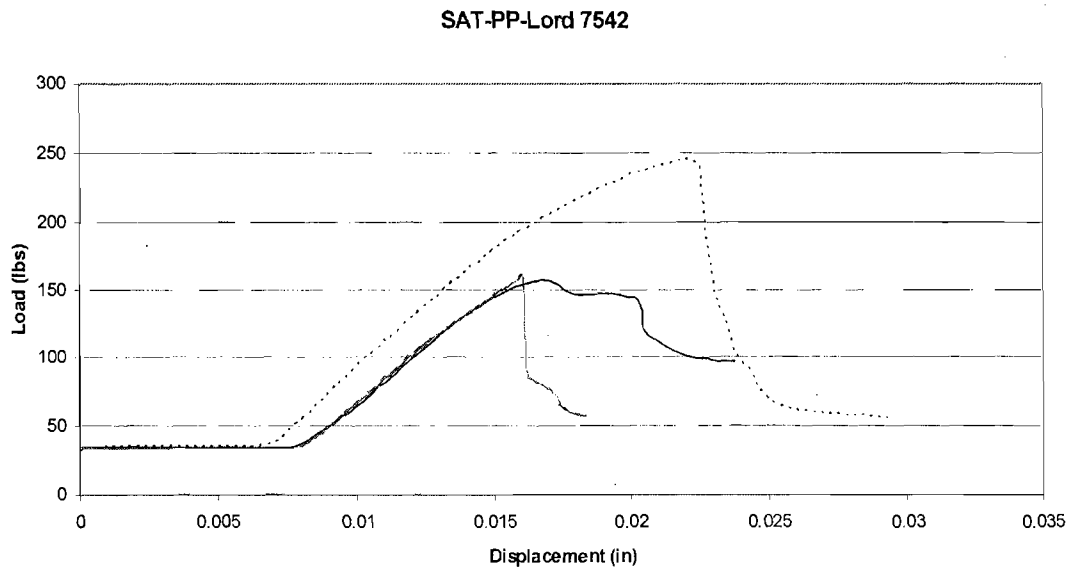


Figure 6-12: Load vs. displacement curves for Surface Activation treated polypropylene bonded with Lord 7542 adhesive.

6.4.8 Surface Activation Polypropylene/Lord 320/322

The parameter group of Surface Activation treated polypropylene thermoplastic adherends with the Lord 320/322 adhesive had a comparative bond strength of 5.5 MPa (798 psi). Only two samples were tested due to failures while loading the samples into the load frame. Load versus displacement curves for the specimens show a significant inconsistency in the peak load as seen in Figure 6-13. However, based on the spot adhesion score of 3.1, a lower strength than the Surface Activation treated polypropylene bonded with the Lord 7542 adhesive would be expected.

6.4.9 Openair® Plasma Nylon/Bondmaster M1315

The parameter group of Openair® plasma treated nylon thermoplastic adherends with the Bondmaster adhesive had the lowest comparative bond strength of any of the nylons tested, 5.4 MPa (783 psi). The load versus displacement curves for the specimens show inconsistency in the peak load as seen in Figure 6-14. This was partially due to the fact that this was the only parameter group where entirely adhesive failure was noted.

6.4.10 Openair® Plasma Polypropylene/3M 8239

The parameter group of Openair® treated polypropylene thermoplastic adherends with the 3M 8239 adhesive had the lowest comparative bond strength of 4.9 MPa (711 psi). The load versus displacement curves for the specimens show significant inconsistency in peak loads as seen in Figure 6-15. This parameter group scored a 3.0 in the spot adhesion test, the lowest acceptable score for quantitative testing to be performed.

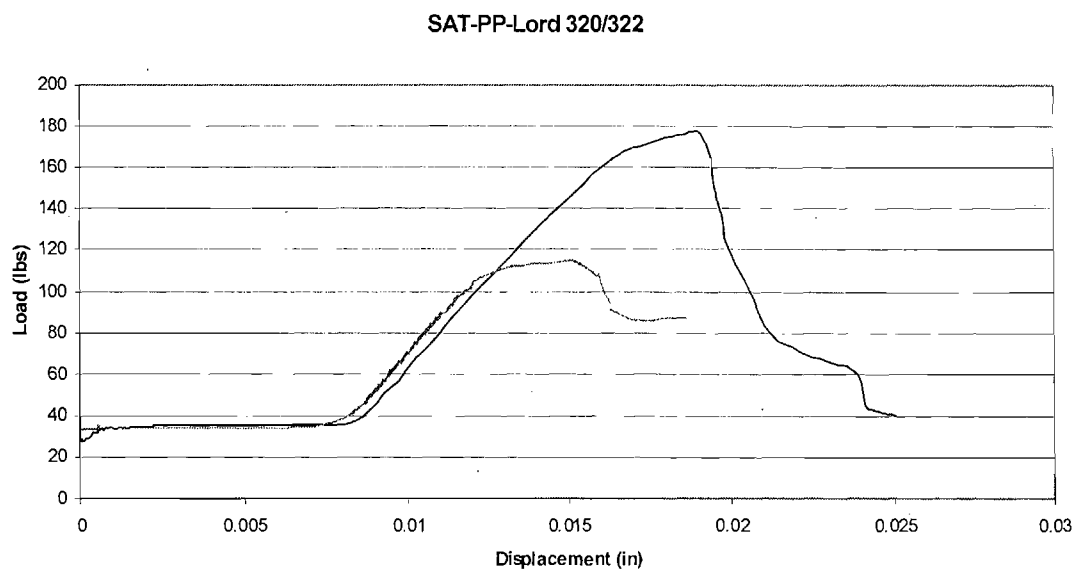


Figure 6-13: Load vs. displacement curves for Surface Activation treated polypropylene bonded with Lord 320/322 adhesive.

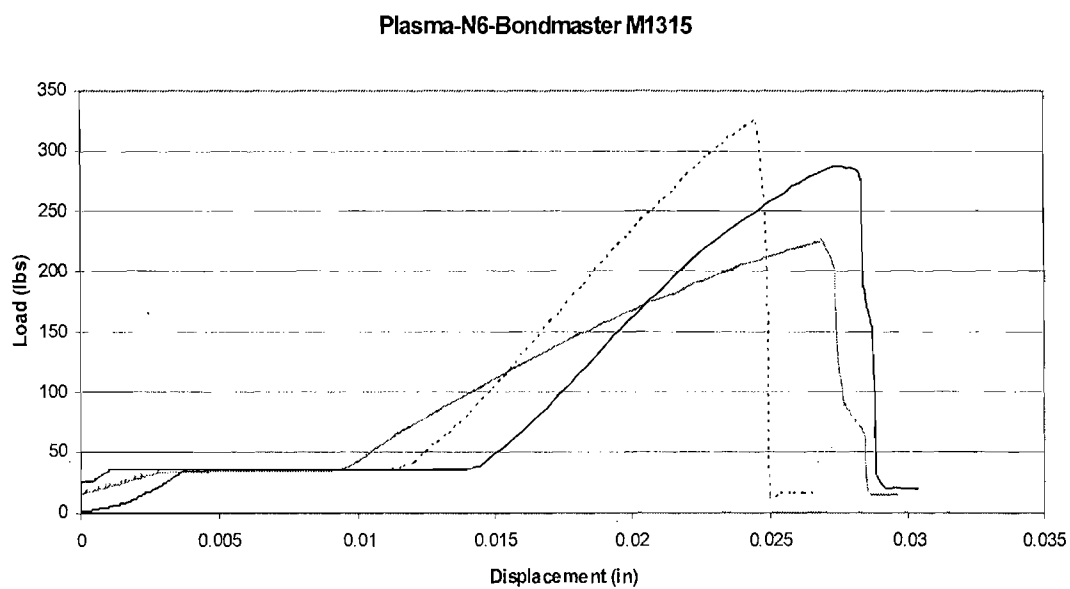


Figure 6-14: Load vs. displacement curves for Openair® plasma treated nylon bonded with Bondmaster M1315 adhesive.

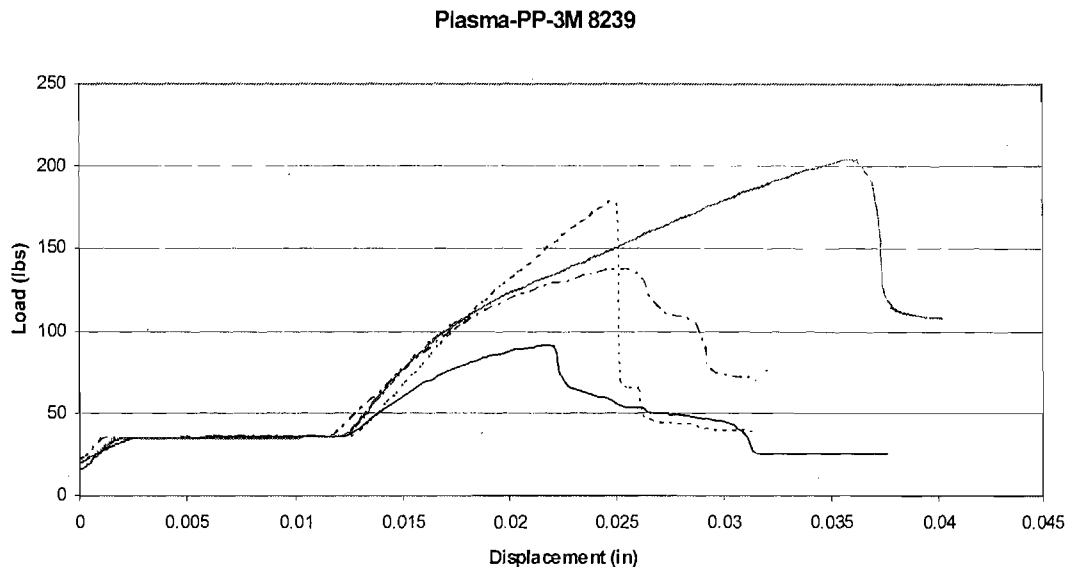


Figure 6-15: Load vs. displacement curves for Openair® plasma treated polypropylene bonded with 3M 8239 adhesive.

6.5 Summary

The highest scoring parameter groups from the spot adhesion test were tested quantitatively using the lap shear test outlined in ASTM D 3163. Specimens were fabricated for each of these high scoring parameter groups. Peak load was established and average bond strength—referred to as comparative bond strength—was calculated to be used as a comparative measure within this investigation only.

From the lap shear test results, the previous conclusion that the nylon thermoplastic composite is capable of higher bond strengths than the polypropylene thermoplastic composites was again confirmed. In addition, the epoxy adhesive achieved higher strengths and more consistent results than the other adhesives investigated. Even though several polypropylene parameter groups scored well in the

spot adhesion test, all polypropylene parameter groups tested had very low comparative bond strengths and load versus displacement curves were inconsistent. It is also important to note that all parameter groups tested quantitatively achieved bond strength an order of magnitude higher than the shear strengths of typical core materials. Thus, further testing of all 10 combinations is recommended.

7 CONCLUSIONS AND RECOMMENDATIONS

In this investigation, over 150 parameter groups of adhesive, surface treatment and thermoplastic composite materials were tested to determine effective bonding procedures for thermoplastic composites. Two testing methods were used: qualitative testing and quantitative testing. The qualitative test method was a spot adhesion test outlined in ASTM D 3808. Many different parameter groups were tested and the highest scoring parameter groups were tested quantitatively using the lap shear test outlined in ASTM D 3163. Ultimately, the best methods identified from this testing can be used to develop joining methods for sandwich composites utilizing thermoplastic facesheets.

Prior to testing, a method was developed to successfully manufacture the thermoplastic facesheets. The key was elimination of contaminants while developing a surface finish acceptable to the automotive industry. The method developed utilized zinc stearate mold release with aluminum tooling surfaces. Aluminum foil was added to the tool interface to improve surface finish. Although this method was found to be suitable, it is recommended that development continue to develop a method capable of Class A surface finish as specified by the automotive industry.

The qualitative test method was chosen because it allowed for simple, inexpensive and quick analysis of a large number of parameter groups. Adhesives and surface treatments were identified to bond continuous carbon fiber nylon and polypropylene

thermoplastic composites. Adhesives initially included epoxies, acrylics, cyanoacrylates and urethanes. In addition to testing as-molded thermoplastics, acid washing, hand sanding, grit blasting, ATmaP® flame, Openair® plasma and Surface Activation (sulfonation) were used.

The spot adhesion test was performed and scores were given to each sample tested. In line with previous research, the nylon thermoplastic scored much higher than the polypropylene thermoplastic. Almost 25% of the parameter groups tested using nylon scored above the minimum score of 3.0 for reasonable adhesion. Scores below this mark were not considered to be high enough for further testing and only one polypropylene parameter group scored above this point in the initial round of testing. Further optimization of several surface treatments resulted in two other parameter groups with the polypropylene thermoplastic.

In all, 10 parameter groups—7 nylon and 3 polypropylene—were identified for quantitative testing. The most successful adhesive were epoxies, though at least one adhesive from each type were tested quantitatively. Even though the surface treatments did appear to improve adhesion, the adhesion performance was more a function of the adhesive used. Of the surface treatments tested, the as-molded and mechanical abrasion methods were removed from quantitative testing due to the potential to introduce contaminants in automotive paint facility. These methods were deemed too risky to test further.

The quantitative testing utilized the lap shear joint test outlined in ASTM D 3163. This test was chosen because bond performance can be easily assessed and the join configuration resembles the geometry of many practical joints. Adherends were

treated and then bonded together in an overlapping fashion with a consistent bond thickness. Next, the lap joint specimens were tested in tension to determine the peak load which allowed for bond strength to be calculated. It must be noted that this strength value can be used only for comparative purposes with other samples tested in the same manner and is thus called comparative bond strength.

The methods used in this investigation were not commonplace, particularly the use of the spot adhesion test. Previous research was performed with only a few parameters, but the spot adhesion test allowed for many different parameters to be tested and analyzed quickly. This test by itself would not carry much merit, but following it with lap shear testing was effective. The combinations that had the highest spot adhesion scores also had the highest comparative bond strengths indicating that the use of the spot adhesion test to identify the best combinations was effective.

The quantitative testing results also identified that the comparative bond strength and consistency of the nylon thermoplastic was better than that of the polypropylene thermoplastic. Of the 10 parameter groups tested, the acid washed nylon with Lord 320/322 epoxy adhesive had the highest strength. In addition, the second highest strength parameter group also was acid washed nylon indicating that perhaps the other surface treatments did not enhance bonding. It must be noted that all adherends were put through the acid wash protocol prior to any other surface treatment in the quantitative round of testing. Thus, acid washing was performed prior to the other surface treatments and was more effective by itself than with the other treatments.

Of the different adhesives investigated, four of top five comparative bond strengths were obtained using Lord 320/322 epoxy. The only variation was the surface treatment method resulting in up to a 15% decrease in comparative bond strength. Thus, while results varied with the surface treatment, both test methods indicated nylon thermoplastic can be effectively bonded utilizing Lord 320/322 epoxy and potentially other epoxies. Further testing of the nylon thermoplastic treated with each of the surface treatments bonded with Lord 320/322 epoxy to determine specific strength values is recommended.

Regarding the polypropylene thermoplastic parameter groups, the comparative bond strengths were significantly lower, even though scores from the qualitative test were similar. Several problems were identified and further testing or dismissal is recommended. However, even the parameter groups with the lowest comparative bond strength were approximately an order of magnitude stronger in shear than typical core materials. Thus, sandwich materials, when placed in shear, would likely fail at in the core prior to bond failure. This warrants further testing to establish specific shear strength properties, given the shortcomings of the lap shear test noted.

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