The Effect of Surface Treatment on the Degradation of Composite Adhesives

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LIST OF ACRONYMS

DCB   Double cantilever beam
FEP   Fluorinated ethylene propylene
TWLS Thick wide area lap shear
CILS   Compression interlaminar shear
IPS   In-plane shear
SRB   Super Release Blue
GB   Grit blast

EXECUTIVE SUMMARY

To ensure the longevity of the commercial fleet, the long term durability of primary aircraft structure must be understood. The degradation of metals and their attachments (mechanical and adhesive) has been rigorously studied over the years. The introduction of composite materials in aerospace applications has presented challenges as methodologies that have successfully been used for metals do not always produce reliable results with new materials. This project considered the effect of surface treatments on composite adherends and accelerated test methods that may be used to compare their long term degradation.

BMS 8-276 form 3 laminates were prepared for bonding using polyester (Precision Fabrics 60001) nylon (Precision Fabrics 52006) and siloxane coated polyester (Super Release Blue or SRB) peel ply. The effect of secondary abrasion was considered by sanding (220 grit) and grit blasting (80 and 220 grit). All coupons were bonded with AF555 (3M) at 350°F that was formulated to be resistant to moisture during bonding.

Using thick adherend wide area lap shear coupons, the AF555 adhesive was shown to be resistant to prebond moisture content. The composite adherends, however, tended to fail by interlaminar shear as the moisture content increased. This occurred for both the low cost and classic material forms.

Of the surfaces prepared from the three peel plies, polyester provided superior shear strength and fracture toughness with cohesive and interlaminar failure modes. Secondary abrasive operations did little to improve adhesion beyond the polyester peel ply, and in some cases lowered the bond strength. Sanded surfaces had slightly higher strain energy release rates than peel ply, while grit blasted surfaces had significantly lower strain energy release rates. The grit blasting operation caused surface damage which may have contributed to the reduced strength.

Combining stress, temperature and moisture was shown to accelerate degradation beyond the effect of these components individually. Temperature accelerated moisture diffusion. The residual shear strength was shown to decrease with creep stress. Crack growth in double cantilever beam specimens was also accelerated using a fluctuating load while immersed in water.

1. INTRODUCTION

The environmental degradation of a material involves a relatively low rate chemical reaction. The reaction rate is usually dependent on temperature, solvent concentration and material stress. In some cases, the simultaneous application of these parameters can increase the reaction rate beyond the sum of their separate effects. The ability of these parameters to accelerate degradation is limited, however. Increasing the temperature or solvent concentration to extreme levels, for instance, can initiate reactions that would not occur even at long durations under normal service exposure conditions. Stress has a similar limitation, high levels of which can induce failure without having an appreciable effect on the reaction rate.

The application of an oscillating load to a material immersed in a hostile environment represents another method of accelerating degradation. The oscillating load can induce distributed damage that can increase the surface area and diffusion rate for the solvent. The distributed damage will also produce localized regions of high stress to further accelerate the degradative process.

A difficulty in combining load, temperature and environment involves the practical problem of supplying equipment in sufficient quantity to perform a statistically significant test within an accelerated time frame. The compact pneumatic creep frames developed for the Environmental Exposure Facility at Washington State University can address this problem. Their operation is intrinsically in load control. While their frequency response is relatively low, the exposure duration needed for environmental degradation allows for the accumulation of a large number of cycles. (Potentially over 3 million in 1000 hours or 42 days).

Of the numerous fluids that may have potential of long term exposure to primary structure in a commercial aircraft, the hot/wet environment has been shown to be the most aggressive. Hot/wet environments are often achieved in the laboratory using humidity controlled ovens. The number and type of coupons proposed for the current work made this type of environmental chamber impractical. Instead, a hot/wet environment of 140F was achieved by immersing coupons in a heated water bath.

2. BACKGROUND

2.1 Failure Modes

An adhesively bonded composite joint typically fails in one of three modes as shown in figure 1. Good adhesion is typically associated with adherend or cohesive failure. The strength of these bonds are a function of the adherend and adhesive strength, respectively. Adhesion failure is due to poor bonding. The strength of the bond is a function of the chemical compatibility between the adherend and adhesive, processing parameters, and impurities. Surface preparation can have a significant impact on the bond strength and is a primary aim of this work.
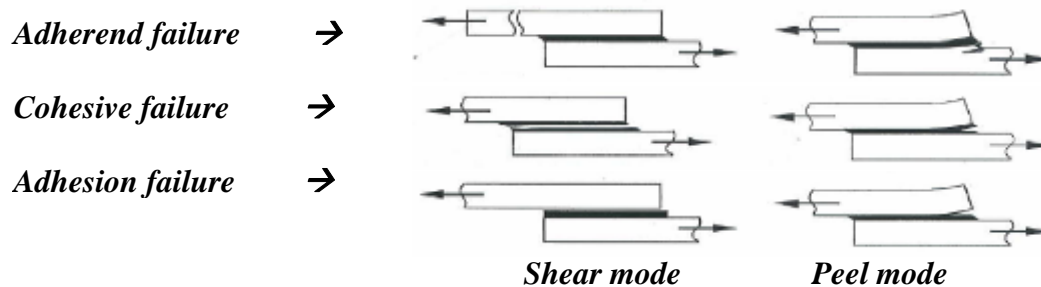

Adherend failure →

Cohesive failure →

Adhesion failure →

Shear mode   *Peel mode*

Figure 1. Failure modes of an adhesively bonded composite joint [1].

2.2 Diffusion

The kinetics of fluid sorption in polymers has been studied for some time, beginning with Fick (1855). Polymers tend to absorb moisture and gain weight in wet environments and desorb moisture and loose weight in dry environments. The magnitude and rate of diffusion will depend on the polymer, its stress state, the solvent, its concentration, and temperature. A one-dimensional Fickian curve is represented by the line LF in figure 2, where a normalized weight change is plotted as a function of the square root of time. Non-Fickian diffusion has also been observed. In some cases the response is elastic (curves A and B) while in other cases the response is associated with degradation (curves C and D). The "Pseudo Fickian" response of curve A corresponds to continuous gradual increase in weight, never attaining equilibrium. Curve B represents a "two stage diffusion" behavior which can be due to a phase change in the polymer. Curve C is usually accompanied by large deformation, damage growth, material break down, and/or mechanical failure. Curve D indicates leaching of material into the solvent with irreversible chemical or physical breakdown of a material.
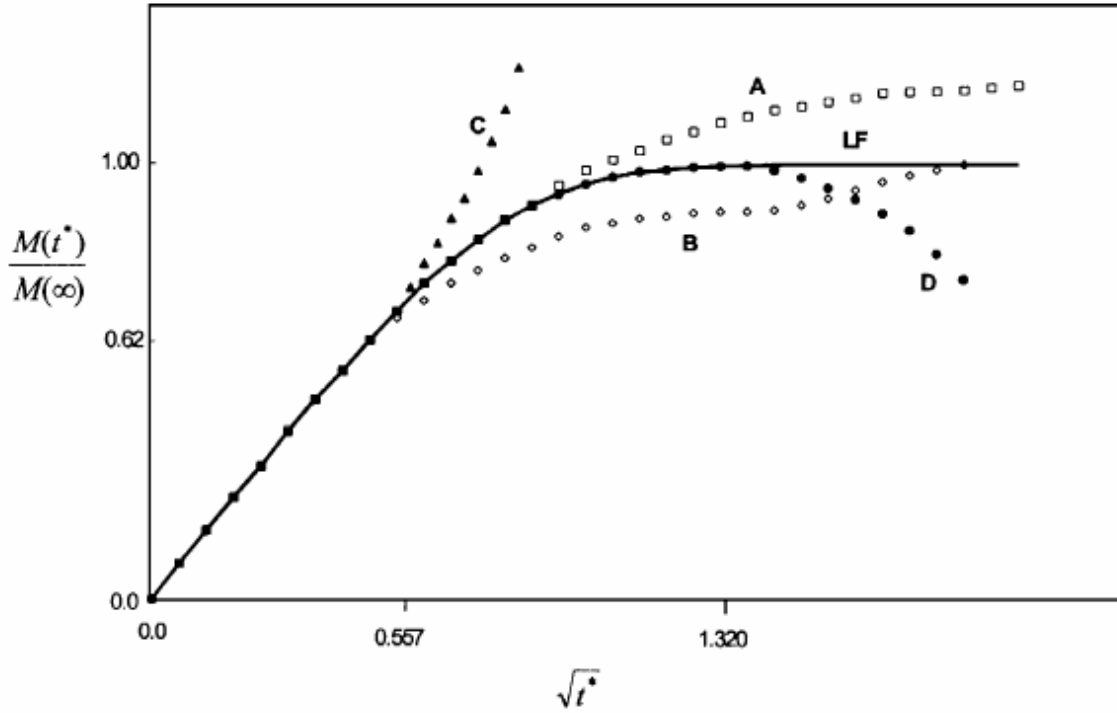
Figure 2. Normalized weight change representing Fickian and non-Fickian polymeric diffusion [2].

Observing the trends depicted in figure 2 are challenging due to the long time scales and large thickness dependence associated with diffusion. In one study, for instance, weight gain observations of graphite/epoxy and glass/epoxy composites followed a benign curve B for three years and beyond that the data shifted towards curves C and D [2].

Moisture tends to lower the glass transition temperature (T_g) of polymers and the strength of the fiber/matrix interface in composites. Glass and carbon fibers do not absorb moisture, although they can degrade in aggressive environments. For composites exposed to hot-wet conditions the most significant loss occurs in the compressive strength [3]. The effect of moisture at the fiber/matrix interface is two-fold. First, the moisture can directly reduce the chemical bonding strength at the interface. Second, the matrix swelling that accompanies moisture absorption tends to minimize beneficial residual cure stresses [4]. The interfacial shear strength is due to mechanical as well as chemical interaction at the interface, the relaxation of residual compressive stresses at the interface reduces the interfacial shear strength [5]. Generally the tensile strength of unidirectional composites is unaffected by moisture absorption. Reductions in the compressive strength of unidirectional composites range from 10%-50% [5].

The foregoing has considered the effects of diffusion on cured materials. Moisture in adherends prior to bonding can interfere with surface wetting, chemical reaction during cure, and induce excessive voids [6]. These adverse effects can be readily mitigated through appropriate drying of the constituents. Thorough drying can require days, however, and rarely occurs in practice. It is helpful, therefore, to understand the effect of pre-bond moisture on bond integrity and interrogate options that reduce its adverse effects.

2.3 Combined Effects

While numerous studies have considered the effects of mechanical stress, temperature or environment on polymers individually, their combined contribution has received less attention. The work that has been done appears to show an effect. Diffusion alone does little to the tensile strength, for instance, while moisture coupled with load and temperature substantially lowered the tensile strength of an e-glass/vinyl-ester composite [7].

Since diffusion and swelling precede chemical reaction and degradation, the effects of moisture can change with exposure duration. At short durations (less than 1000 hours) the tensile strength of an e-glass/epoxy system under immersed creep increased [8]. At long durations (more than 3000 hours) the tensile strength decreased. The tensile strength also decreased at short durations if heat was applied (65C). In this case the strength reduction was due to a degrading fiber-matrix interface that accelerated with stress and temperature.

In comparison to the e-glass systems, the tensile strength of carbon fiber reinforced polymers is less sensitive to immersed creep. This is apparently due to a more robust fiber-matrix interface. Matrix dominated loading, involving transverse and shear stresses, with moisture and temperature did cause a reduction of their respective strengths [9].

A classic example of the significance of combined stress and environment has been observed with Nylon fibers in NO_x [10]. Creep stress alone has a minimal effect on the tensile strength of fiber bundles. In a NO_x environment, however, stress was observed to accelerate degradation substantially. The effect of combined environments was persistent with bare fibers and fiber bundles embedded in a polymer matrix.

Aloha Flight 243 is another example of the significance of combined environments on adhesion [11]. While surface preparation and joint design were significant factors in the failure, the disbond leading to failure occurred under a combined environment of moisture and load.

2.4 Bond Durability

Adhesive bonds are often characterized by their lap shear strength, peel resistance, or residual strength after controlled environmental exposure. Results of this work have shown increased degradation when load and environment are combined [12]. Unfortunately the cohesive laboratory failure modes often don't match adhesive service failure modes, making the relevance of this work to service exposure unclear.

A test method was developed to provide an improved comparison of bonded aluminum joints (ASTM D3762). The method has been termed "wedge crack test" and involves forcing a wedge into a bonded joint with a pre-crack [13]. Crack growth often occurs at the primer surface without plastic deformation of the adherends in less than 24 hours. The failure modes from this coupon also tend to agree with service exposure. The method has been particularly helpful in accelerating crack propagation of aluminum adherends from oxidizing primer surfaces in humid environments.

The durability of adhesively bonded composite joints has also been considered [14, 15]. Surface preparation and contamination were observed to play an important roll in bond integrity. Surface quality was strongly influenced by the peel-ply used in processing. In particular, peel-ply containing silicone agents significantly reduced the strain energy release rates (G_{IC}). Grit blasting tended to increase G_{IC}, but it did not change the adhesive failure mode of surfaces containing silicone.

The foregoing has reviewed some of the progress that has been made in evaluating metallic and composite adhesively bonded joints. While the results of this work have contributed to our understanding of bonded joints, it illustrates the need for additional work. The effect of combining service load and environment, in particular, is not well understood and has received relatively little attention. A method of measuring environmental effects on a reduced time scale is also needed.

Manufactures of commercial composite aircraft are using peel ply and grit blasting surface preparation techniques to bond primary structure. The durability of the adhesive bonds are affected by the adherend surface quality, pre-bond and post-bond moisture content, and service loads. The following will consider how surface preparation affects the integrity of adhesive bonds and investigate test methods that may be used to accelerate degradation.

3. RESULTS

3.1 Materials and Processes

The carbon/epoxy adherends used for adhesive bonding in this study were made from Toray T800/3900-2 (BMS 8-276 Form 1) or T800/3900-2B (BMS 8-276 Form 3). The materials were referred to as classic (Form 1) and low cost (Form 3). Prepreg laminates were vacuum bagged with mold release on the tool side and a peel ply on the top surface. The panels were cured using a recipe provided by Boeing [16]. Vacuum was applied (22 in Hg) and autoclave pressure was raised to 85 psi. The temperature was then raised at 3 F (1.7 °C) per minute to 355 °F (180°C) for 120 to 180 minutes. After the soak, the part was cooled at 5 °F (3 °C) per minute to 140 °F (60 °C) after which the pressure was released and the part was removed from the autoclave.

The composite panels were cured using a polyester (Precision Fabrics 60001), nylon (Precision Fabrics 52006) or siloxane coated polyester (Super Release Blue or SRB) peel ply. The texture of the three fabrics was fine, medium and coarse, respectively.

The composite panels were bonded using 3M AF555 (BMS 5-160 Grade 5). It was provided in a 0.01 inch thick, 0.05 lb/ft^2 areal weight film adhesive form. The peel ply was removed from the part within 20 minutes of bonding. The adhesive was cured at 350F following the prepreg recipe.

Double cantilever beam (DCB) specimens were made from bonded adherends comprised of 10 plies of unidirectional prepreg. A FEP (Fluorinated Ethylene Propylene) separator film was used as a crack initiator. The DCB coupons were 0.16 inches thick, 0.50 inches wide, 13 inches long, and had an initial crack length of 2 inches, as shown in figure 3.
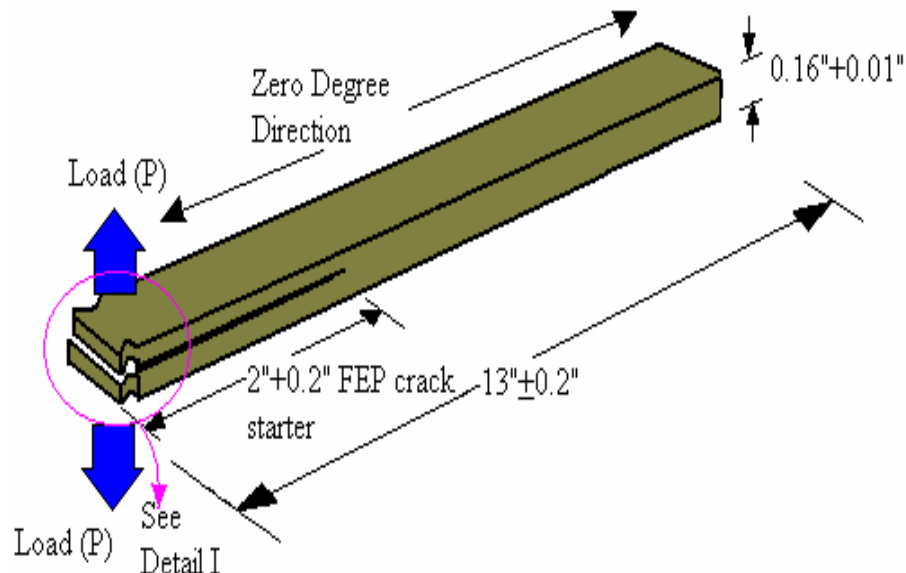

Figure 3. Schematic of double cantilever beam specimen.

Wedge crack specimens were made from bonded adherends comprised of 10 plies of unidirectional prepreg. A FEP (Fluorinated Ethylene Propylene) separator film was used as a crack initiator. The coupons were 0.16 inches thick, 6 inches long, 1 inch wide, and had an initial crack length of 2 inches. The wedge was made of aluminum, was 0.125 inches thick and 1 inch long. The wedge was inserted in the pre-crack flush to the end of the coupon, as shown in figure 4.
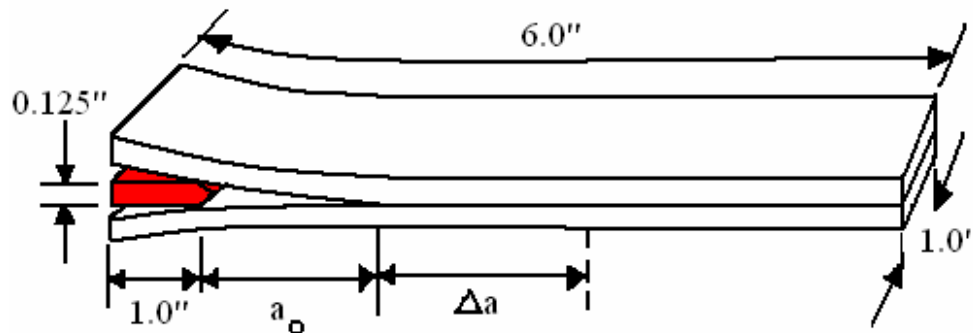
Figure 4. Schematic of wedge crack specimen.

Thick wide area lap shear (TWLS) coupons were made from bonded adherends comprised of 20 unidirectional plies of prepreg. These were formed by bonding 7 inch long by 1 inch wide adherends. The shear region was formed by machining a 0.218 inch wide slot through the adherend into the adhesive on either side of the specimen. The slot ended 3.25 inches from either end of the specimen, leaving a 0.50 inch long gage section, as shown in figure 5.
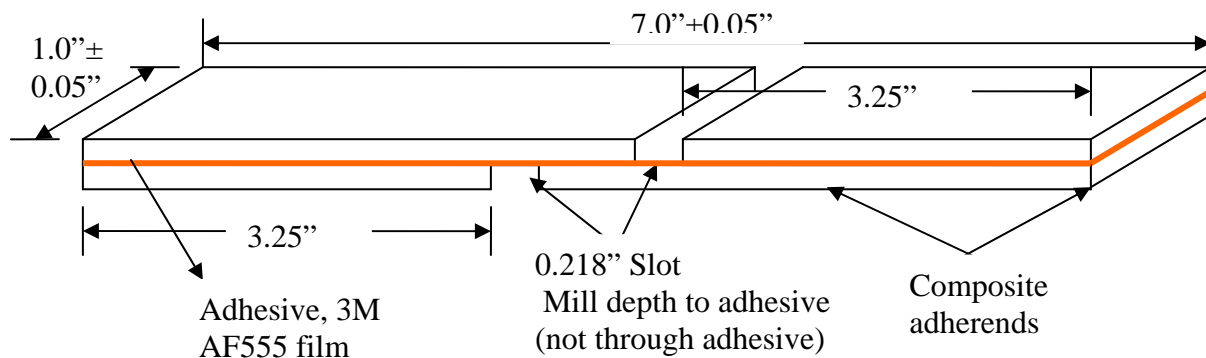
Figure 5. Schematic of thick wide area lap shear specimen.

Compression interlaminar shear (CILS) specimens were made from 24 plies of unidirectional prepreg (no adhesive). These coupons measured 3.18 inches long and 0.50 inches wide. The shear region was formed by machining a 0.10 inch wide slot 0.092 inches deep, or half way through the thickness of the specimen. The slot ended 1.465 inches from either end of the specimen, leaving a 0.25 inch long gage section, as shown in Figure 6.
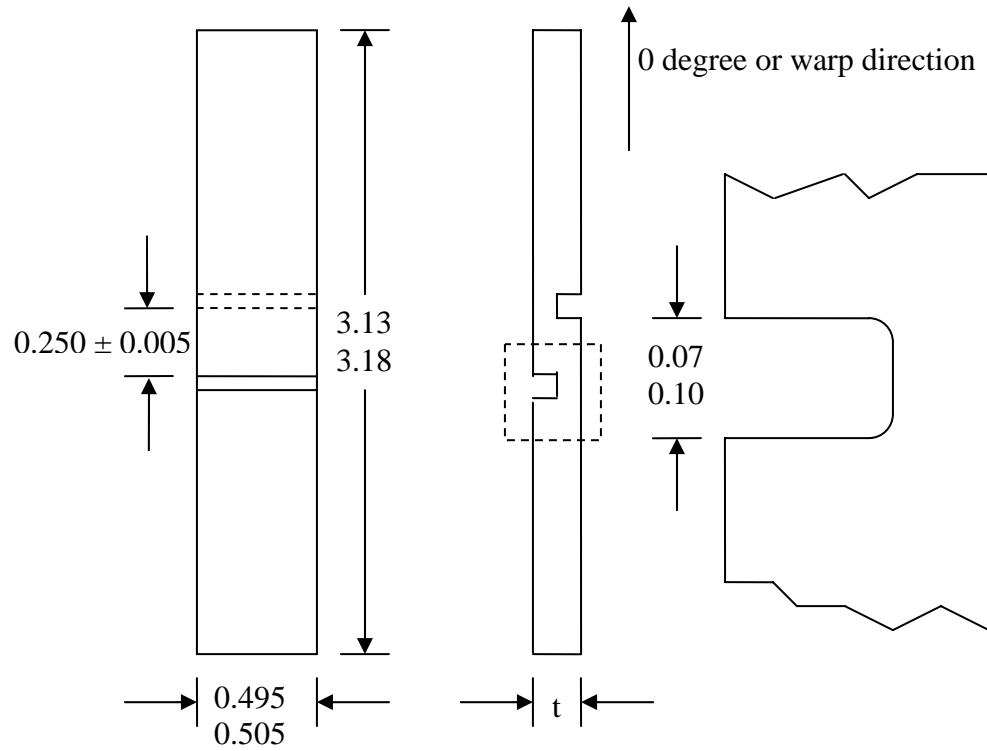
Figure 6. Schematic of compression interlaminar shear specimen.

In-plane shear (IPS) specimens were made from 4 plies of prepreg with a layup of [±45]$_s$. These coupons were 9 inches long, 0.50 inches wide, with 2 inch long tapered glass/epoxy endtabs, as shown in Figure 7.
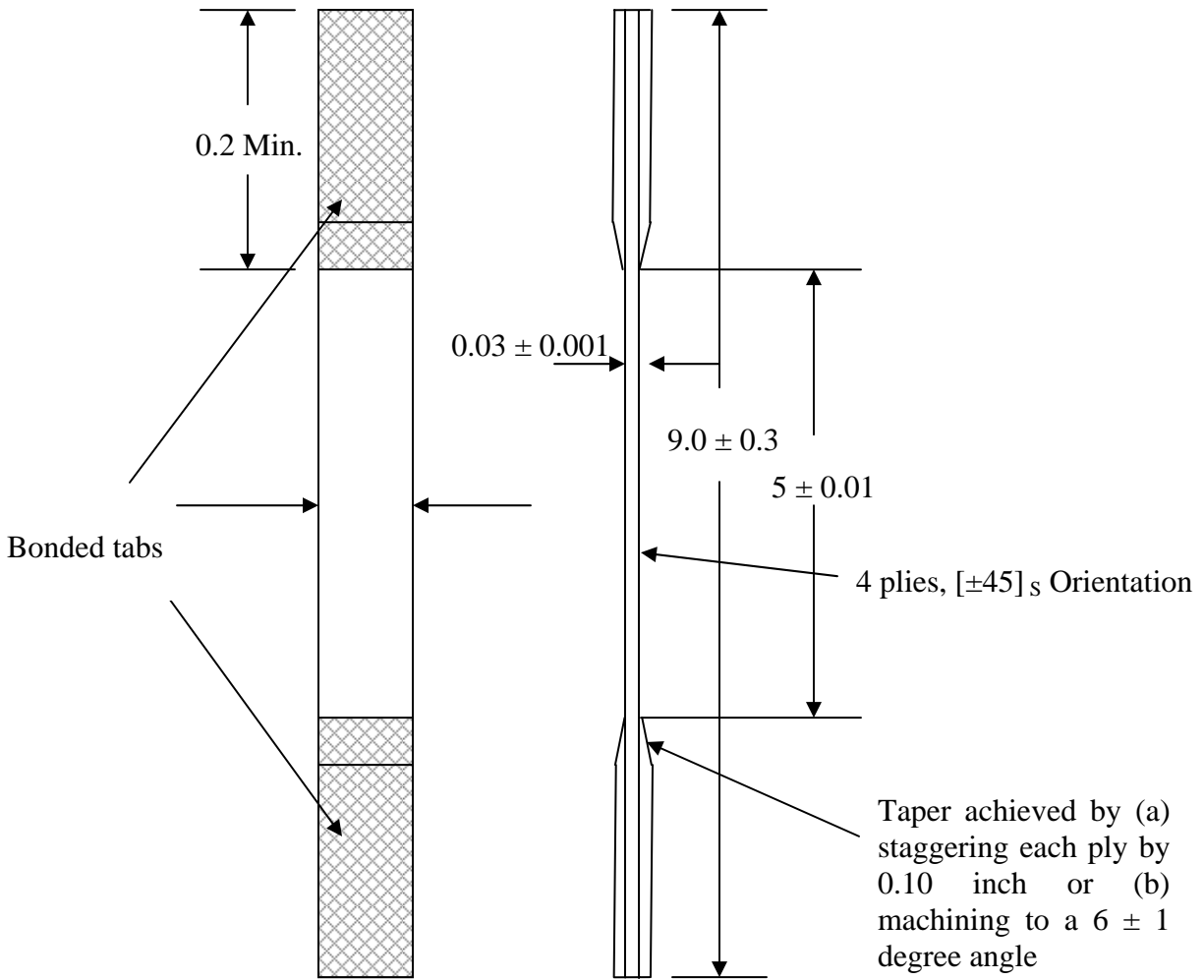
Figure 7. Schematic of in-plane shear specimen.

3.2 Effect of Moisture

Most adhesives are sensitive to the prebond moisture content [17-19]. Accordingly, adhesives and their adherends are typically dried before bonding operations can be performed. The adhesive AF555 (3M) has been formulated to be insensitive to the prebond moisture content. The aim of this portion of the work was to verify the bond quality and environmental durability in the presence of prebond moisture.

TWLS specimens were formed from the low cost form of the prepreg using a polyester peel ply and bonded with dry and wet (1% moisture) adherends. The bonded specimens were immersed in water at 140 ºF for 1000 hours. The coupons were then given a creep load of either 2, 3, or 4 ksi for an additional 1000 hours while immersed in water at 140 F. The residual shear strength of these coupons is presented in Figure 8 and appears to be relatively insensitive to the pre-bond moisture content.
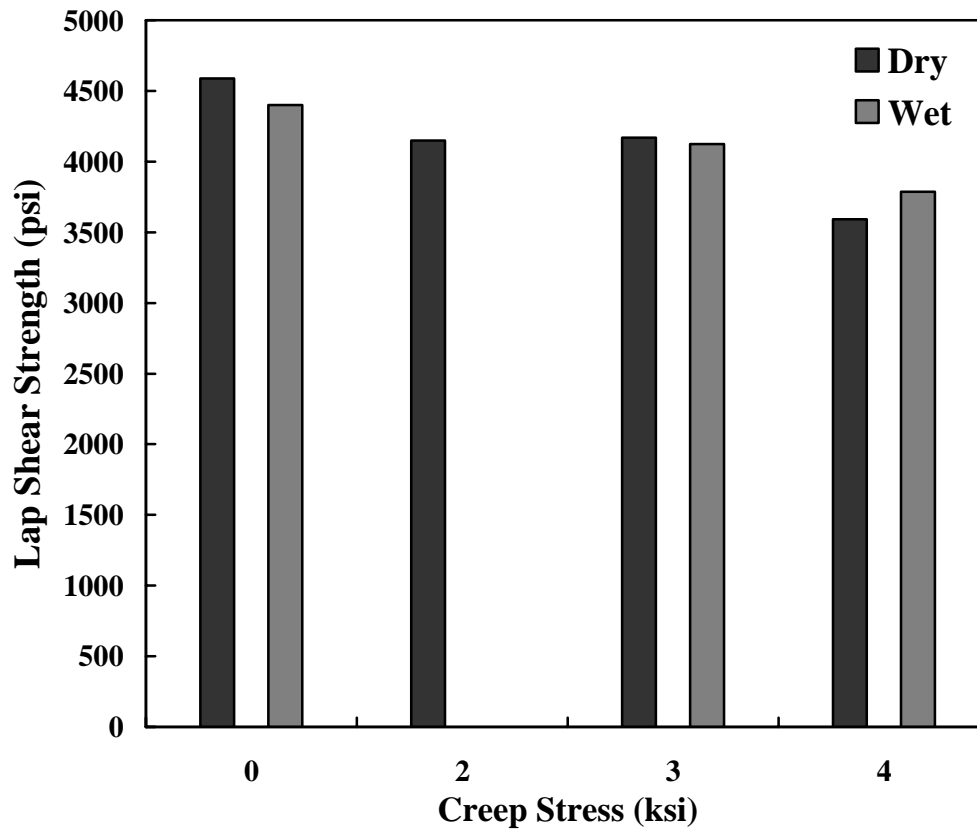
Figure 8. Residual shear strength of TWLS coupons.

Representative failure surfaces of the dry and wet coupons are presented in Figs. 9 and 10, respectively. While the surfaces appear consistent with adhesive failure, closer inspection shows evidence of adherend failure. The failure surfaces show bare fibers with no evidence of the texture of the peel ply. The prepreg used in this work uses a thin film on its surface as a toughening agent. It appears that the disbond from the fibers originated in the toughened region.
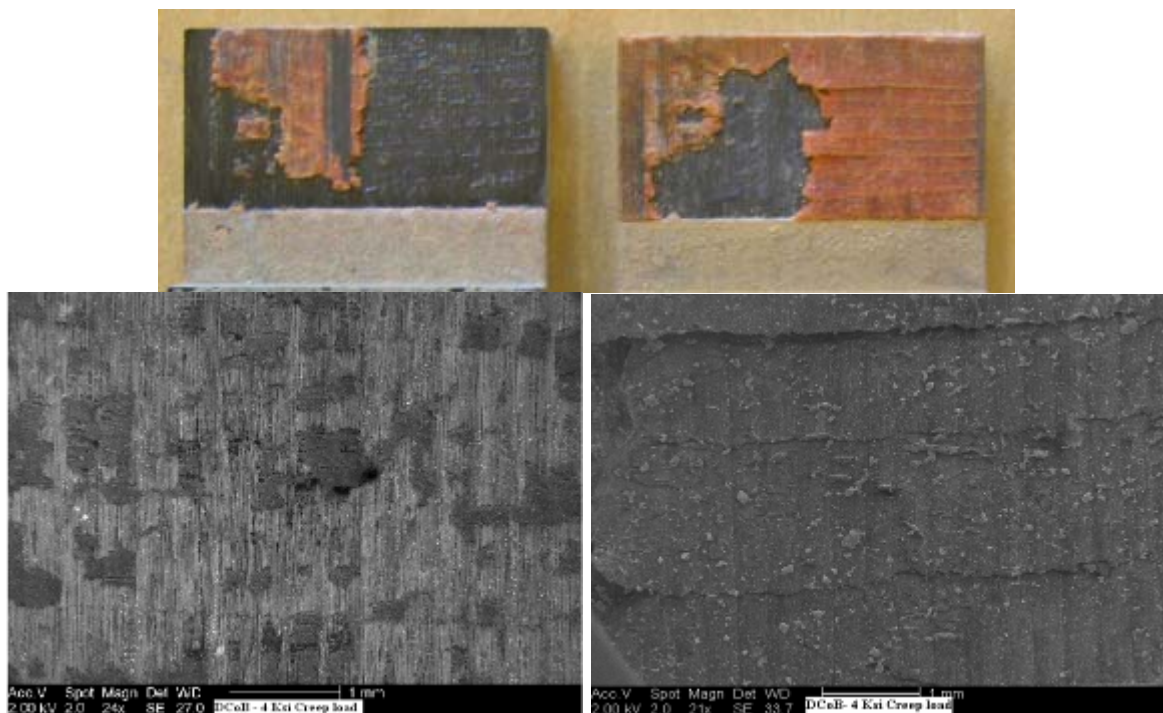
Fig 9. Fractures surfaces of a specimen bonded with dry adherends then creep loaded to 4 ksi while immersed in water at 140F.
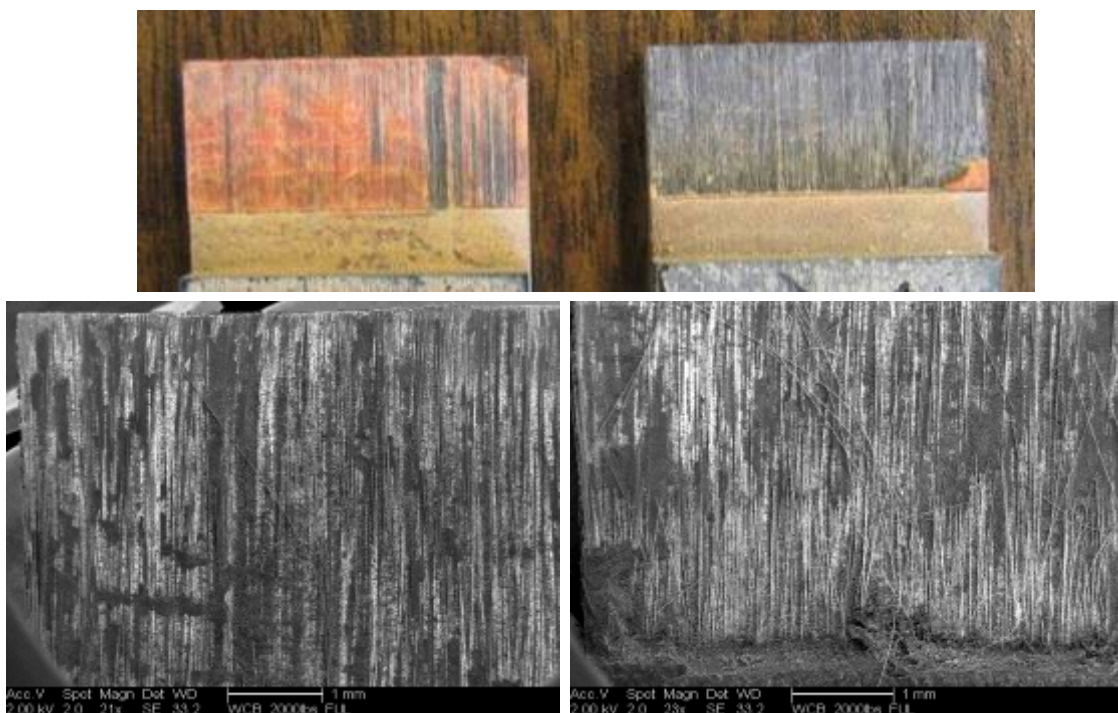

Figure 10. Fracture surfaces of a specimen bonded with wet adherends then creep loaded to 4 ksi while immersed in water at 140F.

The residual shear strength shown in Figure 8 decreased with increasing creep load. While this response was consistent with other adhesives [16, 20-23], there was, nevertheless, concern that the adherend failure mode may have been due to the low cost material formulation. The moisture study was, therefore, included the classic and low cost material forms. CILS and IPS coupons were made from the two material forms to compare their matrix moisture resistance. The coupons were immersed in water at 160F and removed at regular intervals for mechanical testing. The CILS coupons were tested at 180F, while the IPS coupons were tested at room temperature. The average CILS strength is presented in Figure 11, which decreased nearly 20% for both material forms. The average shear modulus from the IPS coupons is presented in Figure 12 as a function of moisture content. The modulus of both material forms decreased 10% at saturation. In both cases the moisture dependence of the classic and low cost material forms was nearly indistinguishable.
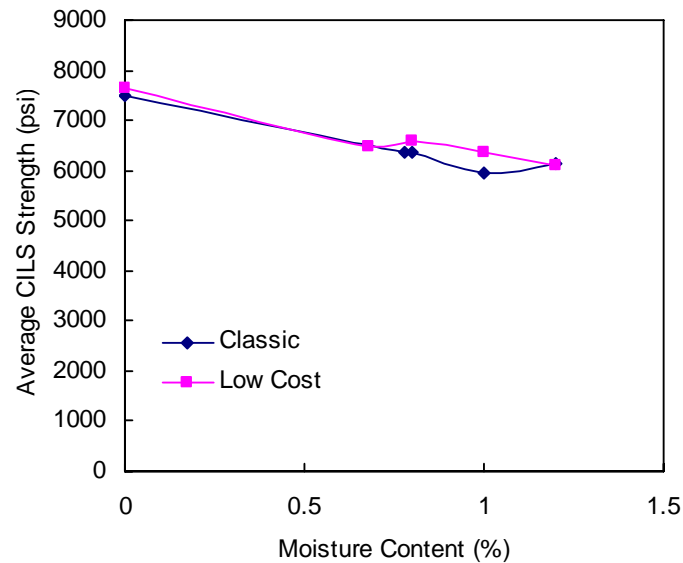
Figure 11. Average CILS strength of the classic and low cost material forms.
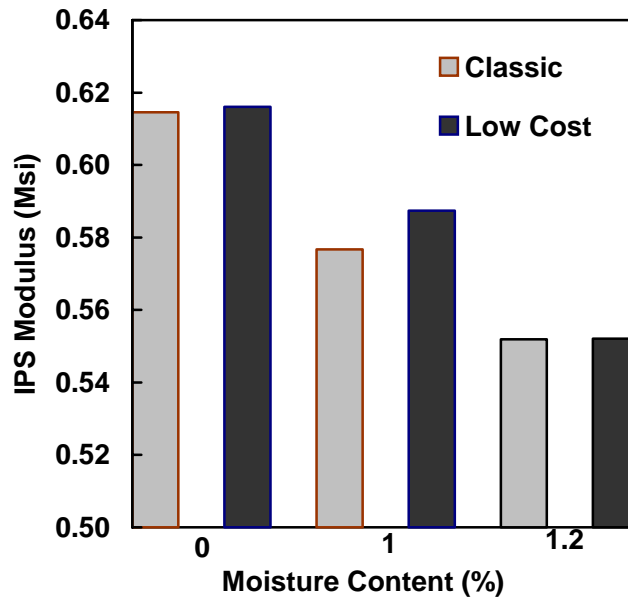
Figure 12. Modulus of IPS coupons as a function of moisture content.

3.3 Effect of Peel Ply

Peel ply is commonly used in autoclave processing of composite laminates. The surface created from peel ply removal can form an effective surface for adhesion. Agents allowing easy removal of the peel ply can affect the integrity of subsequent adhesion, however. To consider these effects, panels were made using polyester, nylon or SRB peel ply.

IPS and DCB coupons were immersed in water at 140F to achieve saturation. The weight change of traveler coupons was periodically recorded. The composite and adhesive were found to have a diffusion coefficient of 0.00106 mm^2/hr and 0.0044 mm^2/hr, respectively, and a saturation level of 1.25% and 3.0%, respectively. The diffusion coefficient and saturation level of a bonded panel was found to be 0.00138 mm^2/hr and 1.41%, respectively. A comparison of the measured weight change with Fick's law is presented in Figure 13, showing the thicker specimens required 6,000 hours to reach saturation.

After reaching saturation, a baseline IPS strength was found from five coupons for each peel ply surface, as shown in Figure 14. The effect of peel ply on the TWLS strength was relatively large, where the polyester peel ply was more than twice as strong as the SRB peel ply. Images of representative failure surfaces are presented in Figure 15. The SRB and Nylon coupons were dominated by adhesive failure, while the polyester coupons had a mixed cohesive/adherend failure. The poor adhesion found with SRB is apparently due to silicone used in this material as a release agent, while the Nylon peel ply has been observed to leave significant amounts of nitrogen and amide groups on the surface [24].
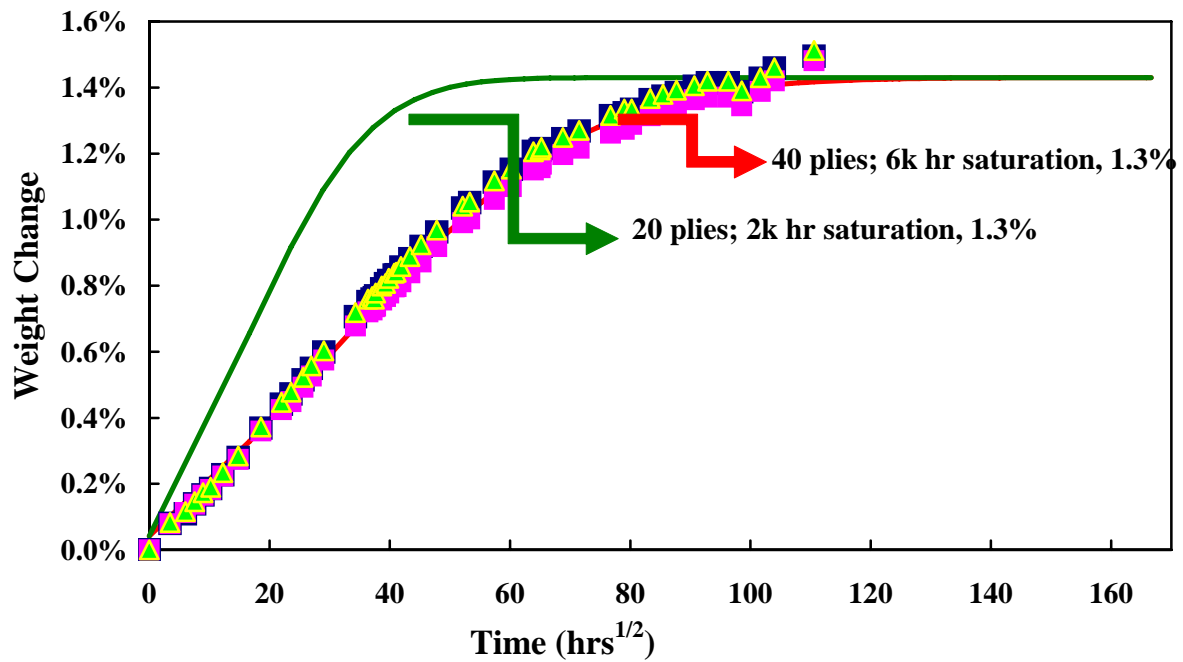
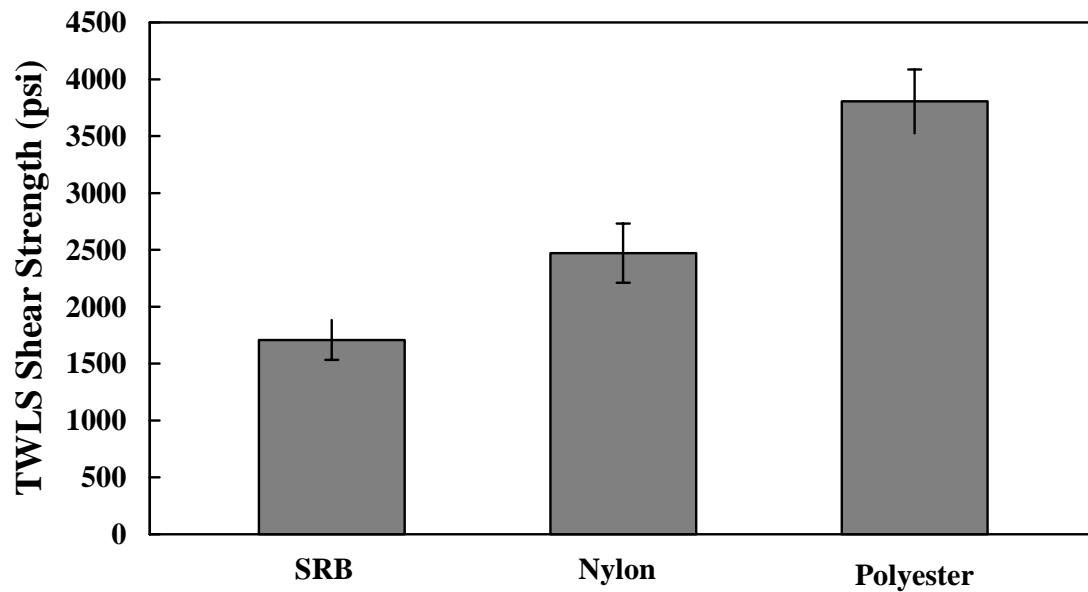Figure 13. Weight gain data of 20 and 40 ply bonded specimens.

Figure 14. Baseline shear strength of saturated TWLS coupons.

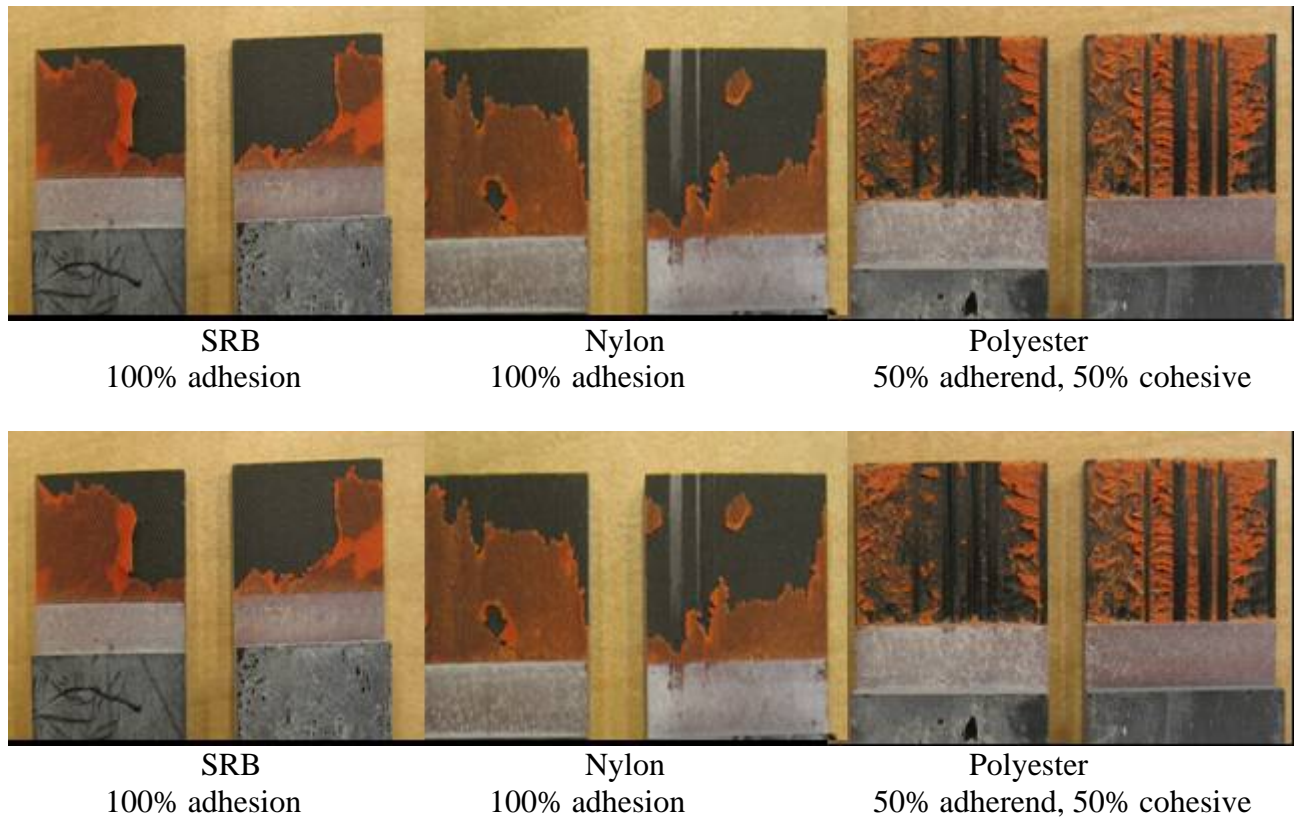|	SRB	Nylon	Polyester
	100% adhesion	100% adhesion	50% adherend, 50% cohesive

Figure 15. Representative failure surfaces of the baseline TWLS coupons.

Ten TWLS coupons from each peel ply were given a creep load of 80% of their respective baseline shear strength while immersed in water at 140F. The average creep rupture time of each peel ply is presented in Figure16. The results suggest that improved adhesion afforded by some peel ply materials also results in greater environmental durability. Representative failure surfaces of the creep rupture specimens are presented in Figure 17. The failure modes are comparable to the baseline TWLS results, while the polyester coupons had slightly more adherend failure.
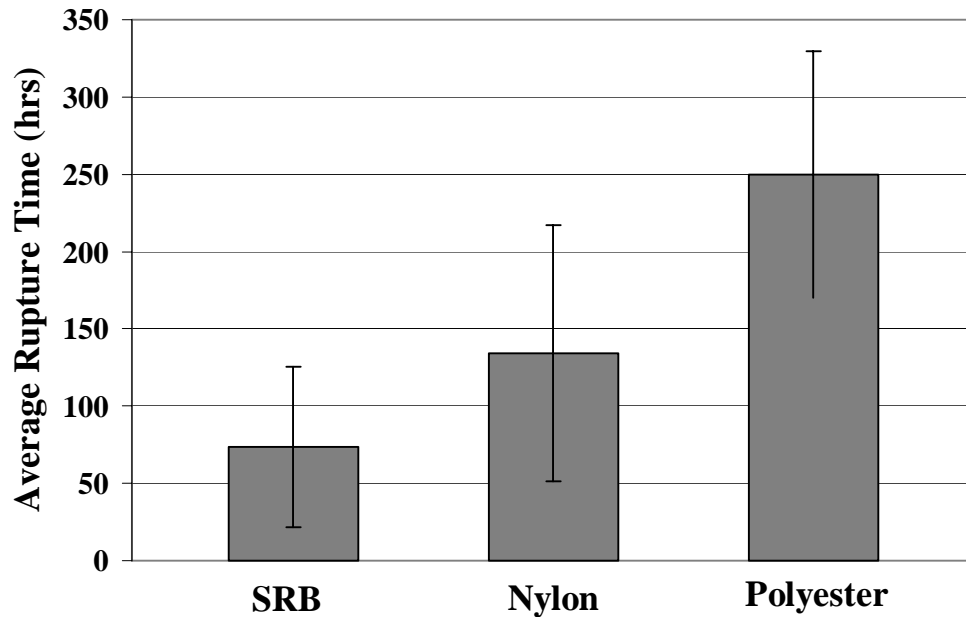
Figure 16. Average creep rupture time as a function of surface peel ply.

SRB	**Nylon**	**Polyester**
100% adhesion	100% adhesion	70% adherend, 30% cohesive
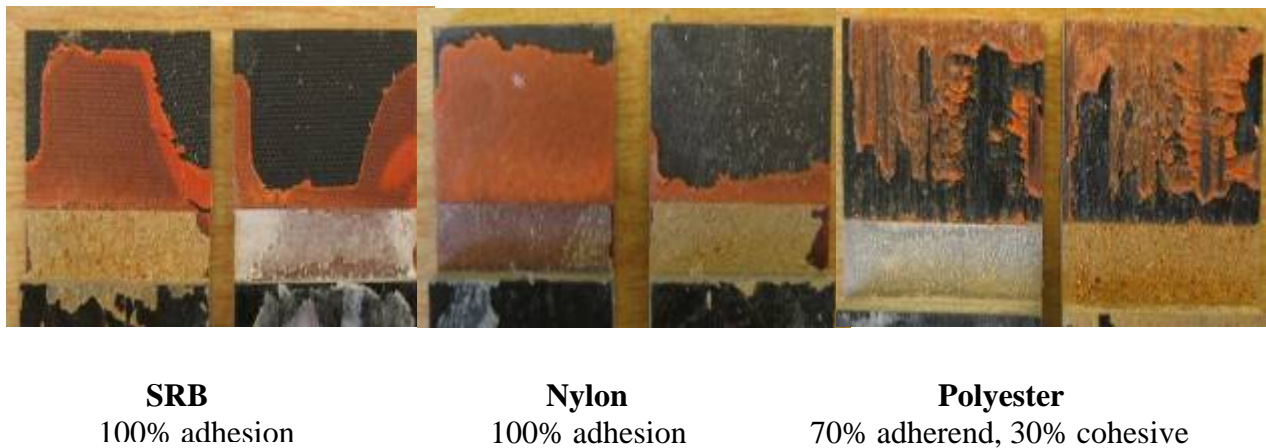
Figure 17. Representative failure surfaces of creep rupture TWLS coupons.

The critical strain energy release rate (G_{IC}) of five DCB coupons from each peel ply exposed to 140F water for 6000 hours is compared in Figure 18. Representative images of their failure surfaces are presented in Figure 19. The effect of peel ply on the strain energy release rate and the failure mode of the DCB coupons is comparable to that found for the TWLS results presented above. The effect of peel ply on the strain energy release rate was much greater than shear strength, however.

Figure 18. Critical mode I strain energy release rate of DCB coupons as a function of peel ply.
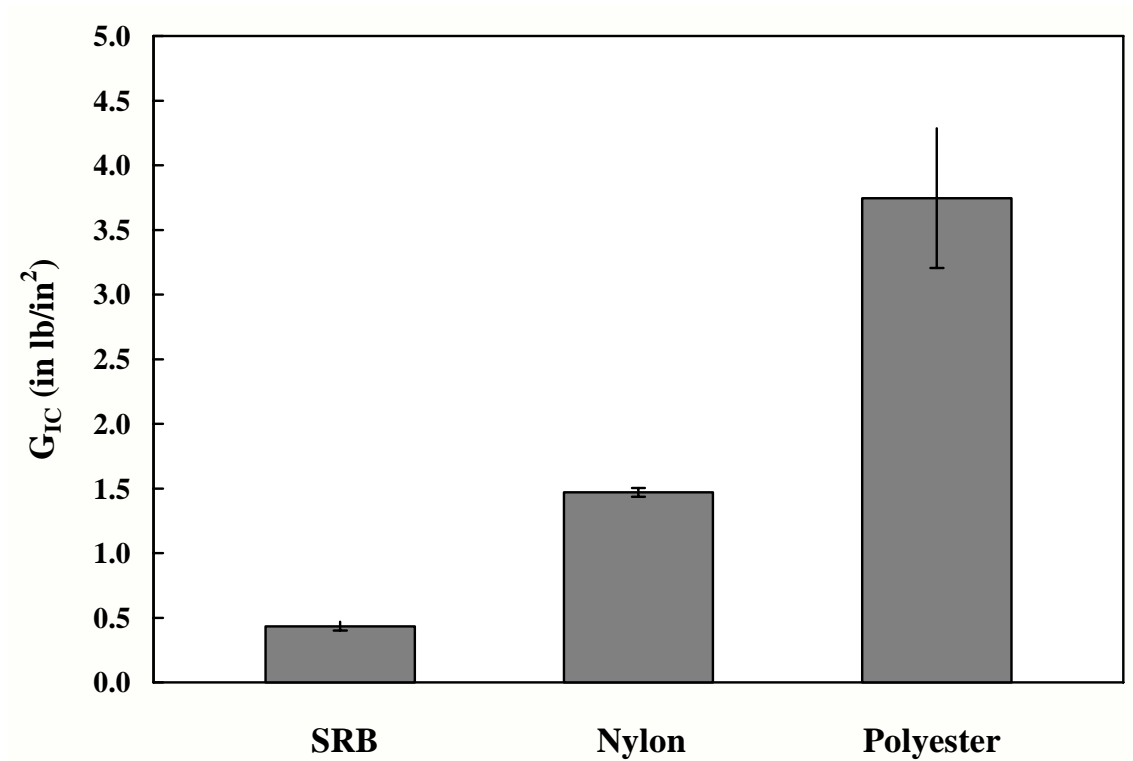

| **SRB** | **Nylon** | **Polyester** |
| 100% adhesion | 90% adhesion, 10% adherend | 100% adherend |
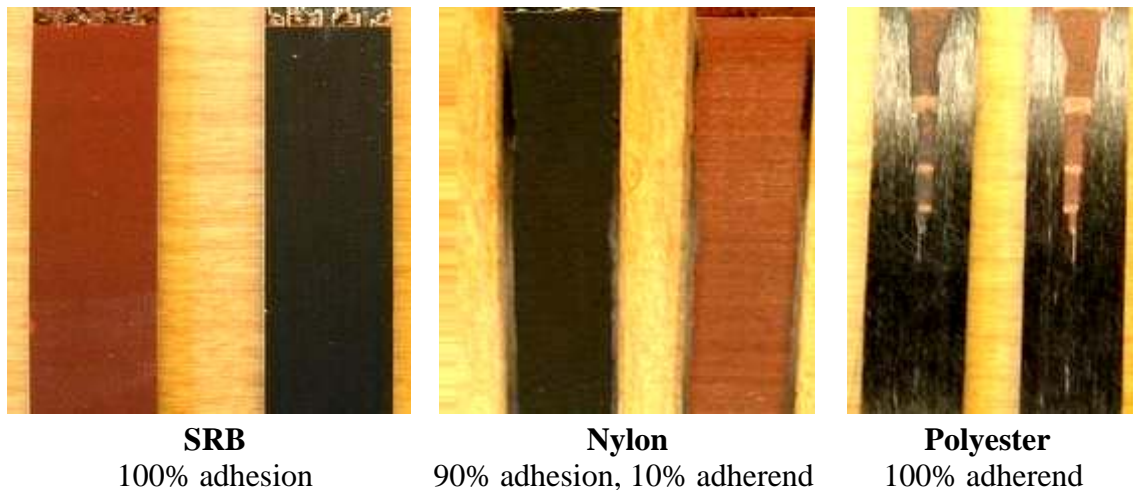
Figure 19. Failure modes of DCB coupons tested after immersed in water for 6000 hours.

The wedge crack coupon has been relatively successful in studying adhesives and surface preperations for bonded aluminum structure [12]. Its application to composite bonded structure has had mixed results, however. The following considers the effect of adherend stiffness on the crack growth of composite wedge crack specimens. The adherend bending stiffness (EI) of the standard aluminum wedge crack specimen is 1571 lb in^2. Composite wedge crack coupons were made with adherends comprising 8, 10, and 12 plies. For comparison the 8, 10, and 12 ply

adherends had a bending stiffness of 365, 696, and 1202 lb in^2, respectively. Panels were prepared using the SRB, Nylon and Polyester peel ply.

Five replicates of each peel ply/adherend combination were immersed in 140F water immediately after wedge insertion and the initial crack length had been measured. The initial crack length for each aherend/peel ply combination is presented in Figure 20. The effect of the initial crack length on the peel ply of the wedge crack specimens is similar to that found for the TWLS and DCB specimens, although the dependence is substantially lower. The effect of adherend bending stiffness is not consistent with the initial crack length. The relatively small sensitivity of the wedge crack specimen suggests adherend bending stiffness effects may be smaller than adhesion process variation.

Wedge crack growth of the composite specimens after 24 hours immersion is compared in Figure 21. The sensitivity of the coupon appears to decrease with increasing adherend stiffness, where the crack growth of the 12 ply adherends is nearly constant. While crack growth is more apparent with the lower stiffness adherends, the results are again not entirely consistent with thickness. The processing induced variation observed in the initial crack length appears to also have influenced the 24 hour crack growth. A variation of the wedge crack method involving a constant load, as apposed to a constant displacement, will be considered in the next section.
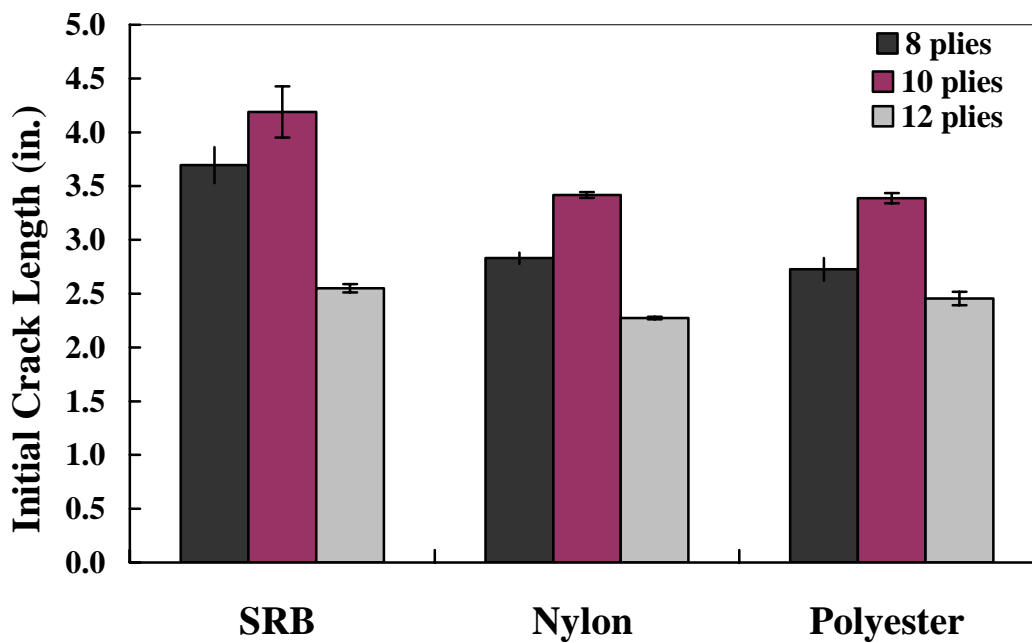

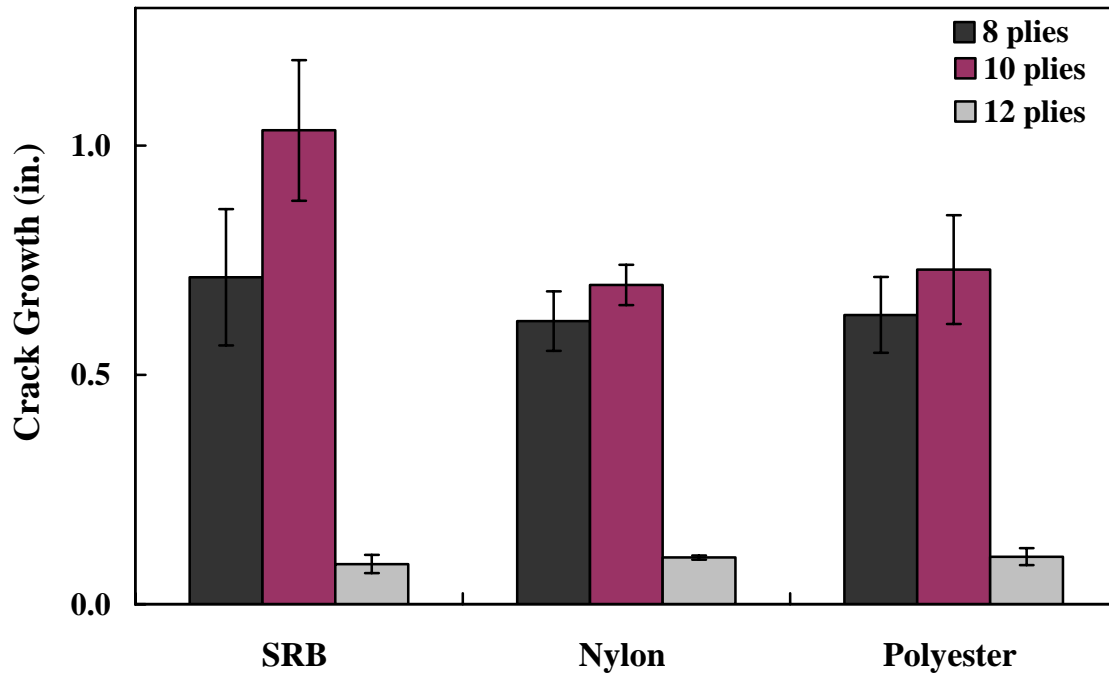Figure 20. Initial crack length of composite wedge crack specimens.

Figure 21. Crack growth of composite wedge crack coupons after immersion in 140F water for 24 hours.

3.4 Effect of Abrasive Surface Treatments

The poor adhesion observed with some peel ply materials has provided motivation to consider secondary surface treatments. The more common treatments involve sanding or grit blasting (GB). To consider the effects of secondary treatments, composite panels were either grit blasted with 80 or 220 grit garnet or sanded using 220 grit sandpaper. The panels were bonded and machined into standard DCB specimens.

Using polyester peel ply as a control, the average G_{IC} of each treatment is presented in Figure 22. The strain energy release rate of the sanded surface was slightly higher than the control, while the grit blasted surfaces were lower. An image of each surface is compared in Figure 23. The texture of the polyester peel ply is apparent on its resin rich surface. The sanding treatment appears to completely remove any evidence of the peel ply, leaving a relatively smooth surface. Both the grit blasted surfaces are relatively rough, showing signs of surface erosion. Representative images of the DCB failure surfaces are presented in Figure 24. The strain energy release rate decreases with increasing adherend failure. Adherend failure, in turn, appears to increase with surface roughness. The pitting from the abrasive techniques may have damaged the fibers and appears to have significantly increased the tendency toward adherend failure.
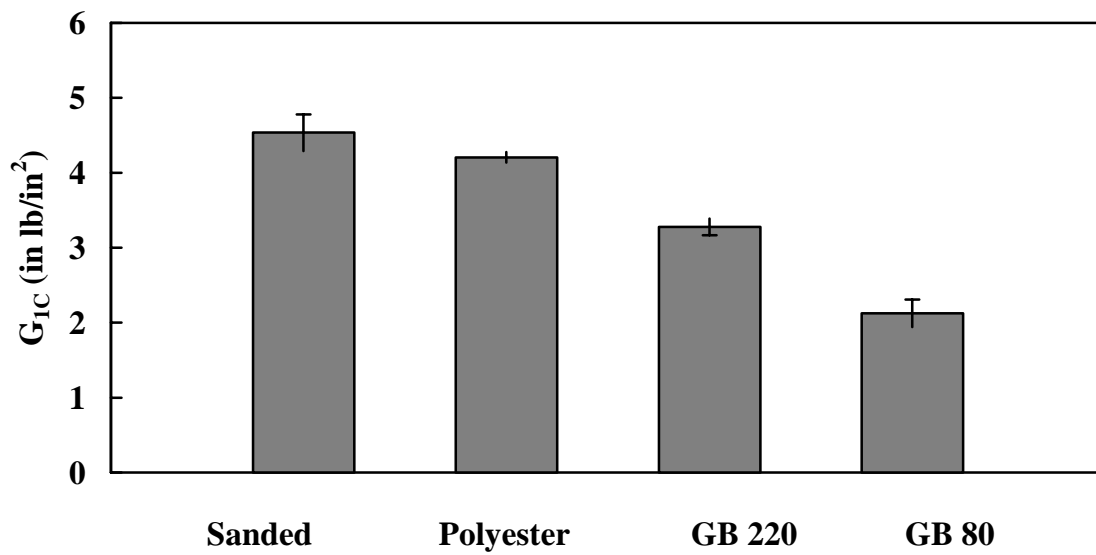
Figure 22. Critical strain energy release rate as a function of surface preparation.
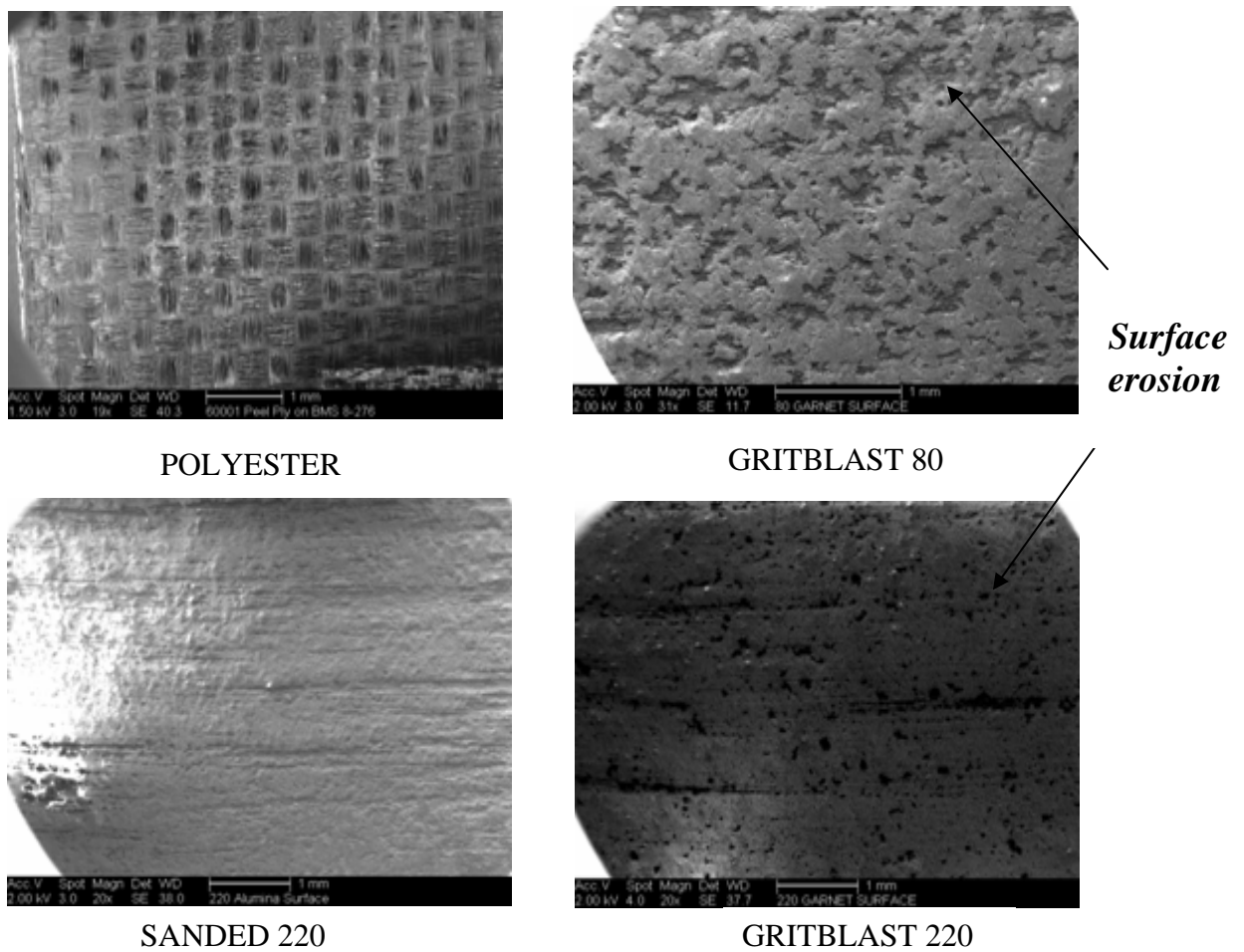

POLYESTER

GRITBLAST 80

Surface erosion

SANDED 220

GRITBLAST 220

Figure 23. SEM images of the polyester peel ply and abrasive surface preparations.

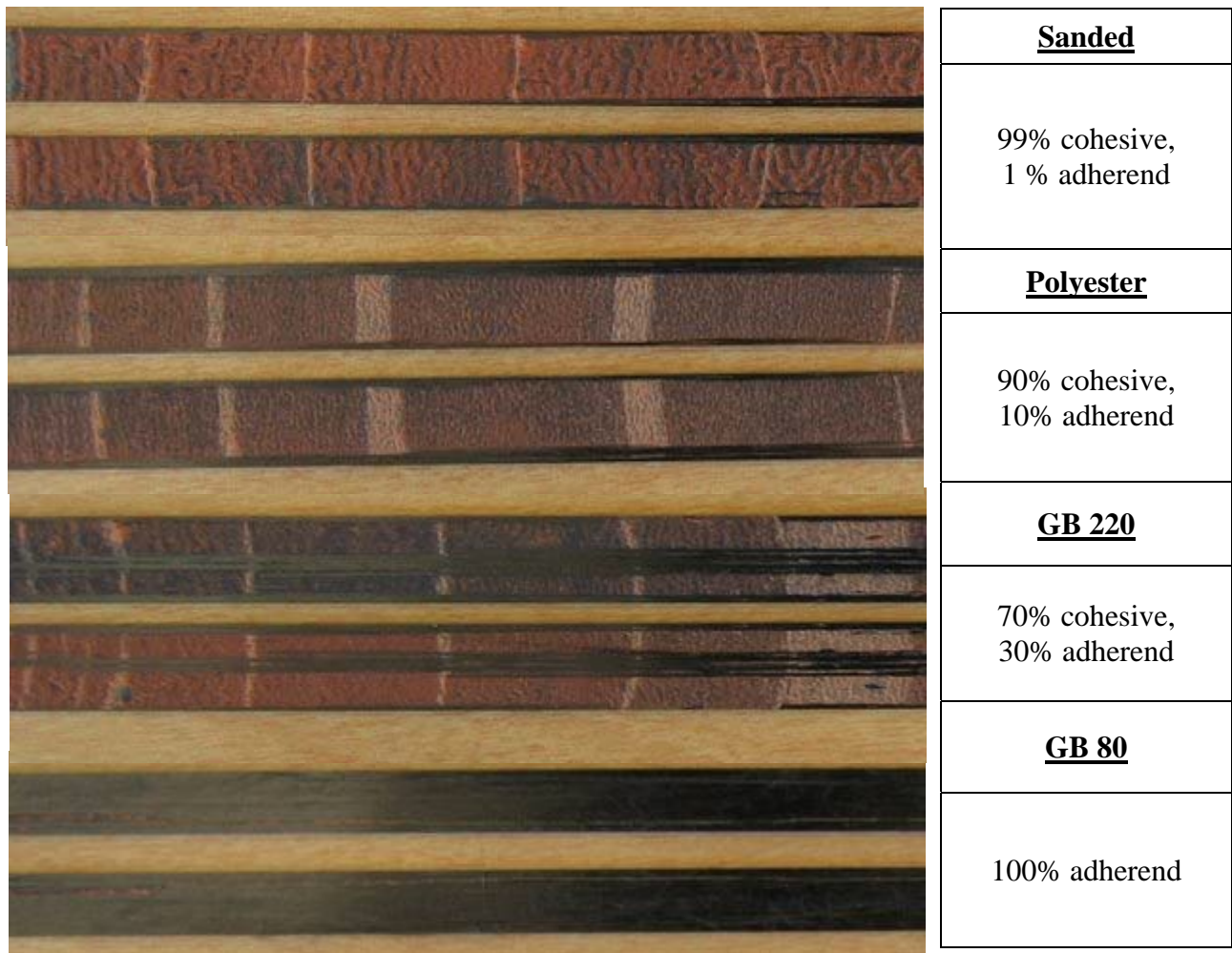|	
Sanded	
	99% cohesive, 1 % adherend
Polyester	
	90% cohesive, 10% adherend
GB 220	
	70% cohesive, 30% adherend
GB 80	
	100% adherend

Fig 24. Representative images of the failure modes of DCB specimens.

To consider if load could accelerate degradation, the DCB specimens were subjected to 90% of their respective baseline crack initiation loads. While immersed in water at 140 °F, constant and fluctuating (0.5 Hz) loads of 6.2 lbs, 8.4 lbs, 9.8 lbs and 10.3 lbs were applied on the GB 80, GB 220, polyester and sanded DCB specimens, respectively. The mean crack growth of each surface treatment is shown in Figs. 25 and 26 under constant and fluctuating load, respectively. The constant load exposure showed little change in crack length, while the fluctuating load showed noticeable crack growth.
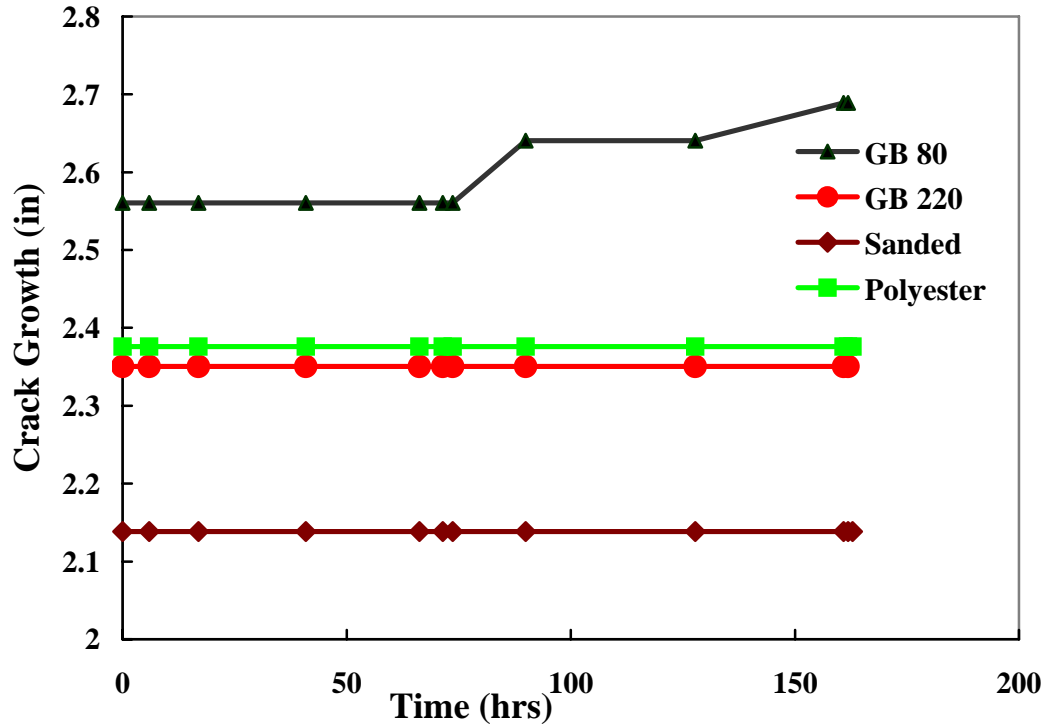
Figure 25. Mean crack growth of the DCB specimens prepared from abrasive techniques under constant loading.
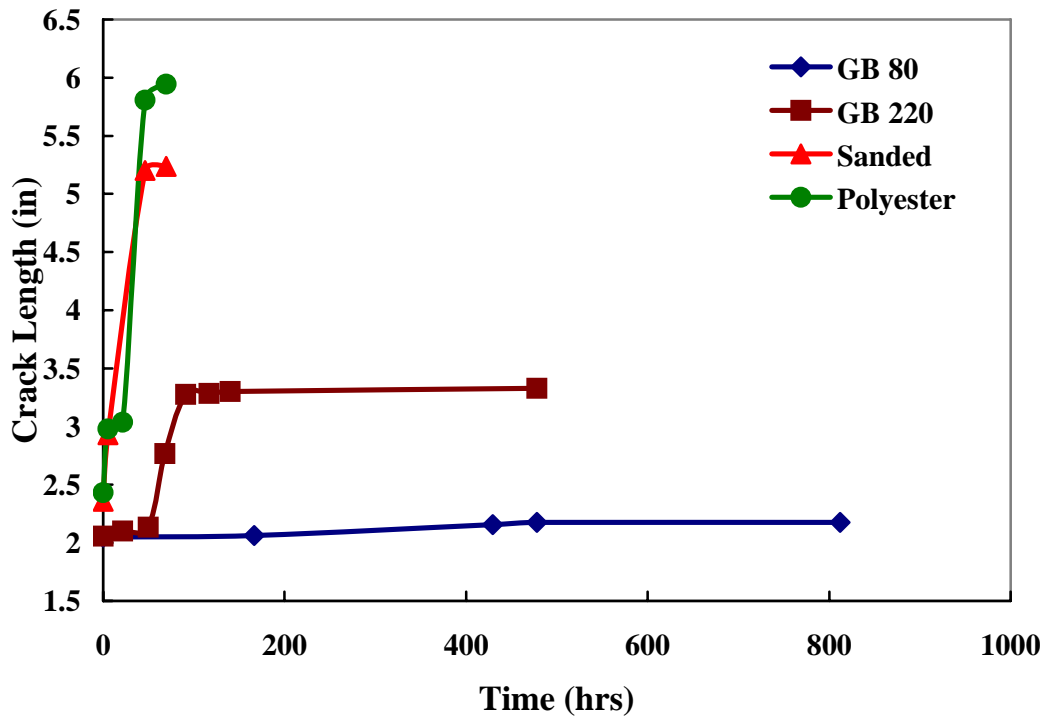

Figure 26. Mean crack growth of the DCB specimens prepared from abrasive techniques under fluctuating load.

While the grit blasted surfaces had a lower strain energy release rate, they exhibited superior crack growth resistance. This is likely due to the criterion for selecting the applied load. Failure of the grit blasted specimens, for instance, continued to be dominated by adherend failure, while the sanded and peel ply surfaces tended to be cohesive failures. Since a weak, but durable bond is of little practical importance, the tests were repeated using a fluctuating load of constant magnitude (9.5 lbs). For this case the crack growth rate of the grit blasted coupons was significantly higher than the peel ply or sanded coupons, as shown in Figure 27.

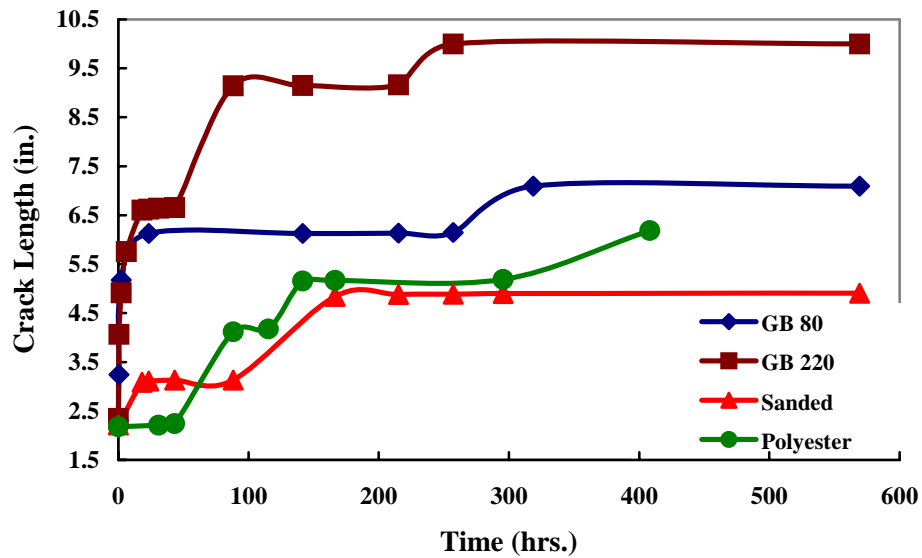Figure 27. Mean crack growth of the DCB specimens prepared from abrasive techniques under a fluctuating loading of 9.5 lbs.

Representative failure modes of coupons exposed to repeated loading are shown in figure 28. The failure modes are similar to that found previously, where increased fracture resistance was associated with cohesive failure.
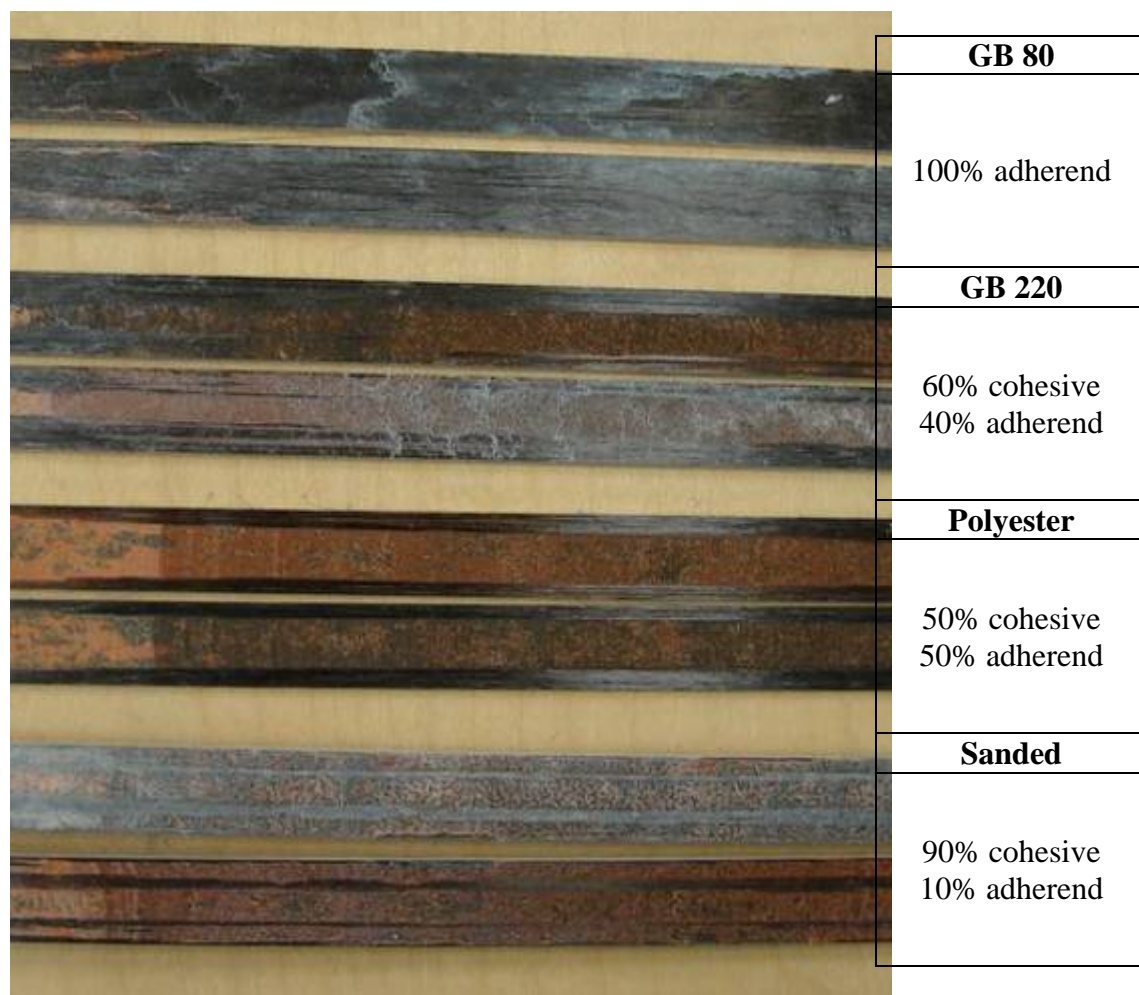
Figure 28. Failure modes of DCB specimens exposed to a fluctuating load of 9.5 lbs.

4. CONCLUSIONS

This project considered the effect of surface preperation on composite adherends and accelerated test methods that may be used to compare their long term degradation.

BMS 8-276 form 3 laminates were processed using polyester, nylon and siloxane coated polyester peel ply. The effect of secondary abrasion was considered by sanding and grit blasting. All coupons were bonded with AF555 (3M) that was formulated to be resistant to moisture during bonding.

The AF555 adhesive was shown to be resistant to prebond adherend moisture content. The composite adherends, however, tended to fail by interlaminar shear as the moisture content increased. This occurred for both the low cost and classic material forms. The tendancy toward adherend failure may have been influenced by a toughening film on the prepreg surface.

Of the surfaces prepared from the three peel plies, polyester provided superior shear strength and fracture toughness with cohesive and interlaminar failure modes. Secondary abrasive operations did little to improve adhesion beyond the polyester peel ply, and in some cases lowered the bond strength. Sanded surfaces had slightly higher strain energy release rates than peel ply, while grit blasted surfaces had significantly lower strain energy release rates. The grit blasting operation caused surface pitting which may have contributed to the reduced strength.

Combining stress, temperature and moisture was shown to accelerate degradation beyond the effect of these components individually. Temperature accelerated moisture diffusion. The residual shear strength was shown to decrease with creep stress. Crack growth in double cantilever beam specimens was also accelerated using a fluctuating load while immersed in water.

5. REFERENCES

1. Tomblin, J., Seneviratne, W., Escobar, P. and Yap, Y. K., "Fatigue and Stress Relaxation of Adhesives in Bonded joints", *DOT/FAA/AR-03/56*, Final report, October 2003

2. Weitsman, Y. J., and Elahi, M. "Effects of Fluids on Deformation, Strength and Durability of Polymeric Composites - An Overview", *Mechanics of Time-Dependent Materials*, Vol. 4.2, pp. 107-126, 2000.

3. Gibson, R. F., "Principles of Composite Material Mechanics", McGraw-Hill, Inc. 1994.

4. Shen, C. H., Springer G., "Moisture Absorption and Desorption of Composite Materials", *Journal of Composite Materials*, Vol.10, pp 2-20, 1999.

5. Bradley, W. L. and Grant, T. S., "The Effect of Moisture absorption on The Interfacial Strength of Polymeric Matrix Composites", *Journal of Material Science*, Vol. 30, pp. 5537-5542, 1995.

6. Bond, D. A., "The Effect of Environmental Moisture on the Performance and Certification of Adhesively Bonded Joints and Repairs", *FAA & CAA Workshop on bonded structures*, Gatwick, 26-27 Oct 2004.

7. Buck S. E., Lischer D. W, Nemat-Nasser S., "The Combined Effects of Load, Temperature and Moisture on the Durability of E-glass/ Vinylester Composite Materials", *Evolving technologies for the competitive edge; Proceedings of the 42nd International SAMPE Symposium and Exhibition*, Anaheim, pp. 444-454, 1997.

8. Abdel-Magid, B., Ziaee, S., Gass, K., Schneider, M.,. "The Combined Effect of Load, Moisture and Temperature on the Properties of E-glass/epoxy Composites," *Composite Structures*, Vol. 71, pp. 320-326, 2005.

9. Browning, C. E., Husman, G. E., and Whitney, J. M., "Moisture effects in Epoxy Matrix Composites", *Composite Materials: Testing and Design: Fourth conference, ASTM STP 617*, pp. 418-496, 1977.

10. Smith, L. V. and DeVries, K. L., "Mechanical Properties of Polymeric Fibers Exposed to Stress in a NO_x Environment", *Polymer*, Vol. 34, 546, 1993.

11. National Transportation Safety Board, "Aircraft accident report- Aloha airlines flight 243, Boeing 737-200, N73711, Near Maui, Hawaii, April 28, 1988".

12. Jurf, R.A., "Environmental Effects on Fracture of Adhesively bonded Joints", *Adhesively Bonded Joints: Testing, Analysis, and Design, ASTM STP 981*, pp.276-288, 1988.

13. Marceau, J. A., Moji, Y., and McMillan, J. C., "A Wedge Test for Evaluating Adhesive Bonded Surface Durability", *Bicentennial of Materials Progress*, SAMPE, Vol. 21, pp. 332-355, 1976.

14. Hart-Smith, L. J, "Peel-Type Durability Test Coupon to assess Interfaces in Bonded, Co-Bonded, and Co-Cured Composite Structures", *McDonnell Douglas paper MDC 97K0042*, MIL-HDBK-17 Meeting, 14-17 April, 1997.

15. Bardis, J. and Kedward, K. "Effects of Surface Preparation on Long- Term Durability of Composite Adhesive Joints", *DOT/FAA/AR-01/8, Final Report*, April 2001.

16. Li, G., Pang, S.S., Woldesenbet, E., Stubblefield, M.A., Mensah, P.F., Ibekwe, S.I., "Investigation of Prepreg Bonded Composite Single Lap Joint", *Composites Part B: Engineering,* Vol. 32.8, pp. 651-658, 2001.

17. McBrierty, V. J., Martin, S. J. and Karasz, F. E., "Understanding Hydrated Polymers: the Perspective of NMR," *Journal of Molecular Liquids*, Vol. 80, Issues 2-3, pp. 179-205, 1999.

18. Ennis, B. C., Morris, C. E. M., Pearce, P. J., "Effects of Humidity on a New Aerospace Adhesive," *Royal Australian Chemical Inst, Polymer Div*, pp. 283-285, 1985.

19. Dodiuk, H.; Drori, L.; Miller, J., "Effect of Moisture in Epoxy Film Adhesives on Their Performance: I. Lap Shear Strength," *Journal of Adhesion*, Vol. 17.1, pp. 33-43, 1984.

20. Shaffer, D. K., Davis, G.D., McNamara, D. K., Shah, T. K., Desai, A., "Durability Properties for Adhesively Bonded Structural Aerospace Applications", *International SAMPE Metals and Metals Processing Conference*, Vol. 3, pp. 629-644, 1992.

21. Roy, A. K., Donaldson, S. L., "Moisture and Temperature Effects on Bonded Composite Double-lap Shear Specimens", *Advanced Materials: Development, Characterization Processing, and Mechanical Behavior, ASME Publication*, Vol. 74, pp. 73-74, 1996.

22. Crasto, A. S., Kim, R. Y. "Environmental Durability of a Composite-to-Composite Adhesive Bond in Infrastructure Applications," *International SAMPE Technical Conference*, Vol. 28, pp. 837-849, 1996.

23. Parker, B. M. "Some Effects of Moisture on Adhesive-Bonded CFRP-CFRP Joints," *Composite Structures*, Vol. 6, pp. 123-139, 1986.

24. Phariss, M. K. M., Flinn, B. D., Ballien, B., Grace, W., VanVoast, P. J., "Evaluation of Peel-Ply Materials on Composite Bond Quality" *SAMPE Fall Technical Conference, 37th ISTC*, 2005.