REMEDIATION OF CONTAMINATED BOND SURFACES: CONTAMINANT MIXTURES

R. Giles Dillingham, Brooke Campbell, Matthew Nichols
BTG Labs
Cincinnati, OH/USA

ABSTRACT

Aerospace manufacturing and repair environments include the very real possibility that bond surfaces presented to the adhesive will not always have the correct composition to ensure acceptable bond performance. There are myriad avenues for contamination of bond surfaces. Contact contamination occurs from unsanitary material handling. Common sources for these contaminants are through substandard wipers, contaminated solvents, and abrasives which contain release agents such as stearates. Aerosol contamination events from airborne substances such as cutting fluids, lubricants, and mold releases are well documented. Another less frequent but real source of contamination is from peel ply that was unintentionally coated with release agent from the manufacturer. Control of adhesive bonding operations to guarantee reliable bond performance requires careful, quantitative bond surface control along with methods for successful remediation of contaminated surfaces. This work describes the development of quantifiable, reliable, and easily deployable techniques for controlling bond surface properties in manufacturing and repair by i. ensuring that the composite surface has been prepared properly for bonding, and ii. if the surface has been identified as having been improperly prepared (e.g. contaminated), establishing quantifiable methods for remediation of the surface.

1. INTRODUCTION

There currently does not exist the same level of confidence in the reliability of composite-composite adhesive bonds that exists in metal-metal adhesive bonds. The low reactivity of the composite surface compared with that of a properly prepared metal surface means that a good interface can be difficult to establish without pretreatments that increase the chemical activity of the surface. These pretreatments are either mechanical (peel ply removal, hand abrasion, grit blasting) or chemical (plasma treatment). However, unlike metal-metal adhesive bonds, composite-composite bonds are relatively insensitive to environmental degradation. Once a good interface has been established between a composite material and an organic adhesive, it is stable to the environment without needing to resort to passivating pretreatments.

Surface treatment processes for composite-composite bonding in aerospace manufacturing and repair are still largely manual, and probably will continue to be for the near future. Partly because these processes are manual, most manufacturing operations and repair procedures do not utilize quantitative control of these processes. Bond failures in composite aircraft are well known, and the lack of clear explanations for the causes of most of these failures results directly from the lack of quantified control over the bonding processes. This unexplained bond performance variability has resulted in a lack of confidence in the ability to manufacture bonded

Copyright 2020. Used by the Society of the Advancement of Material and Process Engineering with permission.

composite aircraft with a reliability that would permit certification. The economic and performance advantages of adhesively bonded primary aircraft structures are well-recognized and have given rise to significant programs such as the DARPA Open Manufacturing TRUST Program [1,6] as well as large internally funded programs at several manufacturers and research organizations [2-4] aimed at developing manufacturing processes and procedures that can provide quantifiable reliability of bonded primary structures.

These programs as well as other recent work in surface and adhesion science outside of the aerospace industry have established the firm scientific foundation necessary for developing truly reliable adhesive bonding processes for composite materials that can be practically deployed in both manufacturing and repair. 'Practically deployed' means that these processes need to be able to accommodate the realities of aerospace manufacturing and repair: bonding environments that are not always well-controlled, and limited training and capabilities of the technicians who exercise these processes.

Aerospace manufacturing and repair environments include the very real possibility that bond surfaces presented to the adhesive will not always have suitable chemical composition and physical properties to ensure acceptable bond performance. There are myriad of avenues for contamination of bond surfaces. Contact contamination occurs from unsanitary material handling. A common source for these contaminants is through the use of substandard wipers, contaminated solvents, and abrasives which contain release agents such as stearates [5]. Aerosol contamination events from airborne substances such as cutting fluids, lubricants, and mold releases have been well documented [6]. Another less frequent but real source of contamination is peel ply that has been unintentionally coated with release agent from the manufacturer [7].

It is currently difficult to protect against unintended contamination events because most surface preparation and bonding procedures consist of following prescribed process steps with no verification of the quality (i.e. cleanliness, surface composition) of the resulting surfaces.

Control of adhesive bonding operations to guarantee reliable bond performance requires careful, quantitative bond surface control. This includes four key components: i. knowledge of the detrimental contaminants present in the bonding environment, ii. Understanding of the threshold amounts of these contaminants that cause degradation of bond performance, iii. reliable methods for detecting these contaminants on the bond surface that can be practically deployed in manufacturing, and iv. methods for successful remediation of contaminated surfaces.

This paper describes some of the results of a recently completed Phase I SBIR that has laid the groundwork for development of quantifiable, reliable, and easily deployable techniques for controlling bond surface properties by i. ensuring the composite surface has been prepared properly for bonding, and ii. if the surface has been identified as having been improperly prepared (e.g. contaminated), establishing methods for remediation of the surface. Successful completion of this work will result in the removal significant barriers to a more widespread adoption both of primary bonded aircraft structures and bonded structural repairs. While previous work in the TRUST program focused on model contaminants consisting of pure, well characterized substances. The current work addresses in part the possibility of contamination by mixtures of pure components, for example mold release + lubricating oils.

Optimum surface treatment and bonding procedures are materials system dependent; i.e. the best treatment and bonding process for a polyimide composite and adhesive will likely be different from that for an epoxy composite and adhesive system, and certainly different from an optimized process for a bonded thermoplastic composite like polyether ether ketone (PEEK). The work described here has focused on a single materials system, surface preparation process, and bonding procedure. The results will be particular to this materials system. However, the concepts, experimental methodologies, and analysis tools are generally applicable to any materials system.

1.1 Remediation of contaminated surfaces

In general, remediation of a compromised surface requires removal of contamination. Contamination can be removed by three approaches: physical, chemical, or mechanical.

An example of a physical approach is removal by dissolving the contaminant in a solvent followed by removal of the resulting solution. In general, this approach cannot remove 100% of a contaminant, although if it reduces the amount of contaminant on the surface below the critical level that affects adhesion, it can likely regenerate a bondable surface.

An example of a chemical approach to contaminant removal is conversion of the contaminant to gaseous species by oxidation using a plasma. This can be effective for small amounts of hydrocarbons, which are eventually oxidized to CO_2 and H_2O, but this approach is frequently ineffective for silicone contaminants if present on the surface in more than miniscule quantities. Silicones oxidize to non-volatile silicas, and when thicker layers of silicone contaminants are exposed to plasmas, the surface of the contaminant film oxidizes to form a silica crust above an unoxidized layer of silicone. Surface energy of the silica crust can be high, but bonding to these surfaces is poor.

Mechanical removal methods include media blasting, abrasion, and even laser treatments, and these approaches depend on ablation of contaminated layers to carry contaminant away from the surface. Media blasting can be very effective at this removal. Abrasion, using abrasive coated paper or an abrasive coated nonwoven fabric (e.g. Scotch-Brite) is not as effective at transporting contaminated particles away from the surface as media blasting, and the process may require more careful pre-cleaning of the contaminated surface prior to abrasion to ensure that contaminant is not simply re-distributed and worked into the surface. Furthermore, mechanical methods have the potential to created physical damage to the laminate surface which can reduce the interlaminar fracture toughness of the composite and reduce the overall fracture toughness.

This work has focused on a combination of physical and mechanical remediation techniques: solvent cleaning of the surface followed by abrasion, with an emphasis on developing techniques with quantifiable endpoints. Successful remediation is defined as creating a surface that results in cohesive failure of DCB specimens in the adhesive or the laminate, with a toughness equivalent to that obtained from uncontaminated specimens. Identifying quantifiable endpoints for the remediation process will ensure that the process is reproducible when deployed in manufacturing and repair scenarios.

Removal of a contaminant by a solvent is a two-step process: i. the solvent is applied to the surface and the contaminant is allowed to dissolve into the solvent and ii. the solution (solvent + contaminant) is removed from the surface.

The dissolution of the contaminant in the solvent is determined by two factors: i. the solubility of the contaminant in the chosen solvent and ii. the ability of the solvent application process (e.g. spray, immersion, agitation, wiping) to facilitate the solution process by agitation. For a manual wiping process on a composite surface, dissolution will be inhibited by a rough surface that prevents contact of the wiper with the contaminated surface. A peel ply surface has deep hills and valleys in the peel ply fabric imprint in the resin cap which can prevent a wiper from contact with the contaminated surface. A peel ply surface that has been sanded has less roughness (as measured by the arithmetic average of the roughness profile, RA) but can still have very high aspect ratio features such as deep scratches and broken fibers that can prevent contact of contaminant with the wiper. The contaminant can "hide" in the nooks and crannies of the abraded surface.

In the case of a manual wiping process, the removal of the contaminant + solvent solution by a dry wipe is critical. This prevents re-deposition of the contaminant as the solvent flashes off. Again, surface roughness inhibits the ability of a dry wipe to contact and remove the solvent solution.

This discussion serves to highlight the fact that the ability of a solvent cleaning process to remediate a contaminated composite laminate surface will be affected by the following:

i. Surface topography (not simply RA, but other aspects of the surface topography)

ii. Solubility of contaminant in the chosen solvent

iii. Nature of the wiper used to apply and remove the solvent

iv. Method (and operator-to-operator reproducibility) of the solvent application and wiping process

2. EXPERIMENTATION

2.1 Application of controlled amounts of contaminants

The contaminant for this phase (Loctite® Frekote 700-NC™, Henkel Corp. blended with equal volumes of 30 wt non-detergent motor oil) was diluted to a fraction of a percent in xylene. Surfaces were contaminated by passing panels through the spray pattern of a high-volume low pressure (HVLP) spray gun at controlled speed. Directly measuring the amount of contaminant on a composite panel is difficult. For this reason, gravimetric measurements were used to determine the areal density (mass of deposited contaminants per unit area) as a function of concentration and spray gun parameters (air pressure and mixture adjustments). 1" x 3" aluminum foil coupons, were passed through the spray pattern at various speeds, and then weighed after allowing 20 minutes for solvent evaporation. Areal density was determined by comparing mass of aluminum foil samples of known area before and after spray deposition of contaminant solutions. For a given concentration and set of spray parameters, the areal density

increased in a linear manner with the residence time of the surface in the spray. The residence time is the amount of time each unit area of surface is exposed to the spray; it is calculated as the width of spray pattern divided by the rate of sample traverse.

2.2 Selection of solvent for silicone remediation

Motor oil is readily removable by a variety of solvents, both polar and non-polar. Silicones are much more problematical due to their lack of solubility in most solvents. Solvents were prescreened for their ability to solubilize silicones by blending 3 ml each of silicone oil and the candidate solvent in a glass vial, capping and shaking until dispersed. The mixture was then allowed to sit for several minutes and then visually evaluated for phase separation (Figure 1). Solvent/silicone mixtures that showed evidence for phase separation were not evaluated further. Quantification of the ability of these solvents to remove silicone from a surface was evaluated by comparing infrared spectra from contaminated ferrotype plate (chrome-plated steel) before and after successive wet + dry wiping cycles. Absorbance is directly proportional to the thickness of the silicone film on the surface and is a quantitative indicator of the ability of the given solvent to remove silicone from the surface. American Fiber and Finishing Rymplecloth™ was the wiper used for both wet and dry wiping. The best performers (MEK, decane, hexane, and ethyl acetate) all gave very similar results; ethyl acetate was chosen for further evaluation because it was the best performer.

Figure 1. Initial evaluation of silicone solubility in candidate solvent. Left: silicone immiscible in solvent. Right: silicone miscible in solvent.

2.3 Selection of mechanical test geometry: lap joints vs double cantilever beams

The stress state in a lap joint under load is complex, including both Mode I and Mode II stresses, and is highest at the ends of the joint. The lack of a uniform stress state along with absence of a defined precrack makes the data very geometry dependent. Sensitivity to the interface is not great. While lap joints are easy to construct and test, they are poor for evaluating the effect of surface treatments and contaminants. DCB specimens, with a defined precrack and pure Mode I stress state, are known to correlate directly with in-service performance [7]. Figure 2 shows failure surfaces for both lap joints and DCB specimens created from DGEBA composites that were either solvent wiped, grit blasted, or plasma treated. All lap joints showed interlaminar failure regardless of surface treatment; DCB failure modes were strongly dependent on surface treatment. The increased sensitivity of the DCB's over lap joints to the specific surface treatment process shown in Figure 2 confirmed the choice of DCB specimens as the appropriate test method for this effort.

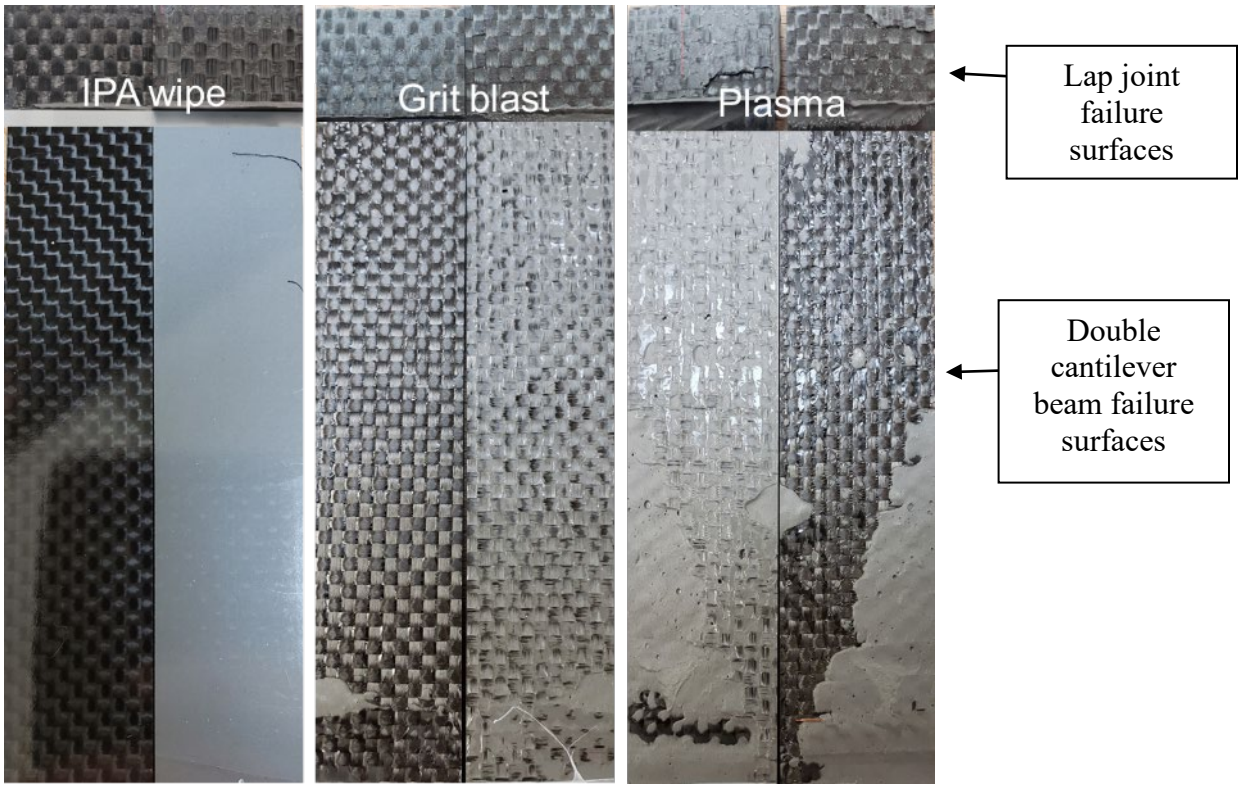

Figure 2. Failure surface for adhesive joints prepared from DGEBA laminates and EA9394 adhesive.

3. RESULTS

3.1 Response of material surface to solvent cleaning and abrasion

Figure 3 shows the effect of the surface preparation process on surface energy as measured by contact angle. The freshly exposed peel ply surface has a very low contact angle (~18°), showing that peel ply removal has created a clean, high-energy surface. Subjecting this surface to solvent cleaning results in an *increase* in the contact angle to about 41°. This is a typical response of a pristine high-energy surface to almost any kind of contact or handling: reactive sites created by the fracture during peel ply removal have been at least partially consumed by reaction and/or adsorption of a few molecular layers of contaminant. Although a well-intentioned solvent cleaning of a highly reactive surface frequently results in a degradation of its reactivity, experience shows that surfaces demonstrating contact angles in this range are still highly bondable. Abrasion + subsequent solvent wiping of this surface does not completely restore the original energy. but does not appear to degrade the surface. Contamination with silicone creates a low-energy surface with ~80° contact angle.

The exposed peel ply surface is fundamentally different from the abraded one: while the unabraded peel ply surface is mostly epoxy resin, the abraded surface consists largely of exposed and fractured graphite fibers.

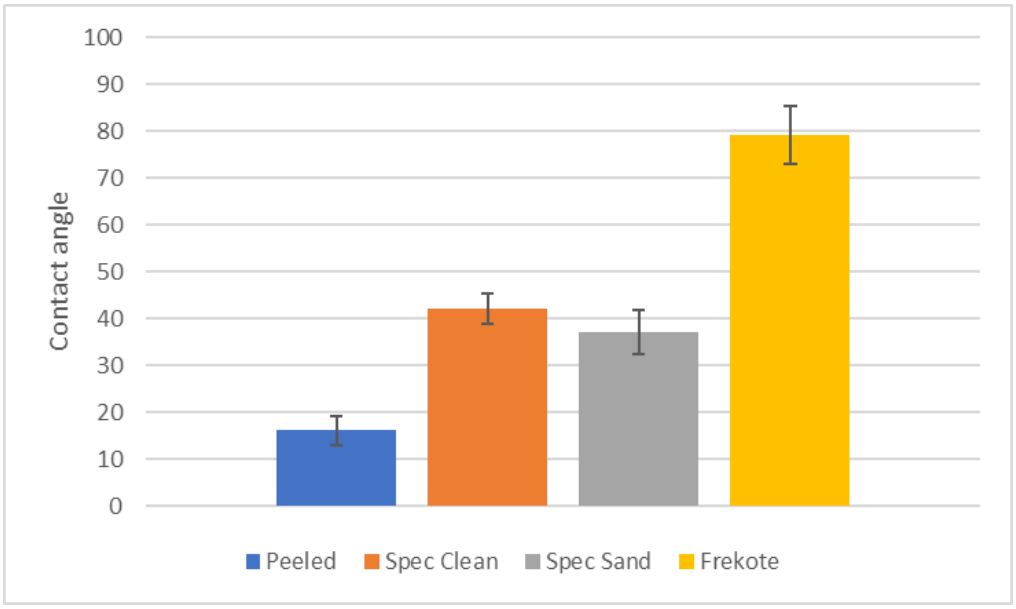

Figure 3. Evolution of contact angle on a freshly exposed peel ply surface with solvent cleaning, abrasion + solvent wiping, and subsequent contamination with silicone.

Profilometry is frequently used to characterize abraded surfaces. Figure 4 shows the effect of the manual abrasion process on the R_A value of these laminates. This surface profile metric (RMS height of surface asperities) is very high for the peel ply surface and is reduced proportional to the amount of abrasion as the asperities are removed. Figure 5 shows an electron micrograph of a manually abraded surface corresponding to fully abraded surface (R_A ~60µin). A large fraction of this surface now consists of abraded (i.e. physically damaged) graphite fiber; the contact angle measured on these surfaces is determined largely by that of the graphite fiber surfaces, not the epoxy matrix resin.

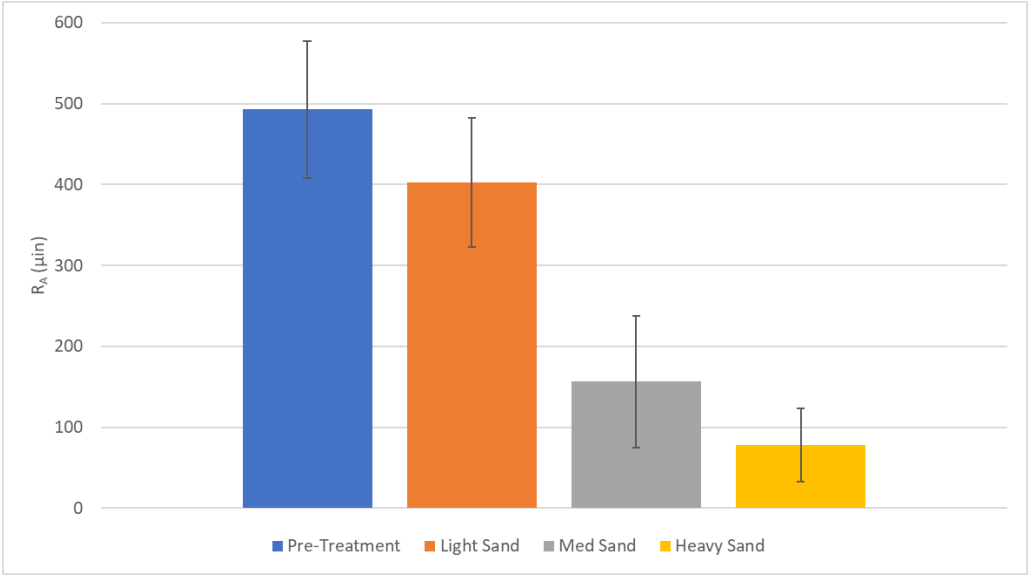

Figure 4. Evolution of R_A with successive sanding cycles.

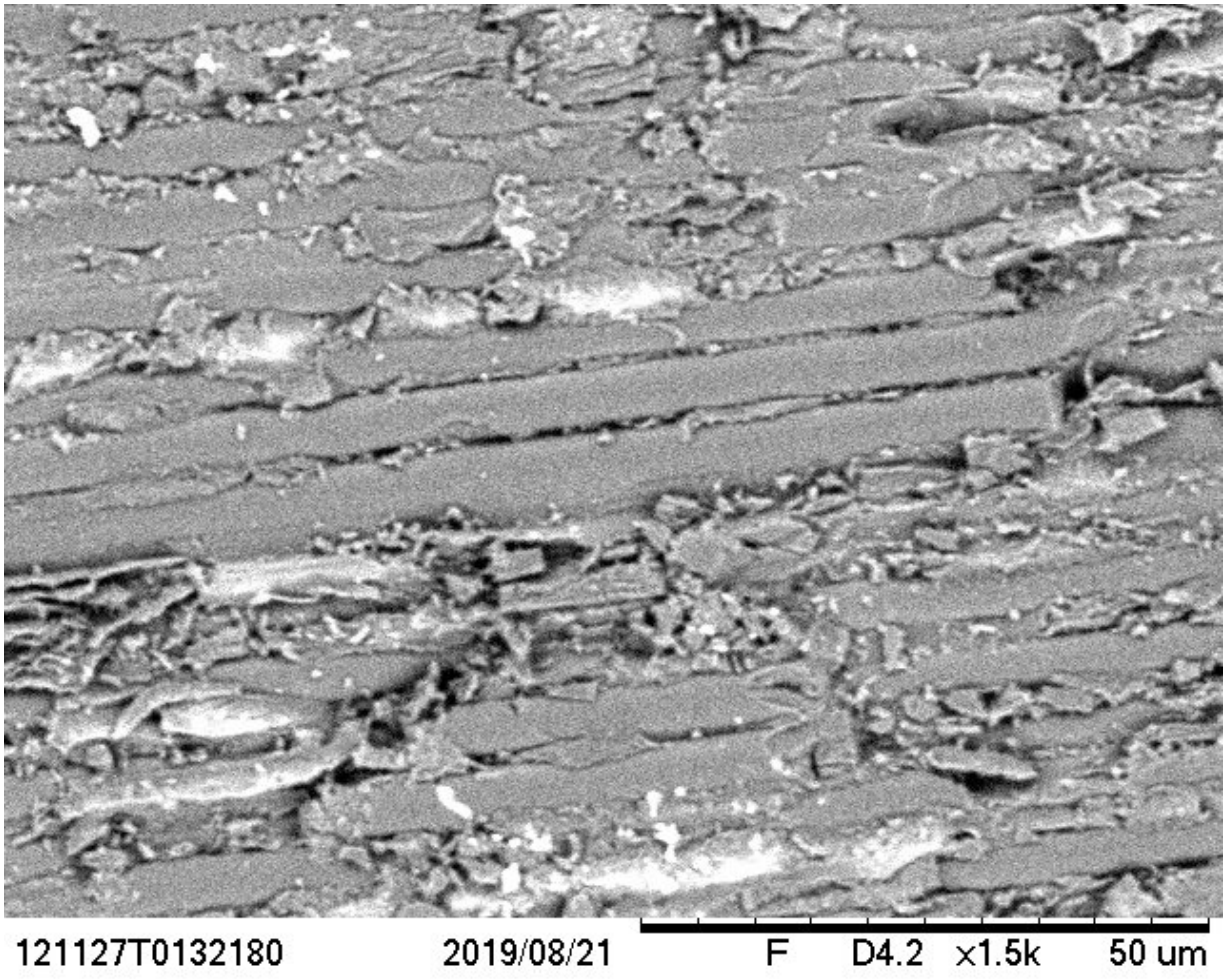

Figure 5. Electron micrograph of an abraded laminate surface corresponding to an R_A of about 60 μin

3.2 Controlled contamination

Figure 6 shows the linearity of the areal density with residence time for silicone. Similar curves were generated for each contaminant mixture and repeated whenever a change in contaminant or adjustment of the apparatus was performed.

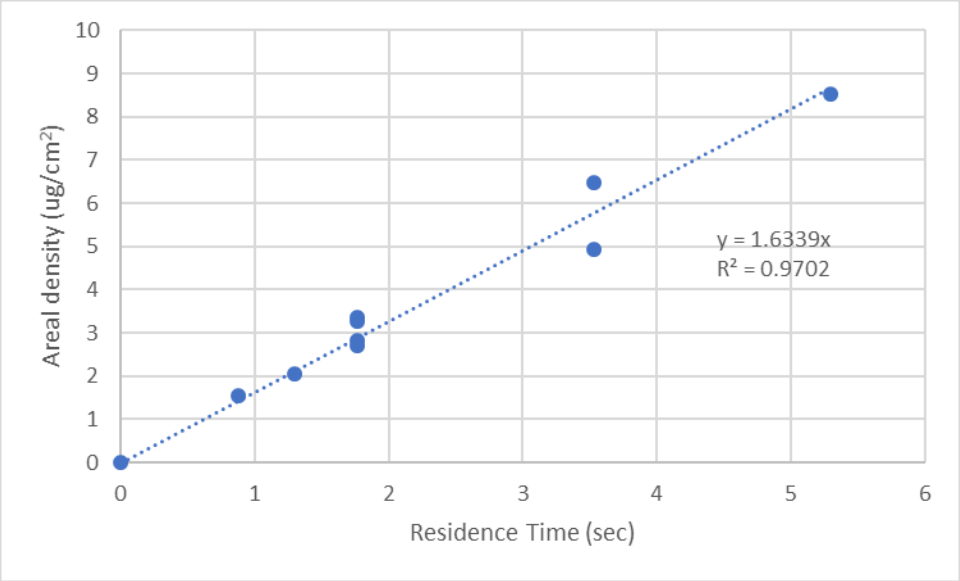

Figure 6. Areal density (mass/unit area) of Frekote 700NC dissolved in xylene.

Gravimetric measurements represent the average areal density over the entire surface; uniformity of deposition was determined by grazing angle Fourier Transform infrared spectroscopy (FTIR) on ferrotype plate (chrome-plated steel) witness coupons that were coated with contaminant at the same time as the foil samples and placed in various locations of the spray pattern.

In order to develop a fundamental understanding of the effects of contamination on adhesive bonding along with remediation, most of the work to date has focused on single component contaminants. However, mixtures of multiple contaminants, particularly immiscible contaminants, have the potential to segregate on a surface. This could have an effect on the ability to detect a contaminant. For example, if a highly detrimental contaminant (such as a silicone) is overlaid by a relatively benign contaminant (such as a mineral oil), the detectability of the detrimental contaminant could be compromised. (This would depend on the detection method used.) In this scenario, a seriously compromised bond surface could possibly be accepted as being suitable for bonding. To initiate investigation into the ability to both detect combined contaminants and to remediate surfaces contaminated in this way, a blend of 50/50 (v/v) Frekote 700/motor oil was used to contaminate composite surfaces. These contaminants are immiscible when neat, but form a single-phase solution in xylene at the dilution used. Figure 7 shows the effect of increasing contaminant level on the measured contact angles on 5320-1 composite surfaces. Although it is unknown whether the contaminant films phase separated to form island structures or discrete layers, the high contact angles for the contaminated surfaces (~90°) suggest that the silicone component has segregated to the top, presenting a pure silicone surface to the water droplet during contact angle measurement. This is expected from a purely energetic standpoint, as the system will tend to minimize surface free energy, which favors low surface tension silicone on the free surface.

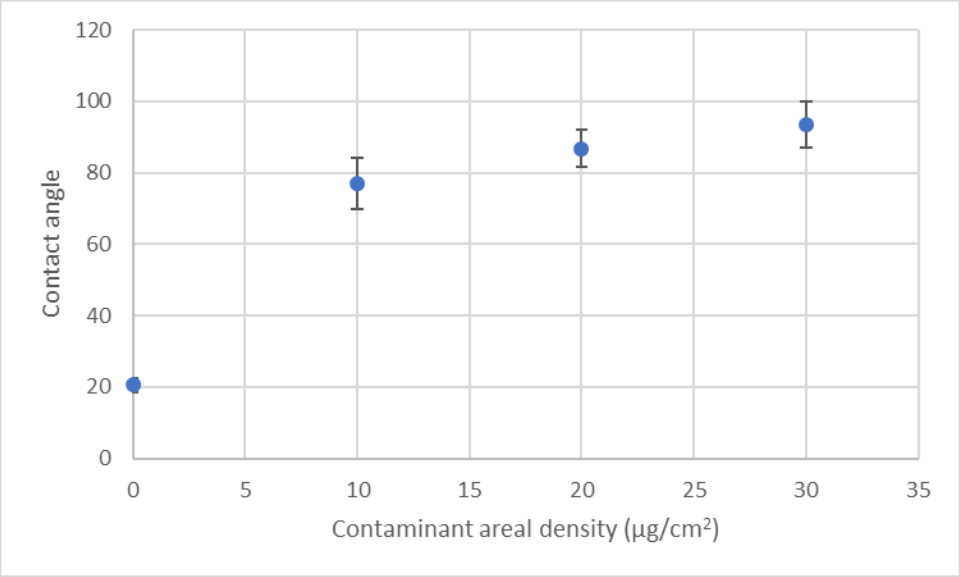

Figure 7. Contact angle on composite surface contaminated with a blend of 50/50 (v/v) Frekote 700NC/30 wt motor oil

3.3 Remediation of surfaces contaminated with mixed contaminants to a quantifiable endpoint

Further contact angle measurements indicated that these contaminated surfaces were readily remediated using solvent cleaning and abrasion process. As an example, Figure 8 shows contact angles obtained from a freshly exposed peel ply surface, after contamination with Frekote 700NC, and after multiple solvent cleaning cycles, and finally after subsequent abrasion.

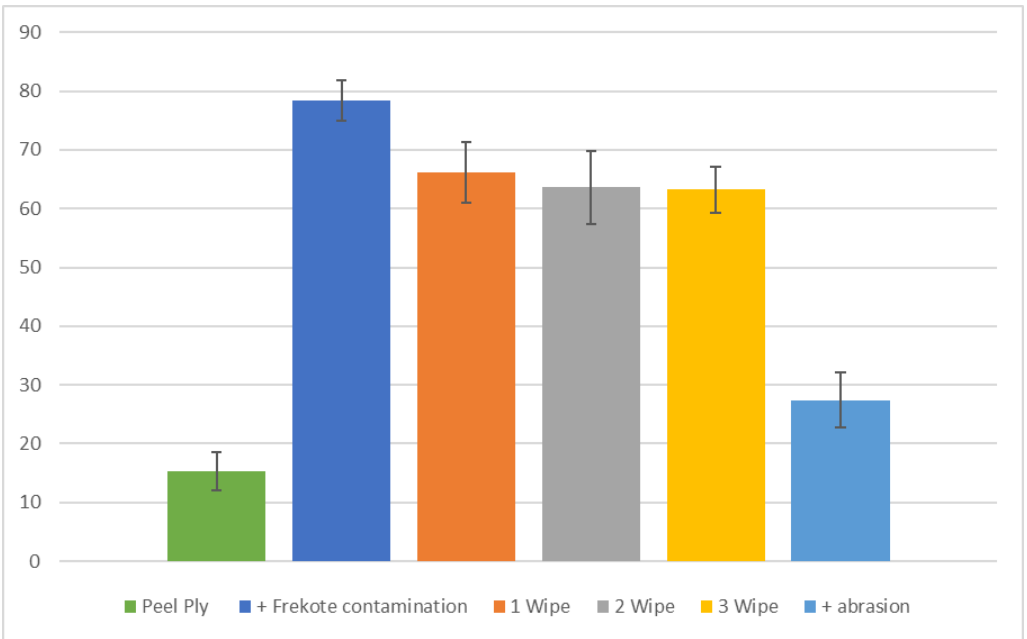

Figure 8. Contact angle on composite surface as-peeled, after contamination (11µg/cm^2 of Frekote 700 NC), multiple solvent cleaning cycles, and abrasion.

Multiple solvent cleaning cycles were unable to restore the original surface properties. However, removal of the bulk of the contaminant via solvent wiping allowed restoration of the original abraded surface properties.

DCB testing of remediated surfaces corresponding to the samples in Figure 8 showed that subjecting the surfaces contaminated with oil + silicone to the standard solvent cleaning + abrasion preparation process successfully regenerated the original bondability. Figure 9 shows the fracture toughness results; Figure 10 shows the fracture surfaces. The contaminated samples failed 100% interfacially at a fracture toughness very close to zero. The fracture toughness values achieved with the remediated surfaces were equivalent to the samples that had been bonded in the freshly peel, uncontaminated condition.

Figure 8 shows that although the fracture toughness for the remediated samples was indistinguishable from the pristine sample, the failure mode appears to have shifted to be more cohesive in the laminate. This may indicate that laminate damage from abrasion has somewhat compromised the cohesive properties of the first ply. This effect has been documented with grit blasted composite laminates

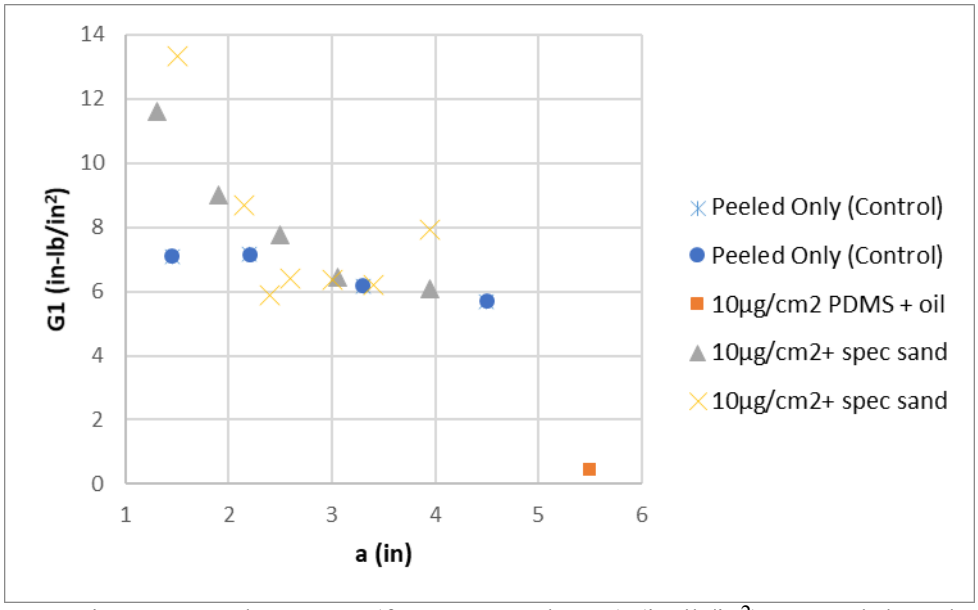

Figure 9. Strain energy release rate (fracture toughness) (in-lb/in^2) vs crack length (in) for composite surfaces as-peeled, after contamination (10µg/cm^2 of 50/50 (v/v) silicone/mineral oil), and solvent cleaning + abrasion. The spec solvent cleaning + abrasion process successfully regenerated a bondable surface.

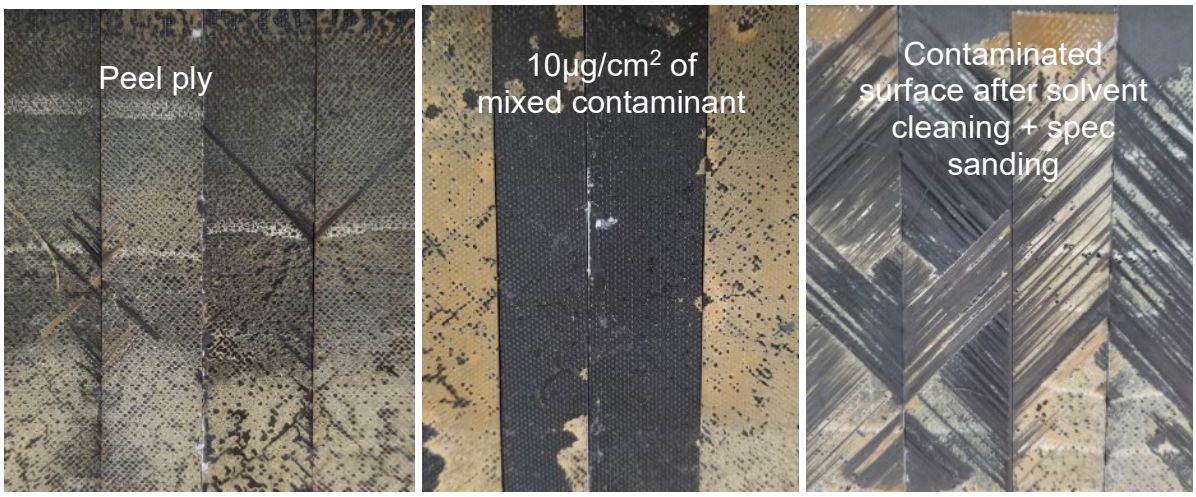

Figure 10. Representative fracture surfaces from samples in Figure 9. The solvent cleaning + abrasion process successfully regenerated a bondable surface.

4. CONCLUSIONS

- All uncontaminated specimens failed essentially 100% cohesively in the adhesive or within the composite
  - Solvent wiping and sanding fresh peel ply surfaces reduced surface energy
  - Sanded peel ply surfaces showed more tendency towards cohesive failure in the first ply
    - Fiber and resin damage from sanding may contribute to lower fracture toughness
- Contamination with ~10µg/cm^2 of either Frekote 700NC or mixtures of Frekote with motor oil resulted in 100% interfacial failures and negligible fracture toughness
  - Contaminant levels on composite surfaces were readily quantified via contact angle measurements
  - Contaminated surfaces failed interfacially with G1c values ~0
- Remediation of silicone/oil contaminated surfaces:
  - Multiple solvent wiping steps were insufficient to remediate a silicone contaminated, abraded surface
  - A combination of solvent cleaning and hand sanding successfully remediated highly contaminated surfaces to restore the original bondability

5. REFERENCES

1. www.compositesworld.com/articles/building-trust-in-bonded-primary-structures
2. Kay Blohowiak, The Boeing Co., personal communication.
3. Upul Palligarayu, NIAR, personal communication.
4. John Webster, Northrop Grumman, personal communication.
5. Steve Twaddle, Brett Bolan, James Mazza, Justin Massey, Ed Harris, personal communications.

6. Johnson Palmer, M., Hanson, B., Clarkson, S., Engelstad, S., Bichon, B., Rousseau, C., Norwood, S., McFarland, J., Popelar, C., Weatherston, M., Oakley, B., Grigoriev, M., MacAdams, L. et al., 2016, “Phase II Report for the TRUST Program,” PMF-02129 Defense Technical Information Center www.dtic.mil