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CENTER OF EXCELLENCE

Thermoplastic Joining Materials Guidance for Aircraft Design and Certification

JAMS 2021 Technical Review

September 29th, 2021

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CMH-17 COMPOSITE MATERIALS HANDBOOK

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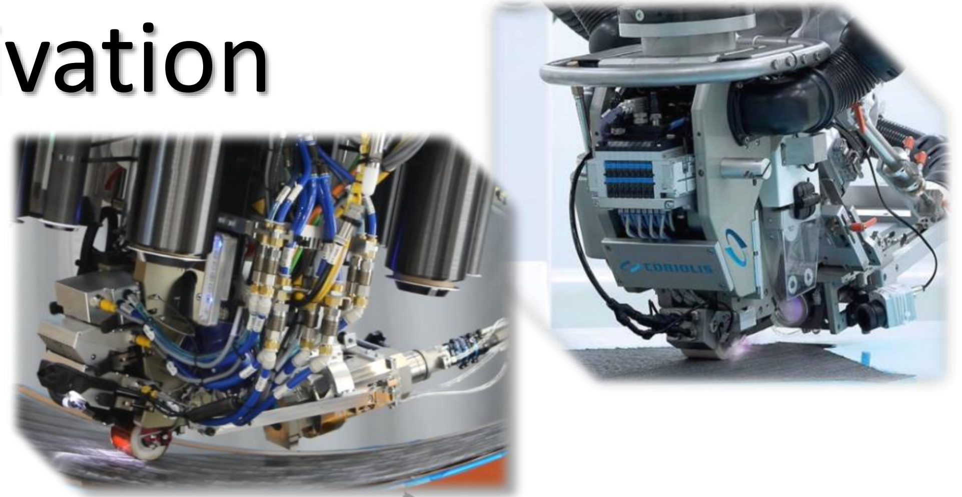
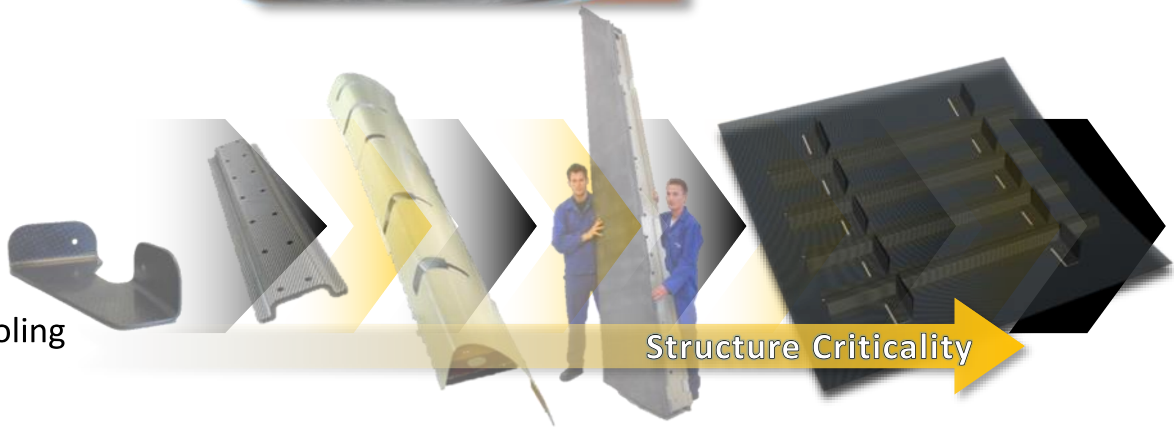
Background & Motivation

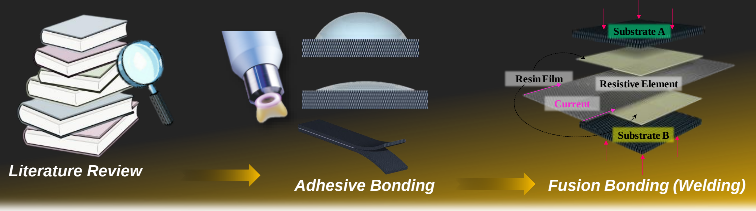


- High-performance thermoplastic resin systems with reinforcement are attractive to aircraft structural applications due to:
  - Ability to integrate into **automated manufacturing methods** & apply unique processing methods (welding) » increase in **production rates** at **low cost**
  - Less stringent cleanroom requirements & material can be stored at ambient temperatures » **low cost**
  - Impact, Chemical, & Environmental Resistance (high material toughness » **increased performance**)
  - Recyclable
- Several challenges have limited their widespread adoption:
  - Large investments in thermoset processing methods (workforce training) and equipment
  - Significant **increase in processing temperatures** compared to thermosets
  - Thermoplastics are sensitive to processing variables, especially the rate of cooling (Tm to Tg) as it relates to the degree of **crystallinity**
  - Lack of established **best practices**
    - **Joining » Adhesive Bonding and Welding**



The primary goal of this research program is to develop a framework for the qualification of thermoplastic joints. Critical processing parameters associated with each joining technique will be identified and protocols will be developed for defining adhesive bonding and welding processes. Research tasks include:

- ***Task 1: Literature Survey and Industry Feedback (SOA Assessment)***
- ***Task 2: Effects of Surface Preparation on Thermoplastic Adhesively Bonded Joints***
- ***Task 3: Effects of Process Parameters on Thermoplastic Welded Joints***
- ***Task 4: Qualification Framework Development***



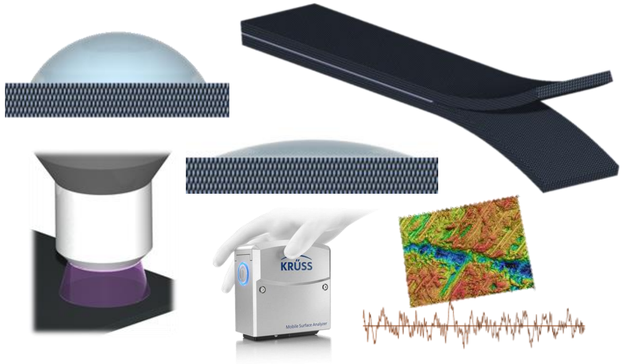
Roadmap of Project – Technical Approach

Task 1
Literature Survey and Industry Feedback

- Conduct literature survey and consult with OEM's to document state-of-the-art joining technologies and applications
- Use industry input and literature findings to tailor research effort to focus on pertinent joining techniques, materials, and processes

Task 2
Effects of Surface Preparation on TP Adhesively Bonded Joints

- Effects of surface preparation techniques on adhesively bonded joints
  - **a) Surface Characterization (2.1)**
    - Surface Free Energy
    - Surface Roughness
  - **b) Joint Testing (2.2)**
    - Lap-Shear
    - Mode-I
- Applicability of standard bonded joint test protocols will be examined

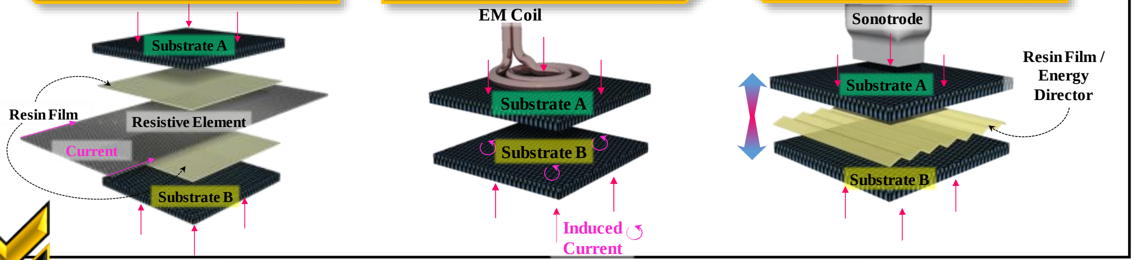


Task 3
Effects of Process Parameters on Thermoplastic Welded Joints

What is a Weld?

- Assessment of critical parameters in the welding process to develop guidelines and recommendations for structural welding
- Effects of surface preparation techniques will be evaluated to investigate potential improvements to welded joint strength and durability

Resistance Welding | **Induction Welding** | **Ultrasonic Welding**

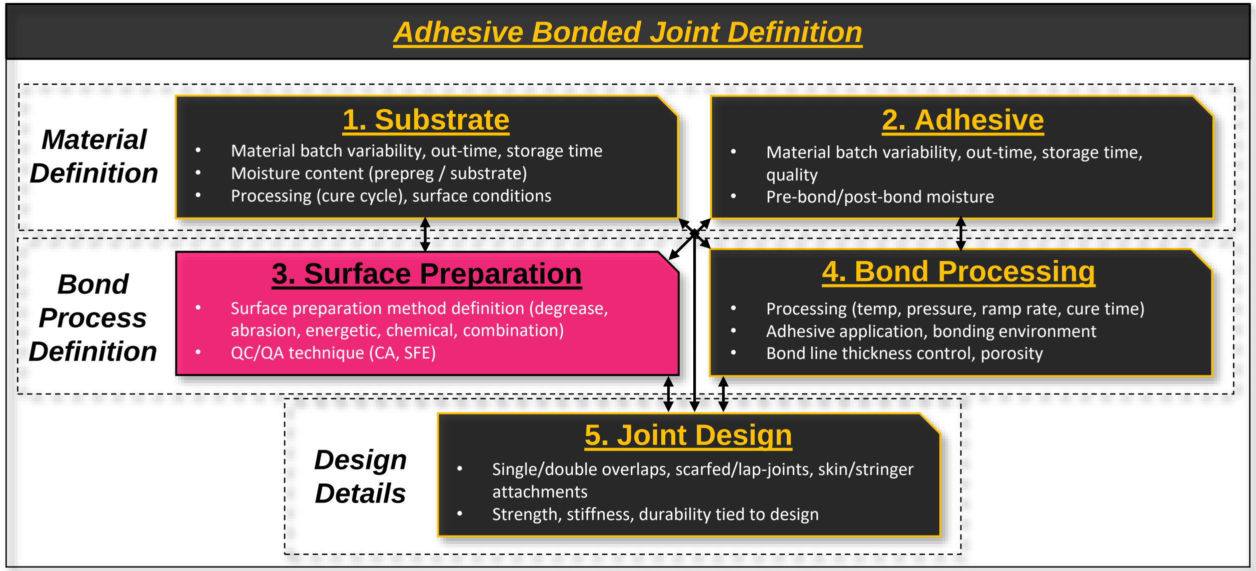


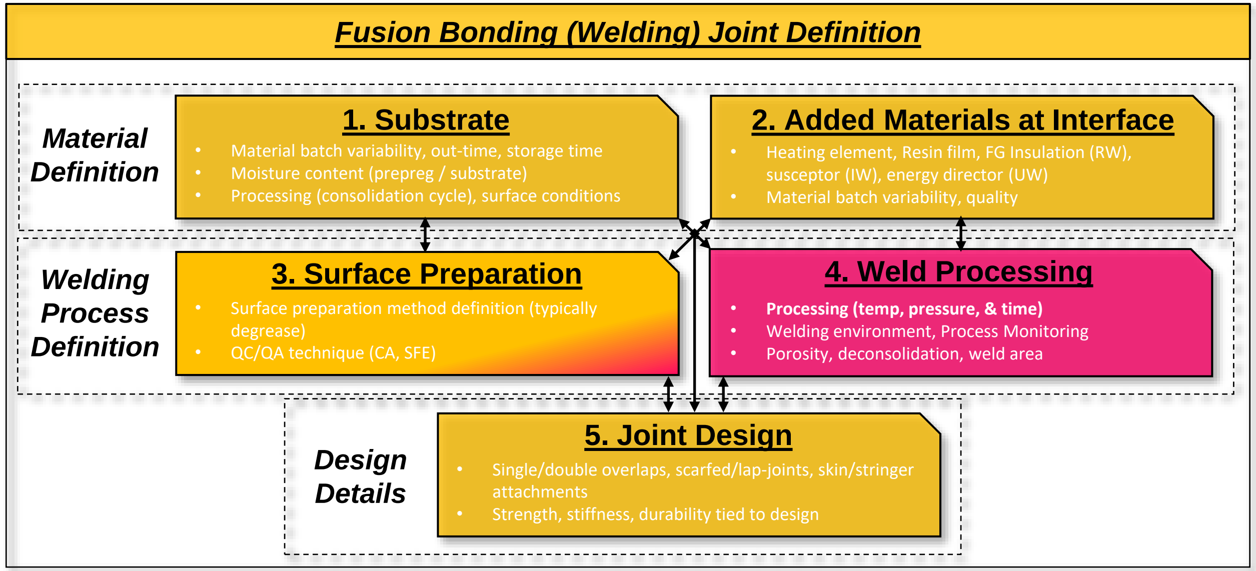
Task 4
Qualification Framework Development

- A framework for qualification will be created in collaboration with industry experts
  - In addition to qualification guidelines, similarities and differences between joining processes will be explored to determine any impact on certification guidelines

Understanding Variability in TP Adhesive Bond & Weld Process

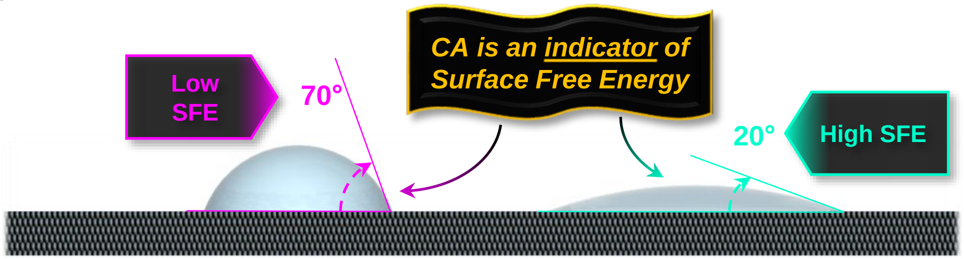
- All factors defined in the joint definition are interrelated[1]
- Identification of critical processing parameters for each joining process is important to ensure those parameters are closely monitored and controlled
  - Expected variation must be related to changes in the structural performance in the characterization process[1]
- **Adhesive bonding**
  - Surface Preparation [cleaning, **chemically activating**, stabilizing (resisting hydration)]
- **Welding:**
  - Surface preparation (cleaning)
  - Weld Processing
    - "Weld cycle"
      - **Temperature (time)**
        - **Processing Temperature:** Promote interfacial intermolecular diffusion (healing)
        - **Cooling Rate:** Crystallinity development
      - **Pressure (time)**
        - Intimate contact development
        - Deconsolidation prevention

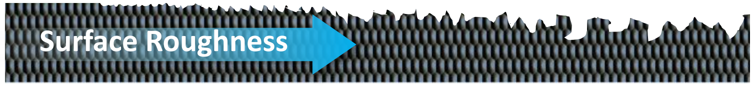




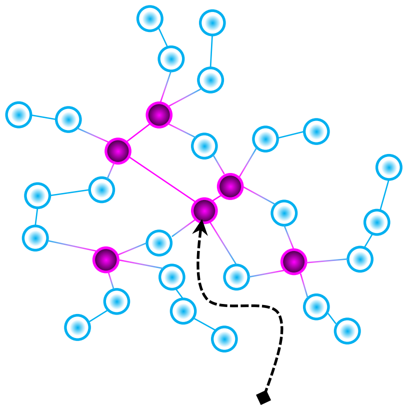
Adhesive Bonding of Reinforced Thermoplastic Composites

- A structural adhesive bond must be accomplished in a way that it predictably and reliably transfers load for the lifetime of the bonded structure
  - Surface preparation process is an important aspect in the bonding process that aims to **clean**, **chemically activate**, and **stabilize** (resist hydration) the substrate surface for bonding
  - Forming strong primary chemical bonds between the adhesive and the substrate has been shown to have greater significance to achieving a successful bond in comparison to the physical characteristics such as surface roughness that promotes mechanical interlocking (keying)
- Thermoplastic materials are generally more challenging to bond than thermoset materials because the surface can be more difficult to chemically activate for bonding:
  - Inherently **low surface free energy »** surface is **not reactive** which does not promote good adhesion
  - Thermoplastic polymers are not locked into a rigid network by cross-linking **»** abrasion surface preparation techniques are not as effective in activating the surface by breaking and opening the polymer chains on the surface[2-6]



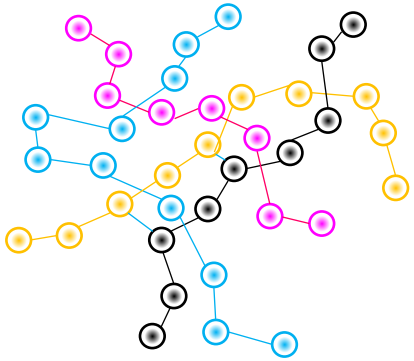


Thermosetting Polymer



Cross-link: strong covalent bonds between polymer chains

Thermoplastic Polymer

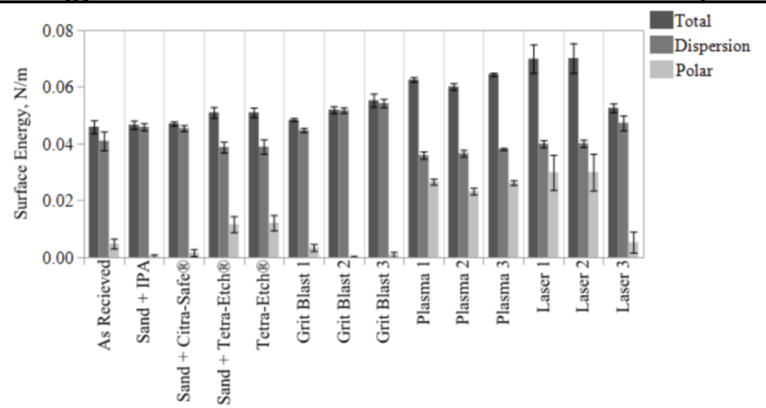


Weak intermolecular forces between polymer chains

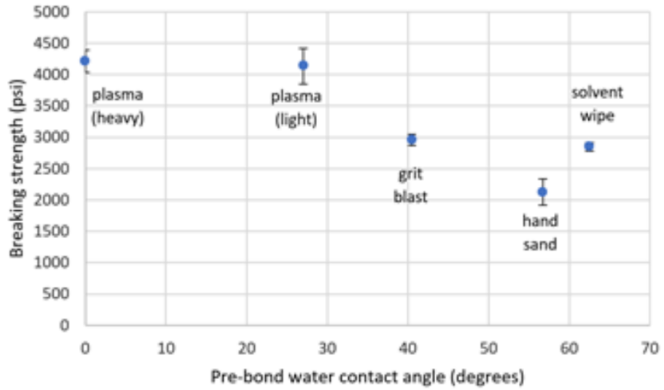
Adhesive Bonding of Thermoplastic Composites – Snapshot of Several Significant Studies in Literature

- **Bonding the Unbondable. Thermoplastics![2]** – The Boeing Company
  - **Key Findings:** Tracey et al. showed that grit blasting is an insufficient surface preparation method for structural bonding PEKK/CF composites to epoxy/CF composites (resulted in low fracture toughness values and >98% adhesion failures). Atmospheric plasma and laser ablation surface treatments resulted in significant increase in surface free energy (specifically polar surface free energy) which corresponded to higher fracture toughness values and predominately acceptable failure modes (cohesion/substrate).
- **Surface Preparation Techniques for Adhesion to Aerospace Thermoplastic Composites[3]** – The Boeing Company
  - **Key Findings:** Schultz et al. showed that abrasion surface preparation techniques tend to only modify the thermoplastic (CF/PEKK) surface morphology with little changes to the surface chemistry & surface free energy. Plasma and chemical treatments primarily affect the surface chemistry and surface energy with little change in the surface morphology. Laser ablation affects the surface chemistry, surface energy, and surface morphology making it more effective for a wide range of materials.
- **The Plasma Treatment of Thermoplastic Fibre Composites for Adhesive Bonding[4]** – Imperial College / University of Surrey, UK
  - **Key Findings:** Blackman et al. revealed that abrasion and solvent cleaning treatments of CF/PEEK substrates displayed an increase in surface roughness and very little change in the chemical composition of the surface. Both plasma & corona treatments dramatically increased the concentration of polar groups present on the surface of the CF/PEEK composite after treatment. Low fracture toughness values were witnessed for thermoplastic bonds when the surfaces were treated with abrasion/solvent cleaning techniques. However, high fracture toughness values were witnessed for thermoset-based composite specimens with the same abrasion/solvent cleaning surface treatment technique. Cohesion failures and high fracture toughness values were achieved for the thermoplastic-based composite specimens with oxygen-plasma and corona treated surfaces.
- **Review – Adhesively-bonded joints and repairs in metallic alloys, polymers, and composite materials: Adhesives, adhesion theories and surface pretreatment[5]** – University of Mersin
  - **Key Findings:** Baldan's review showed typical composite surface treatments include traditional abrasion/solvent cleaning techniques for thermoset composites, while thermoplastic composites require surface chemistry and surface topographical changes to ensure strong and durable bond strengths. The aim of treating thermoplastic composite surfaces is to increase the surface energy of the substrate (adherend) as much as possible.
- **Surface treatment for adhesive bonding: Thermoset vs. thermoplastic composites[6] – BTG Labs / Composites World Article**
  - **Key Findings:** Dillingham suggests adhesive bonds suitable for structural purposes are achievable between most structural materials. Abrasion works on thermoset matrix resins because the polymers are brittle and fracture under abrasion by actual breaking of the polymer chains to create a chemically active surface. This surface can react with an adhesive to form a strong, stable interface. Thermoplastic polymers deform plastically under abrasion rather than fracture, therefore, although the surface is roughened it is still chemically unreactive and wont establish a good bond with an adhesive, coating, or sealant.

Surface Free Energy of CF/PEKK Substrates for Various Surface Prep Methods[3]



PEKK Substrates Bonded w/ Solvay 377S Film Adhesive[6]



Standardized surface preparation techniques such as abrasion (HS/GB) traditionally applied to prepare thermoset-based composites for structural bonding do not effectively chemically activate thermoplastic composite surfaces for adhesive bonding.

Task 2.1 – Surface Characterization Matrix

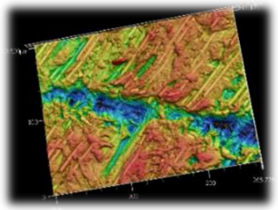
- Various surface preparation methods considered in the screening phase before bonding test specimens
  - Surface Roughness
    - Microscopic Surface Imaging
    - Ra – Arithmetical Mean Roughness Value
  - Surface Free Energy
    - Goniometer
    - Mobile Surface Analyzer

Material	Treatment Type	Treatment		Surface Roughness (Keyonce 20X)	Surface Free Energy (KRUSS)	Surface Free Energy (Goinometer)	Contact Angle (BTG SurfaceAnalyst)
Uni TC1225 (LMPAEK / T700GC)	As Received	As-Received	IPA	6	6	6	6
	Abrasive	Hand Sanding	80 Grit + IPA	6	6	6	6
			150 Grit + IPA	6	6	6	6
			220 Grit + IPA	6	6	6	6
		Grit Blast	80 Grit + IPA	6	6	6	6
			150 Grit + IPA	6	6	6	6
			220 Grit + IPA	6	6	6	6
	Chemical Treatment	Chemical Etching (Tetra Etch)	Etch Time 1	6	6	6	6
			Etch Time 2	6	6	6	6
			Etch Time 3	6	6	6	6
	Energetic	PlasmaTreat Atmospheric Plasma	APT 1 (Speed 1)	6	6	6	6
			APT 2 (Speed 2)	6	6	6	6
			APT 3 (Speed 3)	6	6	6	6
		SurfX Plasma (Argon + Oxygen)	PT 1 (Speed 1)	6	6	6	6
			PT 2 (Speed 2)	6	6	6	6
			PT 3 (Speed 3)	6	6	6	6
		SurfX Plasma (Argon + Nitrogen)	PT 1 (Speed 1)	6	6	6	6
			PT 2 (Speed 2)	6	6	6	6
			PT 3 (Speed 3)	6	6	6	6
	Combination	Hand Sand + IPA + Tetra Etch		6	6	6	6
		Grit Blast + IPA + Tetra Etch		6	6	6	6
		Hand Sand + IPA + APT		6	6	6	6
		Grit Blast + IPA + APT		6	6	6	6

Microscopic Surface Imaging
Keyence VK-X1000

Water Contact Angle
BTG Labs Surface Analyst

Surface Free Energy
KRUSS Mobile Surface Analyzer & Goniometer



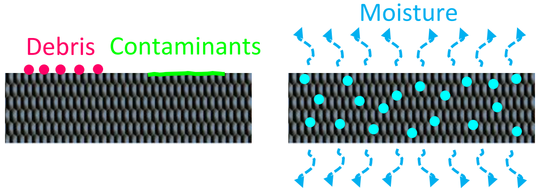

Surface Preparation Process

1. Pre-Treatment

Cleaning

- **Cleaning/Degreasing:** Removal of bulk surface contaminants that could spread on the surface of the substrates throughout the treatment process
  - Isopropyl Alcohol (IPA) with lint-free cloth

- **Drying** of substrates to control moisture content



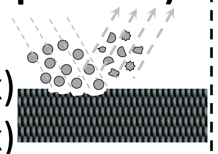
2. Treatment

Activation

Abrasion

- **Hand Sanding (Orbital Sander):**
  - 80-Grit (Al-Ox)
  - 150-Grit (Al-Ox)
  - 220-Grit (Al-Ox)

- **Grit Blasting (Dry 60-psi – 45°):**
  - 80-Grit (Al-Ox)
  - 150-Grit (Al-Ox)
  - 220-Grit (Al-Ox)

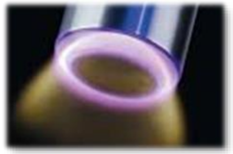


Chemical

- **Chemical Etching (Tetra Etch):**
  - Etch process 1
  - Etch process 2
  - Etch process 3

Energetic

- **Atmospheric Plasma Treatment (Plasmatreat FG 5001)**
  - Process 1
  - Process 2
  - Process 3



- **Plasma Treatment (Surfx Atomflo™ 600)**
  - Process 1
  - Process 2
  - Process 3

Combination

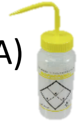
- **Hand Sand + Tetra Etch**
- **Grit Blast + Tetra Etch**
- **Hand Sand + PT**
- **Grit Blast + PT**

Down Selected Parameters

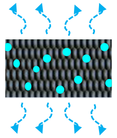
3. Post-Treatment

Stabilization

- **Cleaning:** Certain treatment methods such as sanding can create contaminants or debris on the substrate surface which must be cleaned
  - Isopropyl Alcohol (IPA) with lint-free cloth



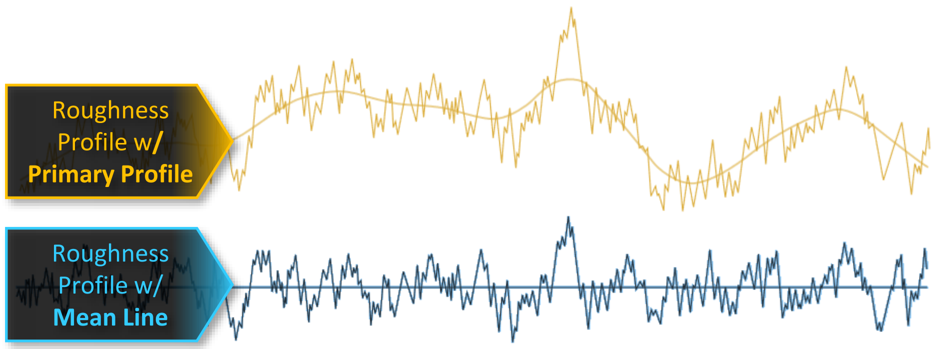
- **Drying** of substrates to control moisture content if treatment method or storage environment increase the moisture content of substrates

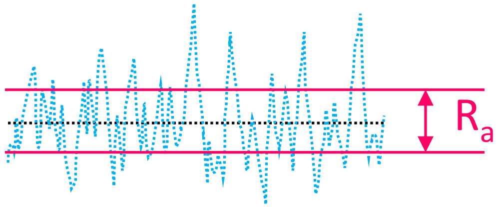


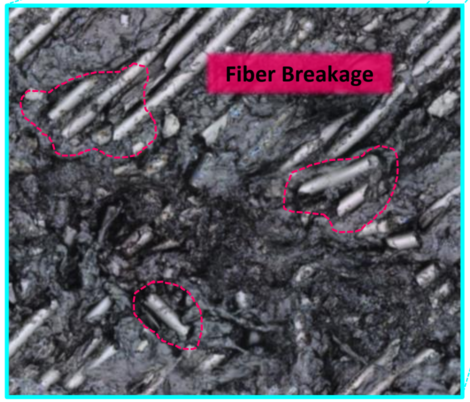
- **Out-time:** Time from completed surface treatment to beginning adhesive cure

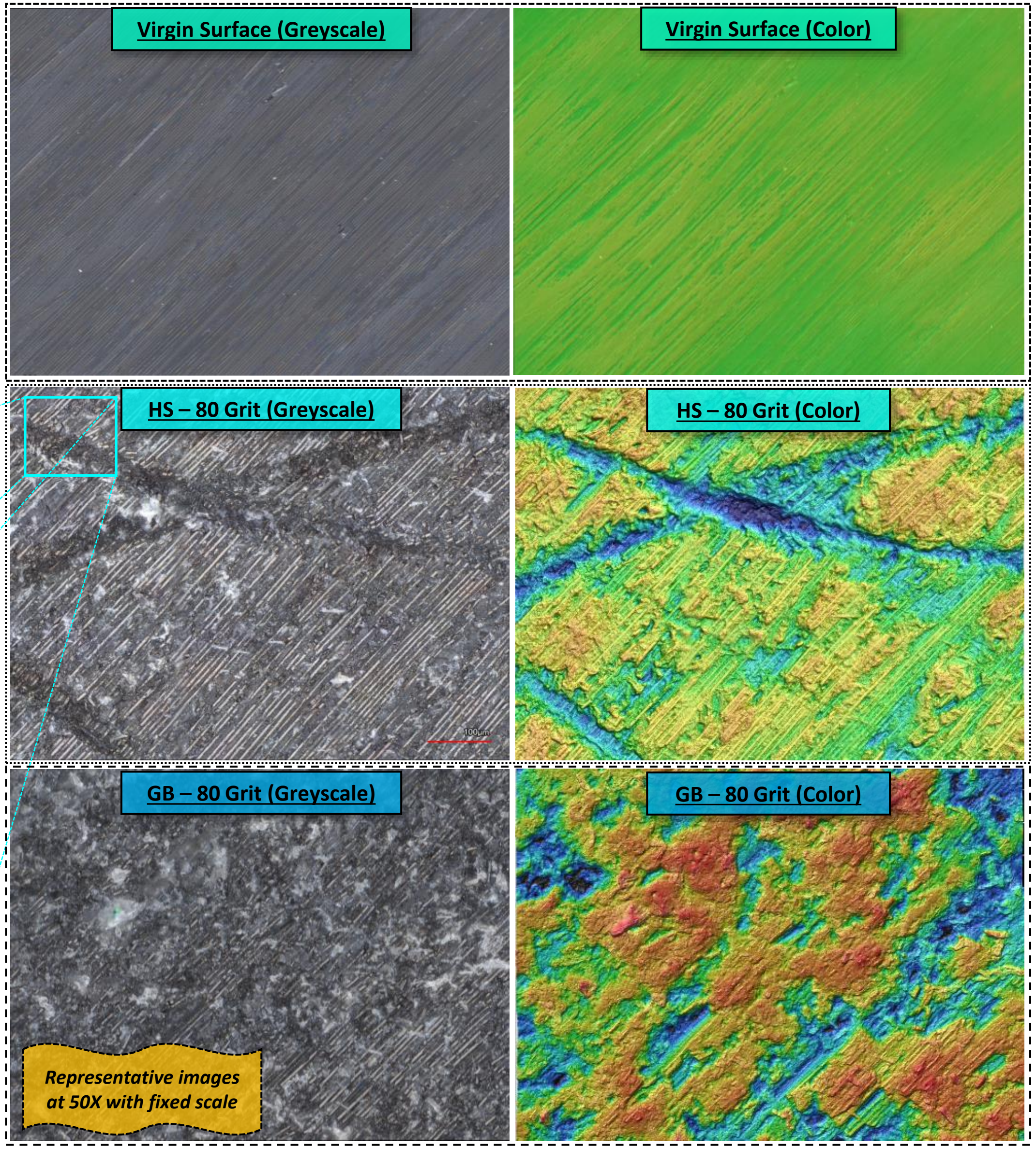
Task 2.1 – Surface Characterization Approach

- **Optical Profiling**: Non-contact measurements with Keyence VK-X1000 Laser Scanning Confocal Microscope
  - EN ISO 4287
    - S_a – Surface Arithmetical Mean Roughness Value
  - Samples examined with 20X magnification



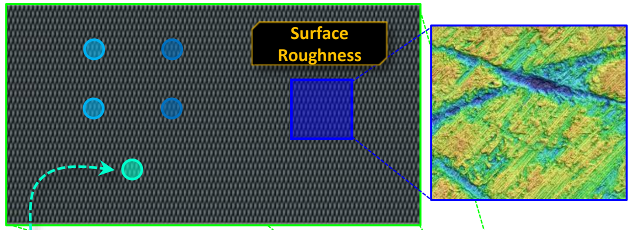


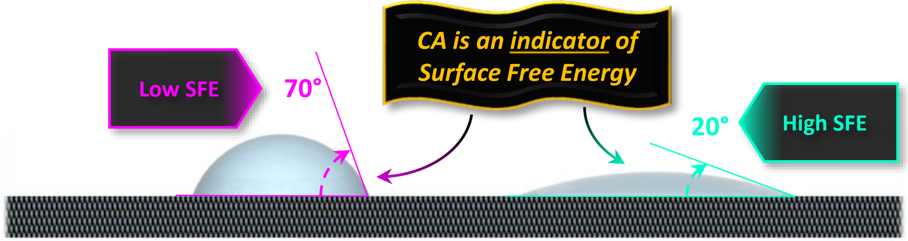


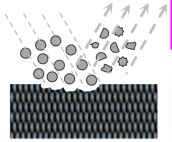


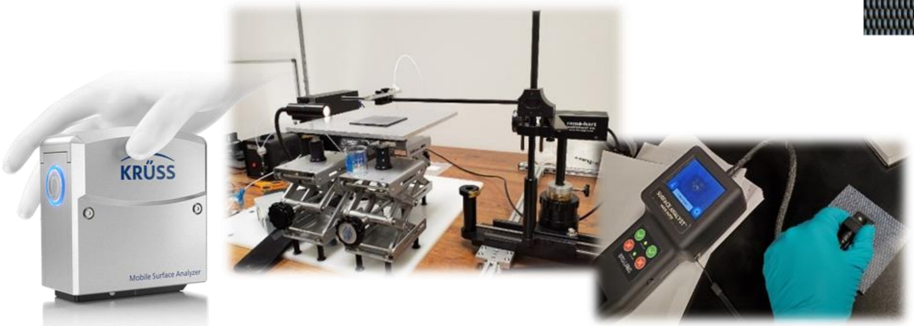
Task 2.1 – Surface Characterization Approach

- Surface Free Energy Measurement
  - (Goniometer) » *Wettability Envelope*
    - Liquid 1 – Deionized Water (High Polar)
    - Liquid 2 – Diiodomethane (High Dispersive)
  - KRUSS
    - Liquid 1 – Distilled Water (High Polar)
    - Liquid 2 – Diiodomethane (High Dispersive)
- Contact angle measurement (BTG Labs Surface Analyst) – HPLC Water
- 10'' x 14'' Panel
  - $[45/0/-45/90]_{2S}$
- Measurement Sequence:
  - Pre-Treatment Contact Angle
  - Post-Treatment:
    - Surface Free Energy
    - Contact Angle
    - Surface Roughness







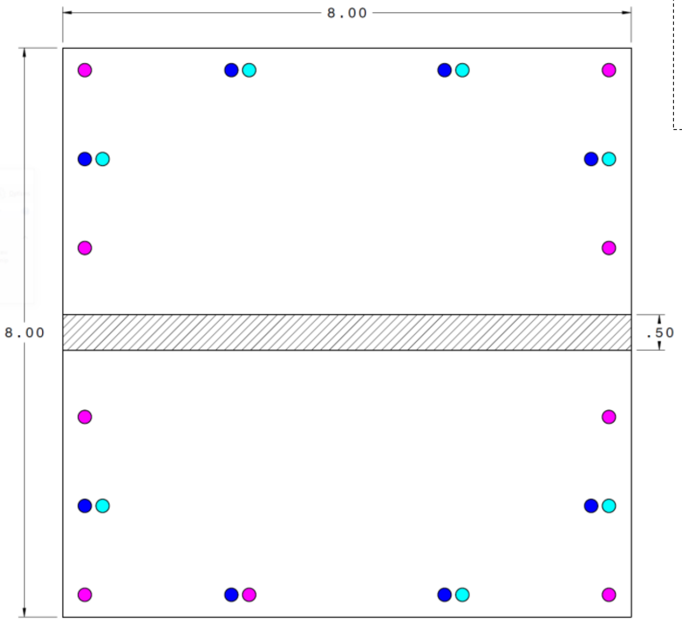


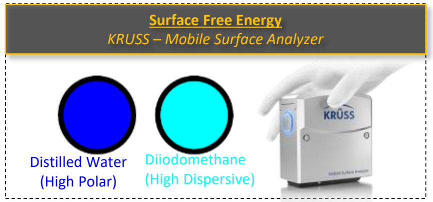
Task 2.2 – Adhesive Bonded Joint Mechanical Testing

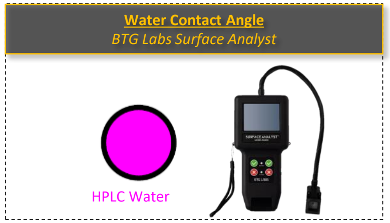
- Substrate M&P Definition
  - Material: Toray TC1225 (LMPAEK / T700GC) 145 GSM 34% RC
  - Layup: $[45/0/-45/90]_{3S}$ (24-ply)
  - Process: Autoclave Consolidation (100-psi)
- Adhesives
  - Paste Adhesive: Hysol EA9394
  - Film Adhesive: Solvay FM300-2M
- Test Methods
  - ASTM D3165 (Single Lap Joint)
  - ASTM D5528 (DCB – Mode I)
- Surface Preparation In-Process QC
  - Contact Angle (Surface Analyst)
  - Surface Free Energy (MSA)

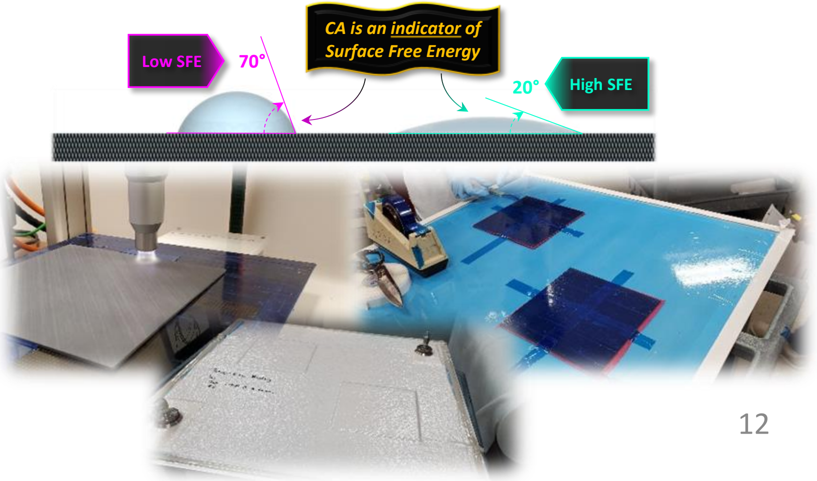
Material	Treatment Type	Treatment		ASTM D3165		ASTM D5528	
				Paste	Film	Paste	Film
Uni TC1225 (LMPAEK / T700GC)	Degrease	As-Received	IPA	5	5		
	Abrasive	Hand Sanding	80 Grit + IPA	5	5		
			150 Grit + IPA	5	5		
		Grit Blast	80 Grit + IPA	5	5		
	Energetic	Atmospheric Plasma	APT 1 (Speed 1)	5	5	5	5
		Plasma (AR+O)	PT 1 (Speed 1)	5	5		
		Plasma (AR+N)	PT 1 (Speed 1)	5	5		
	Combination	Hand Sand + IPA + APT		5	5		
		Grit Blast + IPA + APT		5	5		

Surface Preparation
QC Measurement Locations



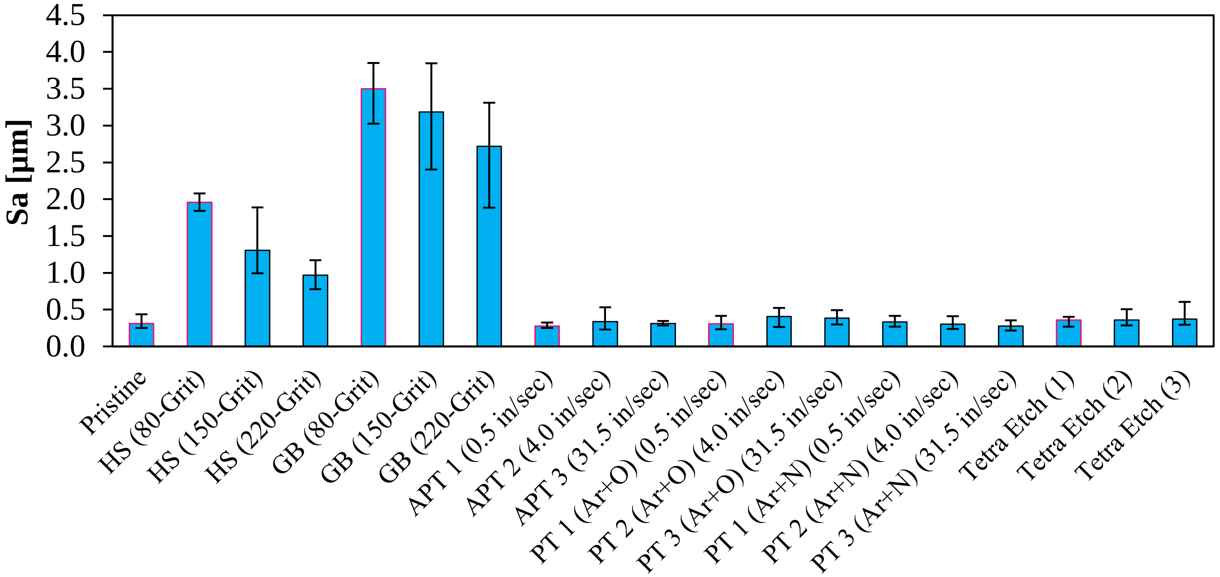


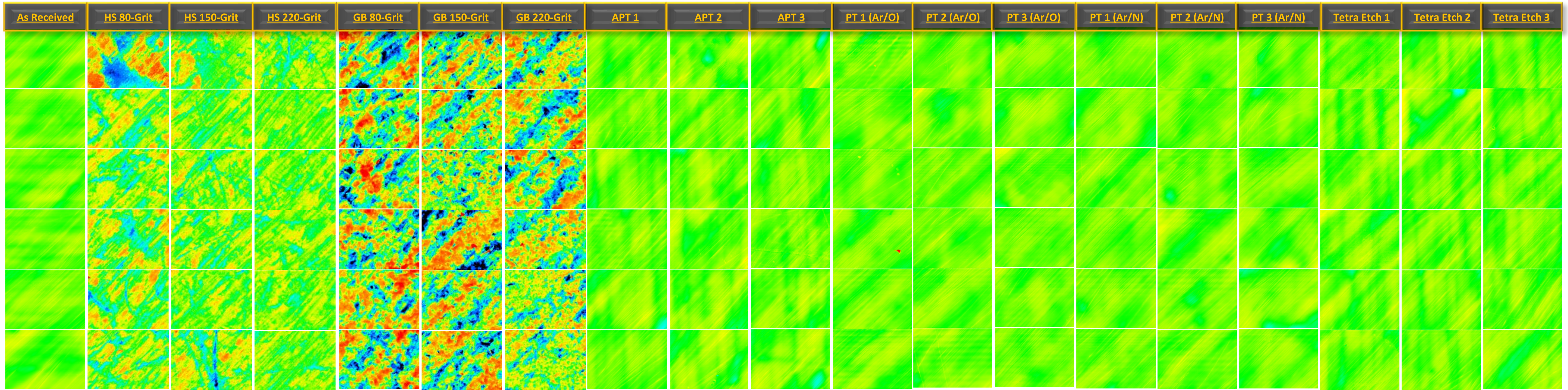




Task 2.1 – Surface Characterization Results

- Higher surface roughness witnessed with grit blasting compared to hand sanding
- No significant change in surface roughness using APT, PT, or TetraEtch® treatments



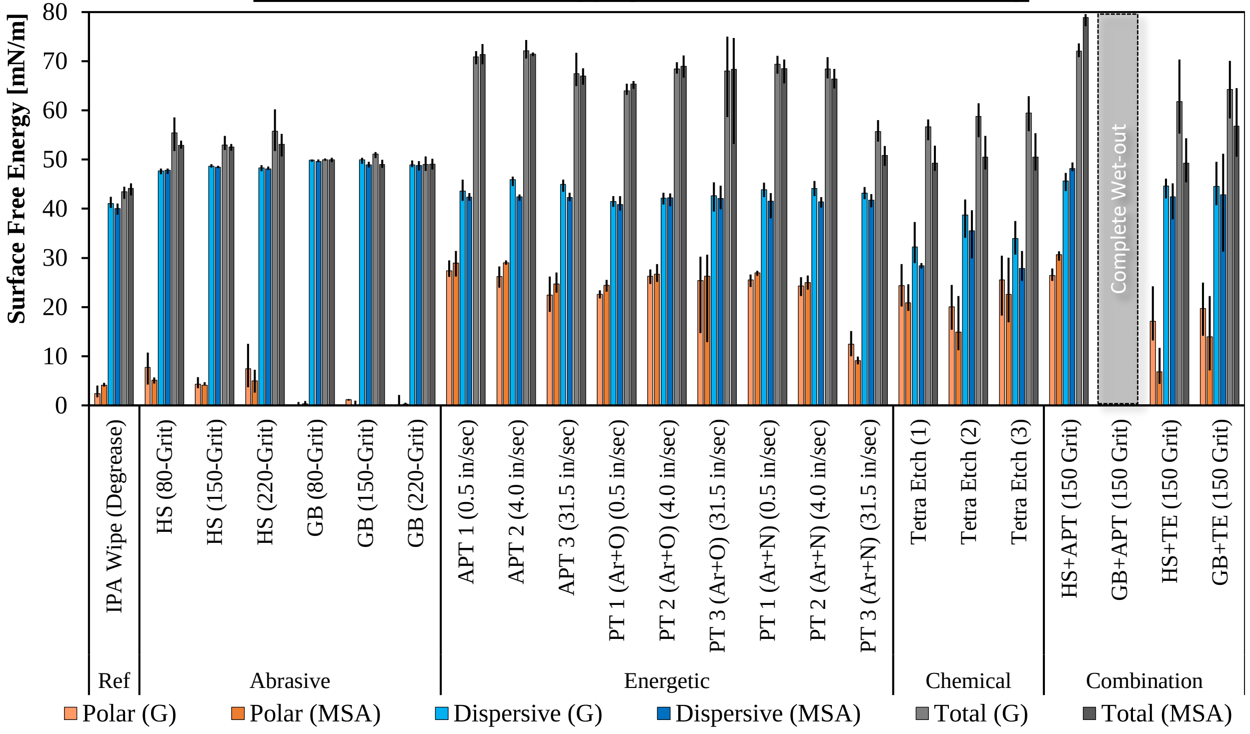


Task 2.1 – Surface Characterization Results

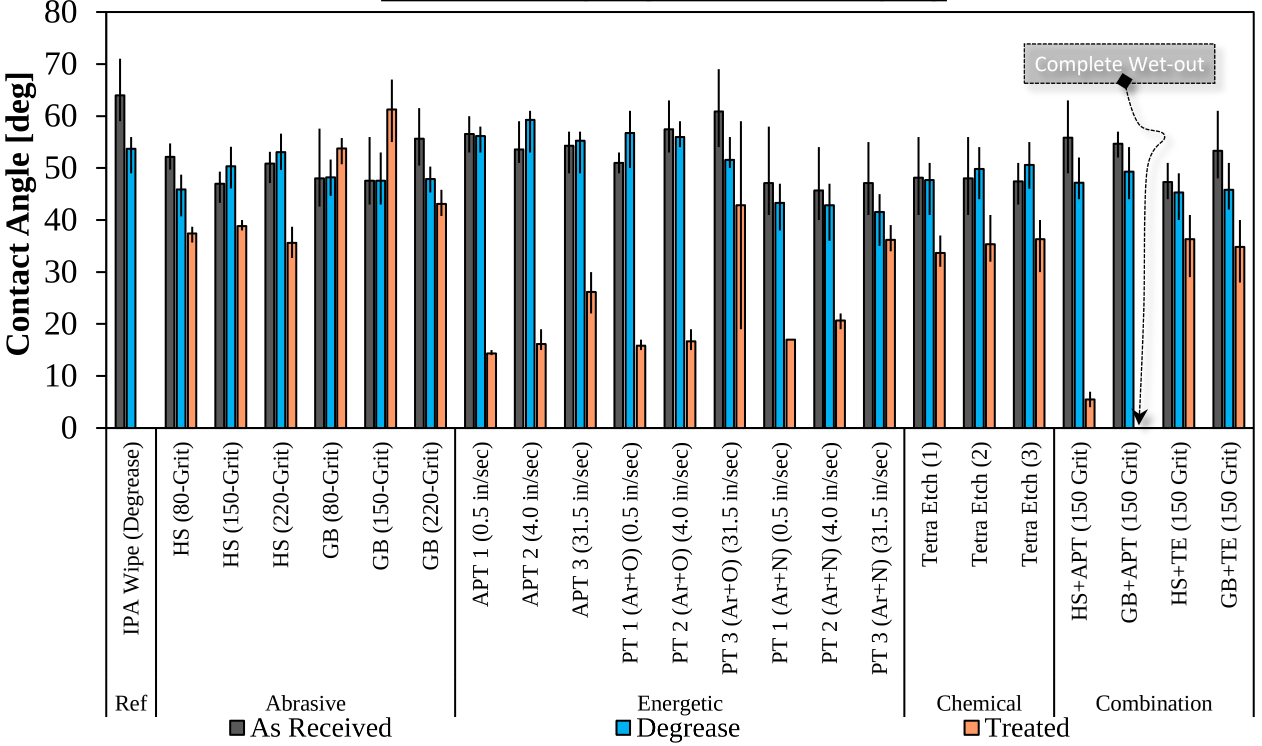
- Significant increase in polar surface free energy with energetic, chemical, and combination treatments
- No significant change in polar component from abrasive methods
- Higher variability associated with TetraEtch® and a decrease in the dispersive component was witnessed lowering the total SFE
- Surface free energy decreased at faster process speeds for energetic surface treatments

- Reduction in contact angle was most significant for energetic surface treatments (higher SFE)
- Contact angle increased as the processing speed increased for energetic surface treatments and higher variability was noticed for the faster processing speeds
- CA and SFE measurements indicate the energetic treatments at 0.5 in/sec processing speed were the most repeatable and reliable method to activate the substrate surface for bonding

Surface Free Energy (Goniometer and MSA)

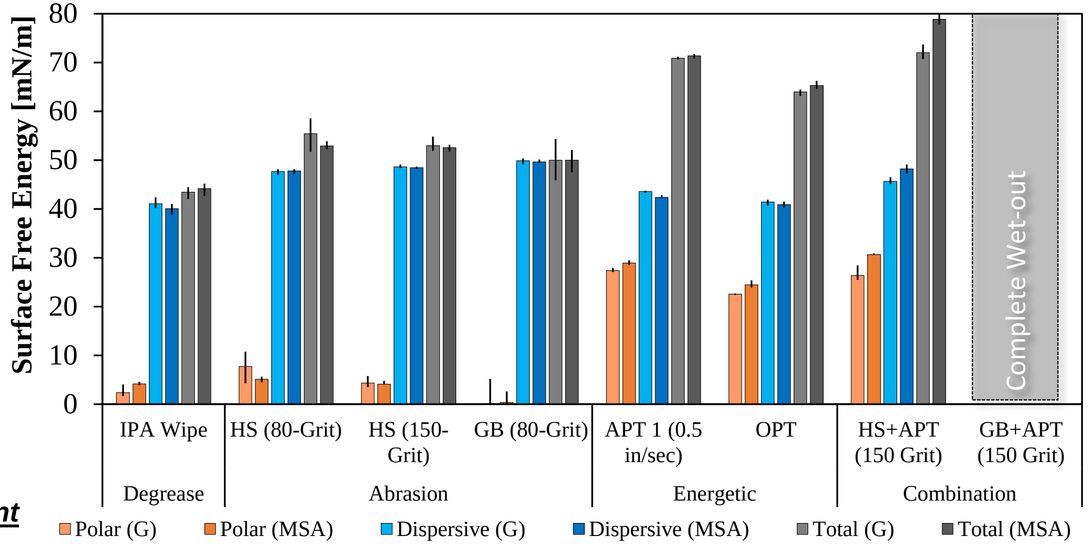


Contact Angle (Surface Analyst)

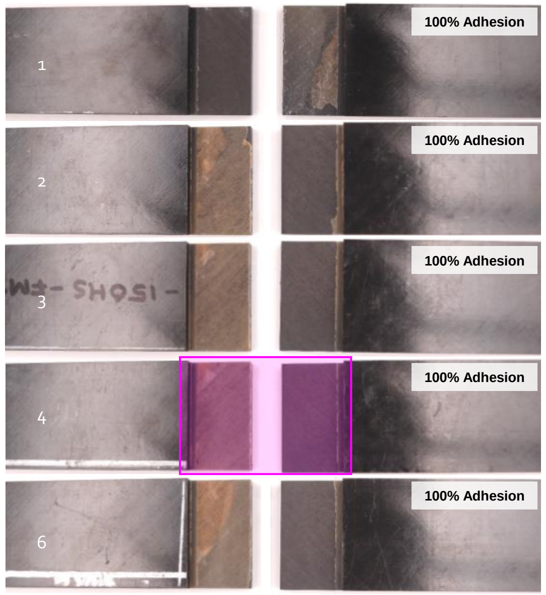


Task 2.2 – Single Lap-Shear Strength Results

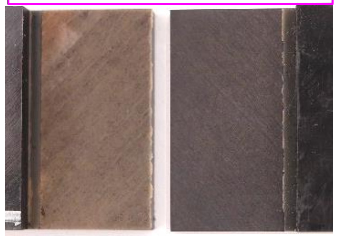
- Similar trends in strength and failure modes witnessed between paste and film adhesive results for the various surface preparation methods
- 100% adhesion failures for all degrease and abrasion surface treatments
- Although a higher surface free energy was recorded for combination treatments, a lower strength was witnessed in comparison to atmospheric plasma only treatments
- Surface roughness did not significantly influence the apparent shear strength results » considering the chemical composition of the surface is more significant than the physical characteristics of the surface such as surface roughness



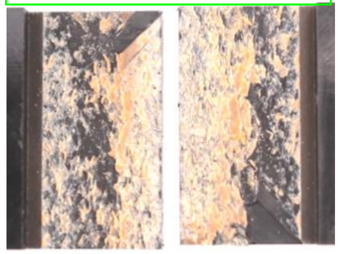
Abrasion: 150G Hand Sand



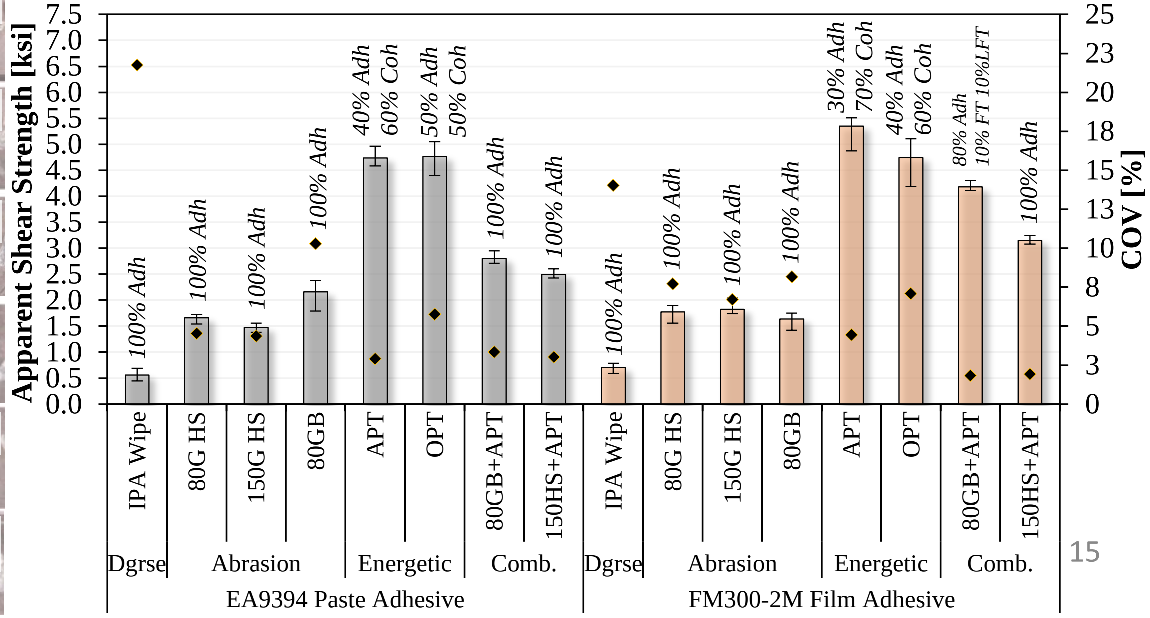
150G Hand Sand
100% Adhesion (4)



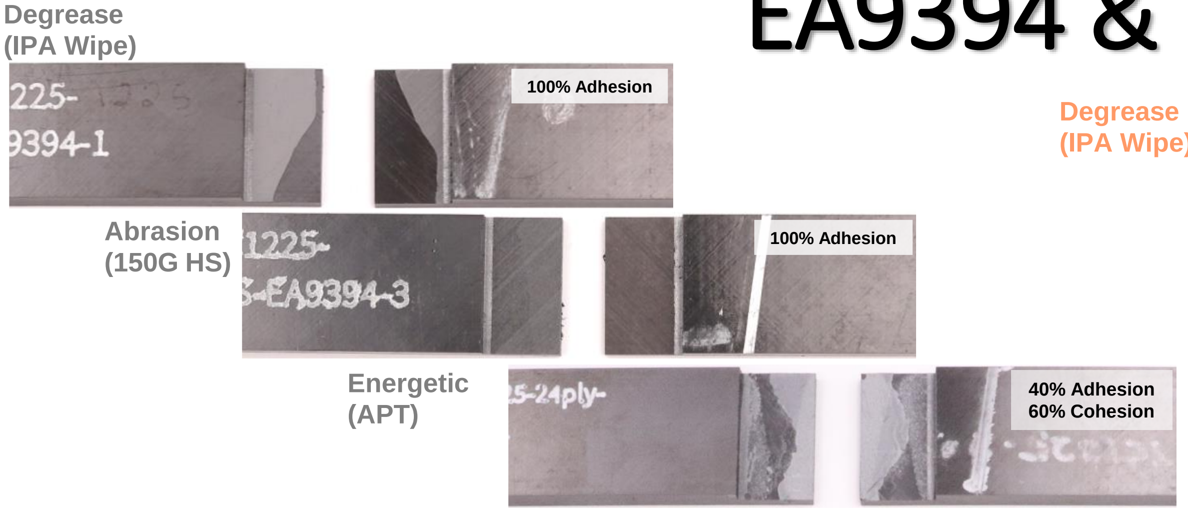
APT
20% Adh, 70% Coh, 10% sub (6)

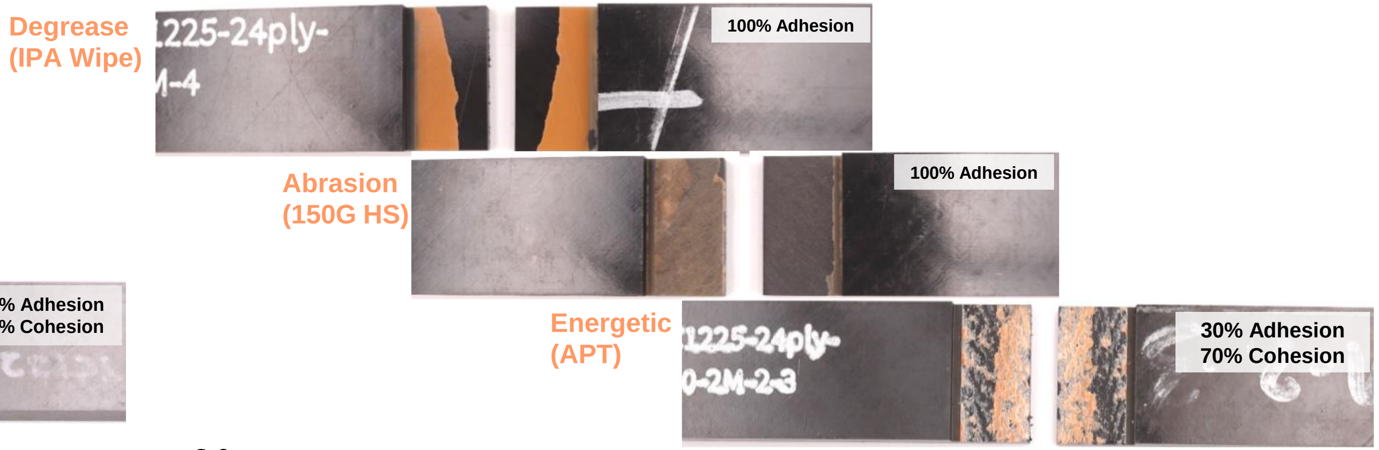


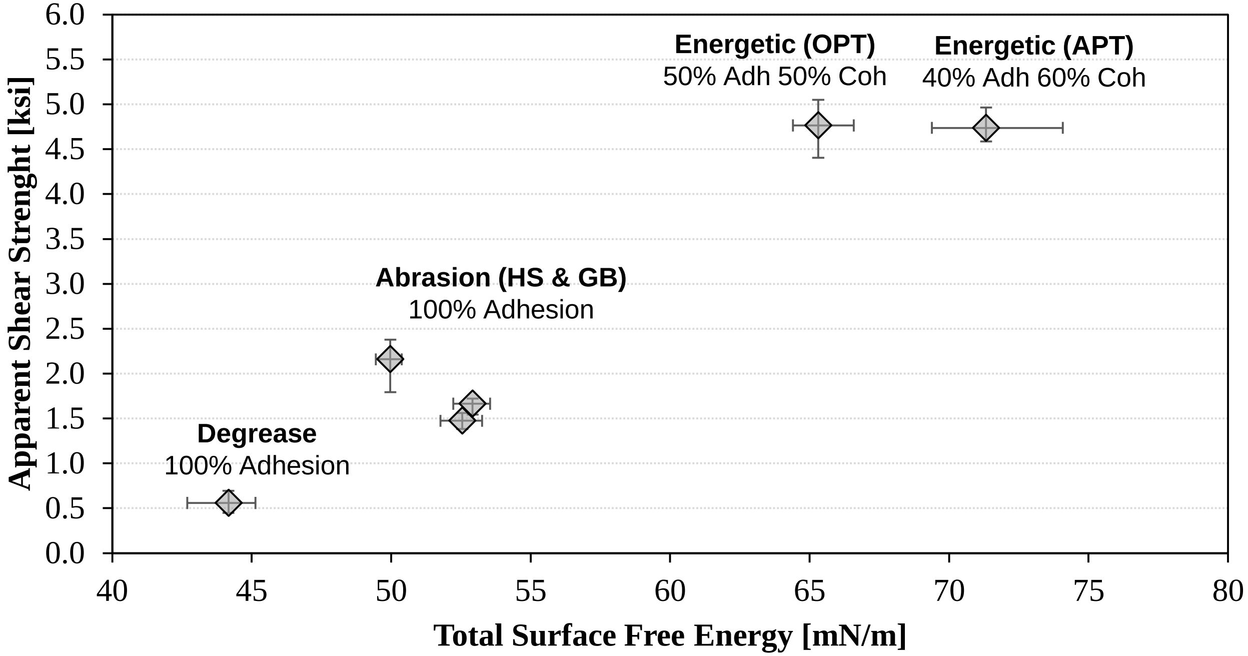
Energetic: Atmospheric Plasma Treatment

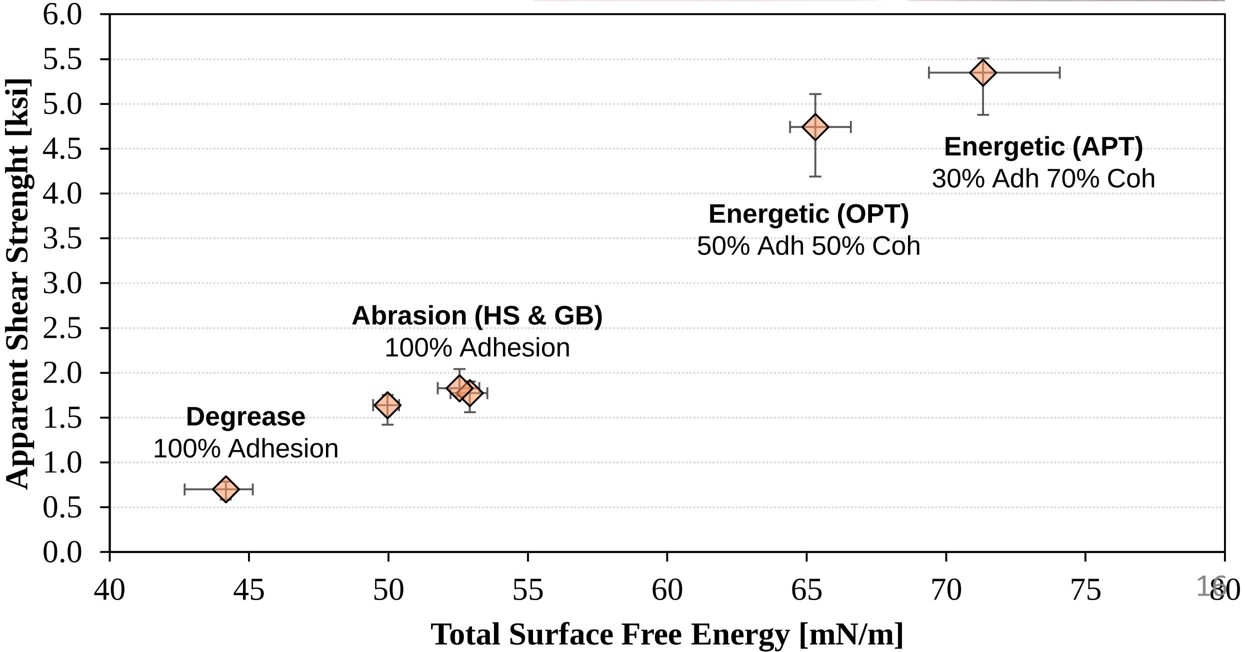


SFE Relationship w/ Shear Strength EA9394 & FM300-2M



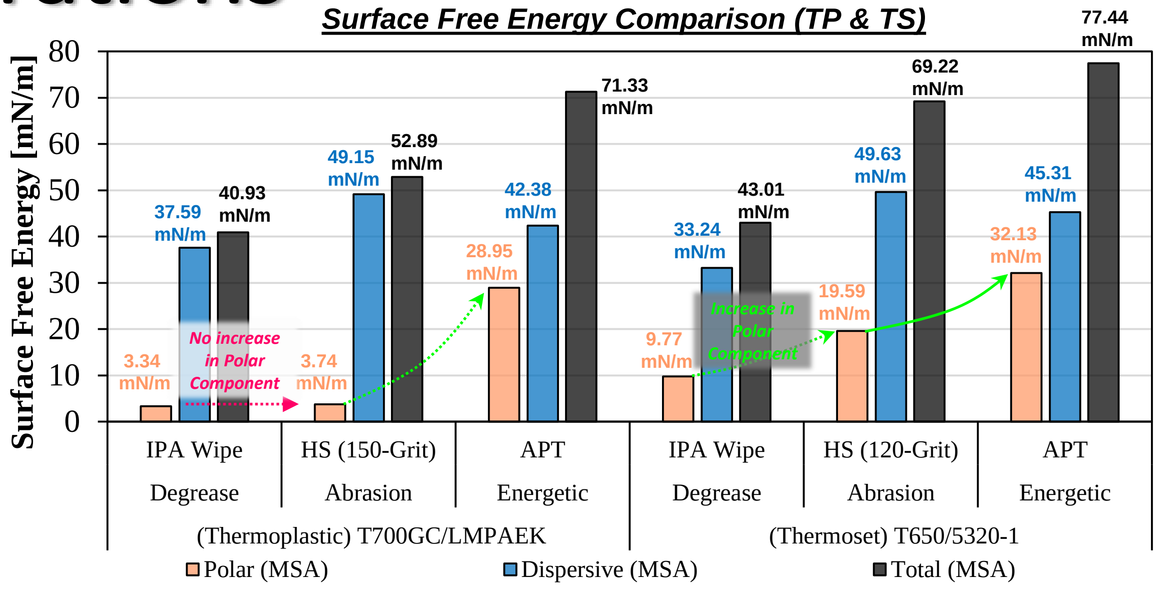


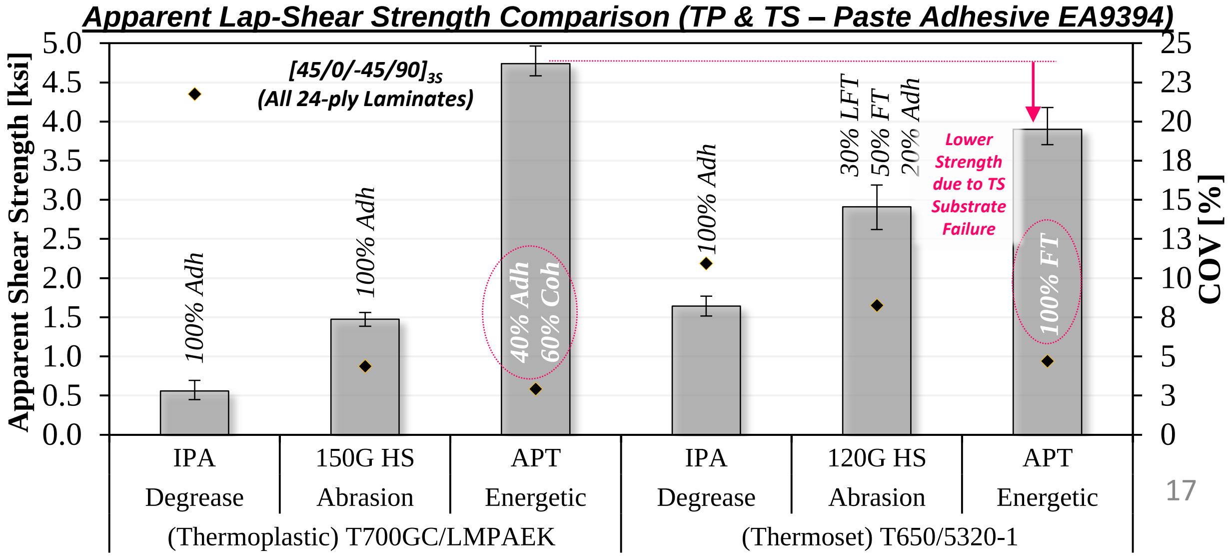




Thermoplastic and Thermoset Adhesive Bonding Considerations

- As mentioned previously, abrasive surface preparation techniques are often associated with increased bond strength and durability when treating thermosets, which is erroneously interpreted as a result from the mechanical interlocking (keying) due to the increased surface area & roughness instead of chemical bonds
- In reality, the overall reactivity of the surface is increased as the inert oxide layer is removed from the surface of the thermoset substrate and the polymer chains are opened (chemically activated)
- First ply substrate failures are often witnessed with thermoset adhesively bonded joints (properly designed joint)
  - This isn't always the case when bonding thermoplastic composites with epoxy adhesives designed for thermosets due to the increase in strength (toughness) associated with thermoplastic substrates

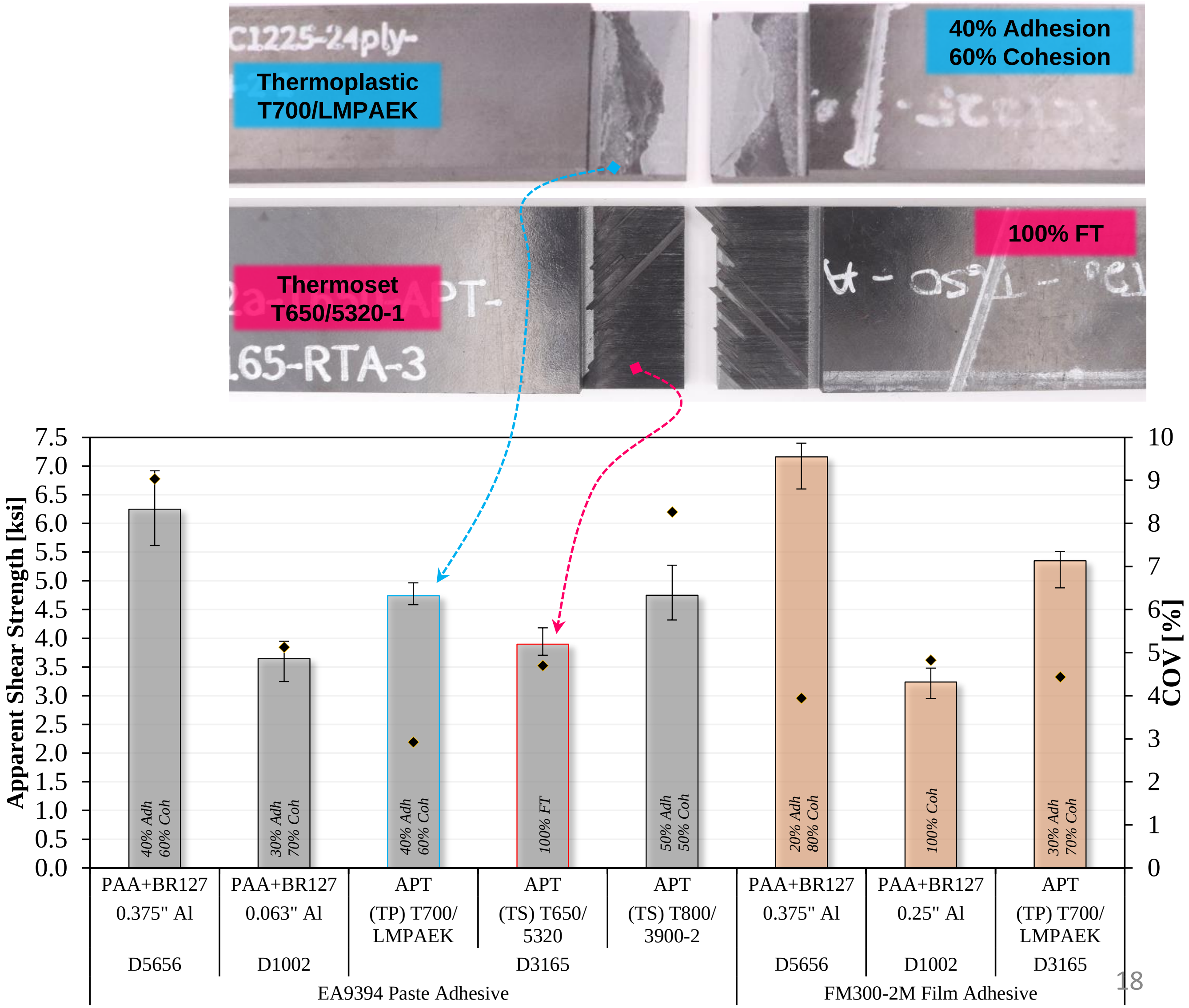




Comparison of Substrate and Adhesive Properties

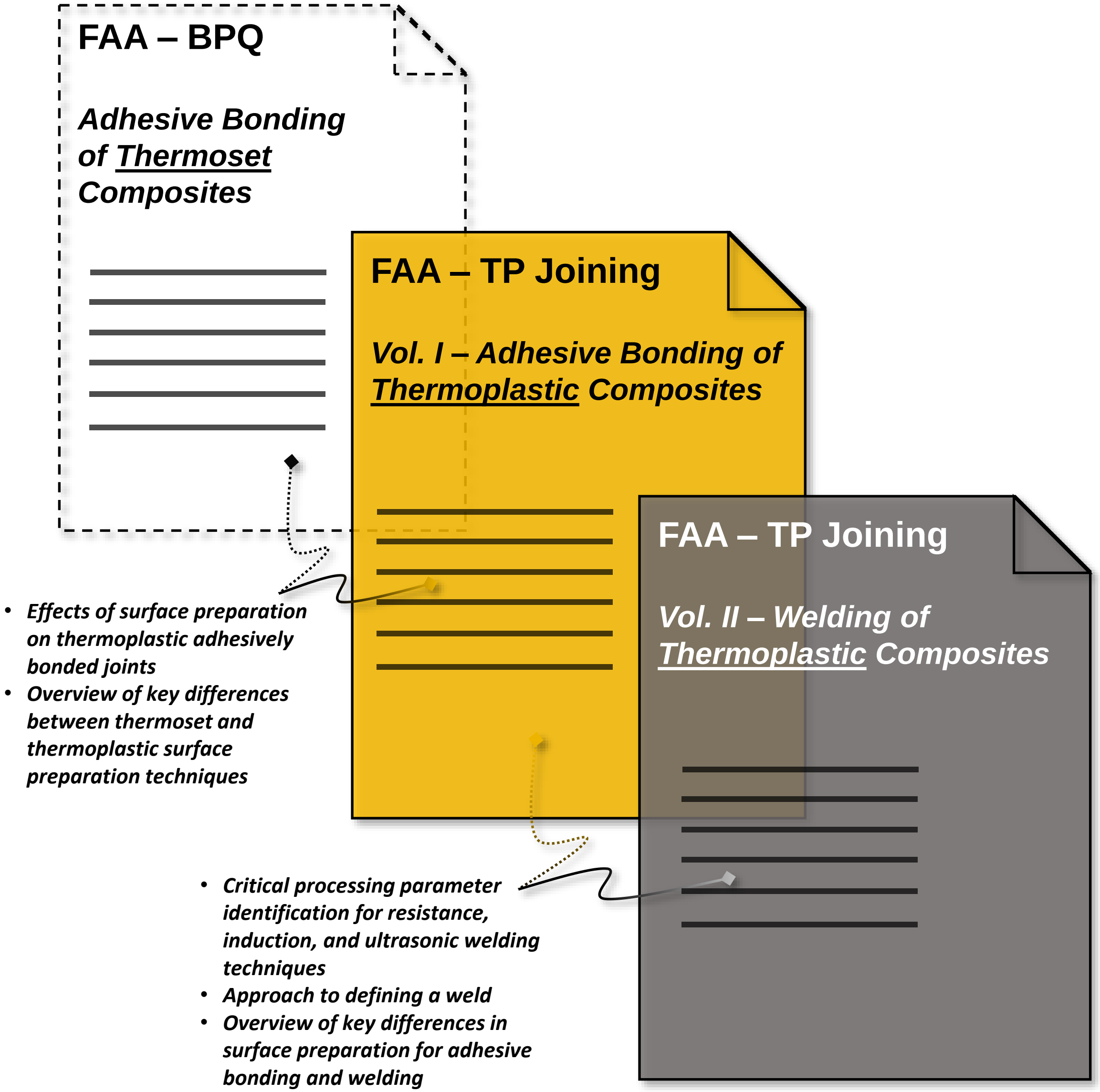
- Thermoset & Thermoplastic Substrate Interlaminar Property Comparison
  - Toray TC1225 (Thermoplastic)
    - Mode I Interlaminar Fracture Toughness G_{IC}= **2.1 kJ/m²**
    - Mode II Interlaminar Fracture Toughness G_{IIC}= **2.6 kJ/m²**
  - T650/5320 (Thermoset)
    - Mode I Interlaminar Fracture Toughness G_{IC}= **0.109 kJ/m²**
    - Mode II Interlaminar Fracture Toughness G_{IIC}= **0.746 kJ/m²**
  - T800/3900-2 (Thermoset)
    - Mode I Interlaminar Fracture Toughness G_{IC}=**0.419 kJ/m²**
    - Mode II Interlaminar Fracture Toughness G_{IIC} = **1.187 kJ/m²**
- Various Substrate Bond Properties (EA9394 & FM300-2M)
  - ASTM D5656 (thick metal adherends)
    - Al 2024 T351 (0.375" thick)
  - ASTM D1002 (thin metal adherends)
    - Al 2024 T351 (0.063" thick)
  - ASTM D3165 (composite adherends)
    - T700/LMPAEK (24-ply – APT)
    - T650/5320-1 (24-ply – APT) (Paste Adhesive only)
    - T800/3900-2 (24-ply – APT) (Paste Adhesive only)

Higher interlaminar properties associated with thermoplastics can change failure mode in comparison to thermoset composites. Bond interfacial strength is then highly interrogated.



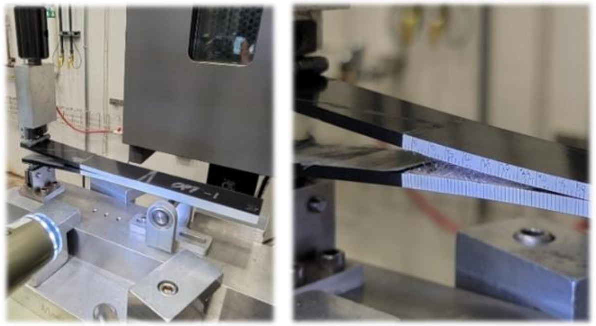
Adhesive Bonding of Thermoplastic Composites Summary

- As with any bond process (thermoset or thermoplastic), the **surface preparation process** is critical in achieving a **strong reliable bond**
- Abrasion surface preparation techniques that have been historically used to prepare thermoset composites are insufficient for thermoplastic composites because the surface is not chemically activated in the abrasion process
- Atmospheric plasma treatment can increase the surface free energy (specifically the polar surface free energy) and chemically activate the substrate to form a strong bond with the adhesive
- Minimal substrate failures were witnessed with thermoplastic bond failures due to the increase in interlaminar properties associated with thermoplastics over thermosets
- Findings will be reported in a series of reports:
  - **Thermoplastic Structural Joining Materials Guidance for Aircraft Design and Certification**
    - **Vol. I – Adhesive Bonding of Reinforced Thermoplastic Composites**
    - Vol. II – Welding of Reinforced Thermoplastic Composites



Looking Forward / Future Work

- Benefit to Aviation
  - Generating guidance materials for adhesive bonding and welding reinforced thermoplastic composites
  - Identification of critical processing parameters in the adhesive bonding and weld processes to aid in establishing process controls



- Next Steps:
  - Complete adhesive bond DCB testing
  - Documentation of findings in Vol I. Report
    - **Thermoplastic Structural Joining Materials Guidance for Aircraft Design and Certification**
      - **Vol. I – Adhesive Bonding of Reinforced Thermoplastic Composites**
  - Thermoplastic Welding Studies

Contact & References

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  - Brandon Saathoff (bsaathoff@niar.wichita.edu)

1. Ashforth, C., Ilcewicz, L., “Certification of Bonded Aircraft Structure and Repairs,” FAA, STO-MP-AVT-266.
2. Tracey, A. C., Dalal, H., Belcher, M. A. (Tony), Ferriell, D. R., Hall, K. L., Blohowiak, K. Y., Thomas, S. K., Blohowiak, D. A., Johnson, B. S., Grace, W. B., Voast, P. J., “Bonding the Unbondable: Thermoplastics!,” CAMX 2017 (Orlando, FL 2017), The Composites and Advanced Material Expo.
3. Shultz, K. A., Davis, A. C., “Surface Preparation Techniques for Adhesion to Aerospace Thermoplastic Composites,” SAMPE 2017 (Seattle, WA 2017), Society for the Advancement of Material Process and Engineering.
4. Blackman, B., Kinlock, A. J., Watts, J. F., “The Plasma Treatment of Thermoplastic Fibre Composites for Adhesive Bonding,” 1993.
5. Baldan, A. “Review - Adhesively-bonded joints and repairs in metallic alloys, polymers and composite materials: Adhesives, adhesion theories and surface pretreatment,” Journals of Material Science, 2004.
6. “Surface treatment for adhesive bonding: Thermoset vs. Thermoplastic composites,” Composites World, 2020.