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NASA TEERM Cr6+ Free Bond Primer Replacement Project

ASETS Defense 2016

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Global Substances Program
Raytheon Missile Systems
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NASA TEERM

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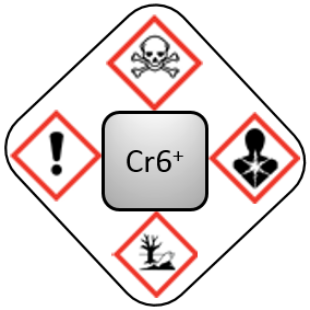
Cr6+ Free Bond Primer Replacement

Goal:

Produce Joint Test Protocol to provide data necessary to justify use of DFARS-compliant hexavalent chromium free bond primers for aerospace applications



Advantages

- Chromate inhibitors anticipated to provide superior corrosion protection
- Structural performance up to 300°F
- Adhesion strength with multiple substrates, surface preparations, & adhesive systems
- Demonstrated performance meeting aerospace/defense requirements for decades
- Preservation of surface
  - Allows extended shelf life (years) prior to bonding

Disadvantages

- Contains known human carcinogen
- Most hazardous through inhalation = Priming and sanding!!!
- Reactivation typically requires scuff sanding
- Solvent based system – volatile organic compounds (VOCs)
- Increasingly Regulated Globally
  - REACH, RoHS, DFARS, etc.
- Restrictions and Regulatory Compliance Driving up the Cost
  - Procurement and Use and Safety

Consortium Members/Major Tasks

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INDUSTRY

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BOEING
LOCKHEED MARTIN
BOMBARDIER the evolution of mobility
TEXTRON AVIATION
Pratt & Whitney · Sikorsky · United Technologies · Otis · United Technologies Research Center · United Technologies · UTC Aerospace Systems
GE Aviation
NORTHROP GRUMMAN
HARRIS
Piper

GOVERNMENT

NAVAIR
AFRL THE AIR FORCE RESEARCH LABORATORY LEAD | DISCOVER | DEVELOP | DELIVER
NASA

ACADEMIA

UMASS LOWELL
TURI TOXICS USE REDUCTION INSTITUTE UMASS LOWELL

- Generate Joint Test Protocol (entire team)
- Locate Potential Suppliers (NASA TEERM)
- Generate SOW (sub-team)
- Evaluate Quotes/Select Supplier(entire team)
- Manage supplier relations (Raytheon)
- Materials management (Bombardier)
- Condition Panels (AFRL)
- Salt Fog Testing (NASA)
- Wedge Crack Testing (NAVAIR)
- Evaluation of Adhesion/Corrosion (NASA/UTC)
- Statistical Analysis of Data (TURI)
- Report (sub-team)
- Peer Review (entire team)
- Publish Data/Article (NASA/TURI)

Complete
Currently In Work
Pending

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Joint Test Protocol

- Evaluation Tests
  - Neutral Salt Spray Testing for Corrosion Resistance (ASTM B117)
  - Wedge Crack Extension Testing for Adhesion (ASTM D3762)
- Substrates – Aluminum alloys
  - 7075-T6
  - 2024-T3
  - 2219
- Surface Preparations
  - Grit Blast Only
  - Grit Blast/Sol Gel (3M AC-130-2)
  - Phosphoric Acid Anodize (ASTM D3933)
    - Using AmChem 6-16 deoxidizer – contains Cr6+

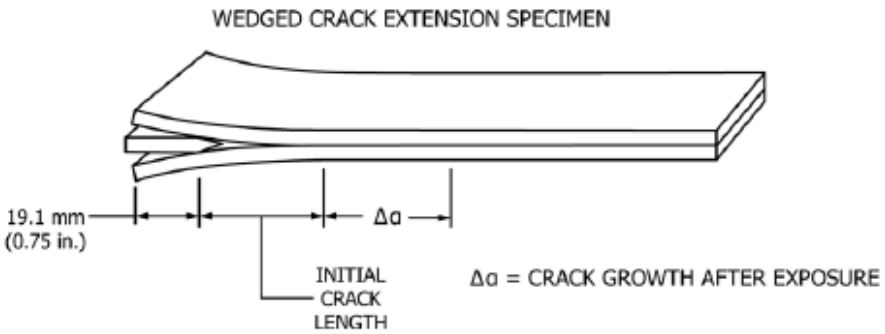

FIG. 1 Crack Extension Specimen Configuration

- Primers - Baseline Material – Cytec BR-127
  - 3M
    - EW 5000-ET: corrosion inhibitor package does not contain chromates
    - EW 5005: corrosion inhibitor package does not contain chromates, not yet commercially available
  - Cytec -Solvay
    - BR-127 NC: no corrosion inhibitor package
    - BR-252: corrosion inhibitor package does not contain chromates
    - BR-6747-1-NC: no corrosion inhibitor package
- Adhesives
  - 3M AF 163-2K (knit carrier, areal weight: 0.045 pounds/ft^2)
  - Cytec FM73 (knit carrier, areal weight: 0.045 pounds/ft^2)

3M

CYTEC
SOLVAY GROUP

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Project Overview

- Consortium Members generated a JTP and a SOW to have the surface preparations, priming, and bonding completed at a single supplier.
  - Triumph Fabrications Ft. Worth selected and contracted
    - Includes language regarding the process for the various procedures
    - Not considered proprietary by Triumph and no NDAs were required – all materials provided
      - Surface Prep/Bond Primers/Adhesive Bonding

Triumph Group, Inc.

- Second set of PAA/BR127 test panels tested in parallel prepared by Textron Aviation using their process
  - Instead of AmChem deox, PAD was used
- NAVAIR performing wedge crack testing (ASTM D3762)
  - Two different environmental conditions; 9-week exposures, 168 hour increment inspections
    - Neutral Salt Fog (NSF) Testing (ASTM B117)
    - Elevated Temperature/Humidity (140°F/ 95-100% RH)
- NASA performed corrosion resistance testing on bond primer only panels
    - Neutral Salt Fog (NSF) Testing (ASTM B117)
      - 1000 hours with 168 hour increment inspections

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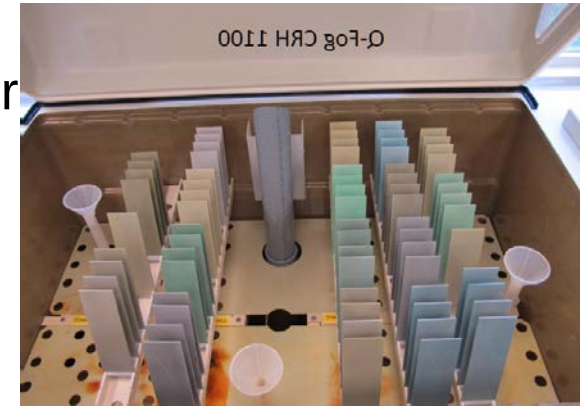
Salt Fog Testing

- 10” X 3” 2024 Al panels shipped to Triumph for preparation
  - Phosphoric acid anodize, grit blast, or grit blast/sol-gel
  - Apply primer and bond, as required
- Application of primers done IAW manufacturers instructions
- 3M and Cytec representatives on site for application

- Panels were scribed with Roland Modela MDX-40
  - X/Y speed = 10mm/sec ; spindle rpm =5000
  - Tool = 1/16” 4 flute carbide ball end mill

- Panels underwent neutral salt fog testing
  - IAW ASTM B117 at NASA Kennedy Space Center
  - 40 days IAW BMS5-89, 5-137, ASTM E1826
    - (1000 hours)



2024 GB Only Surface Prep – NSF @ 1008 hours

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2024 – GB/AC-130 Surface Prep NSF @ 1008 hours

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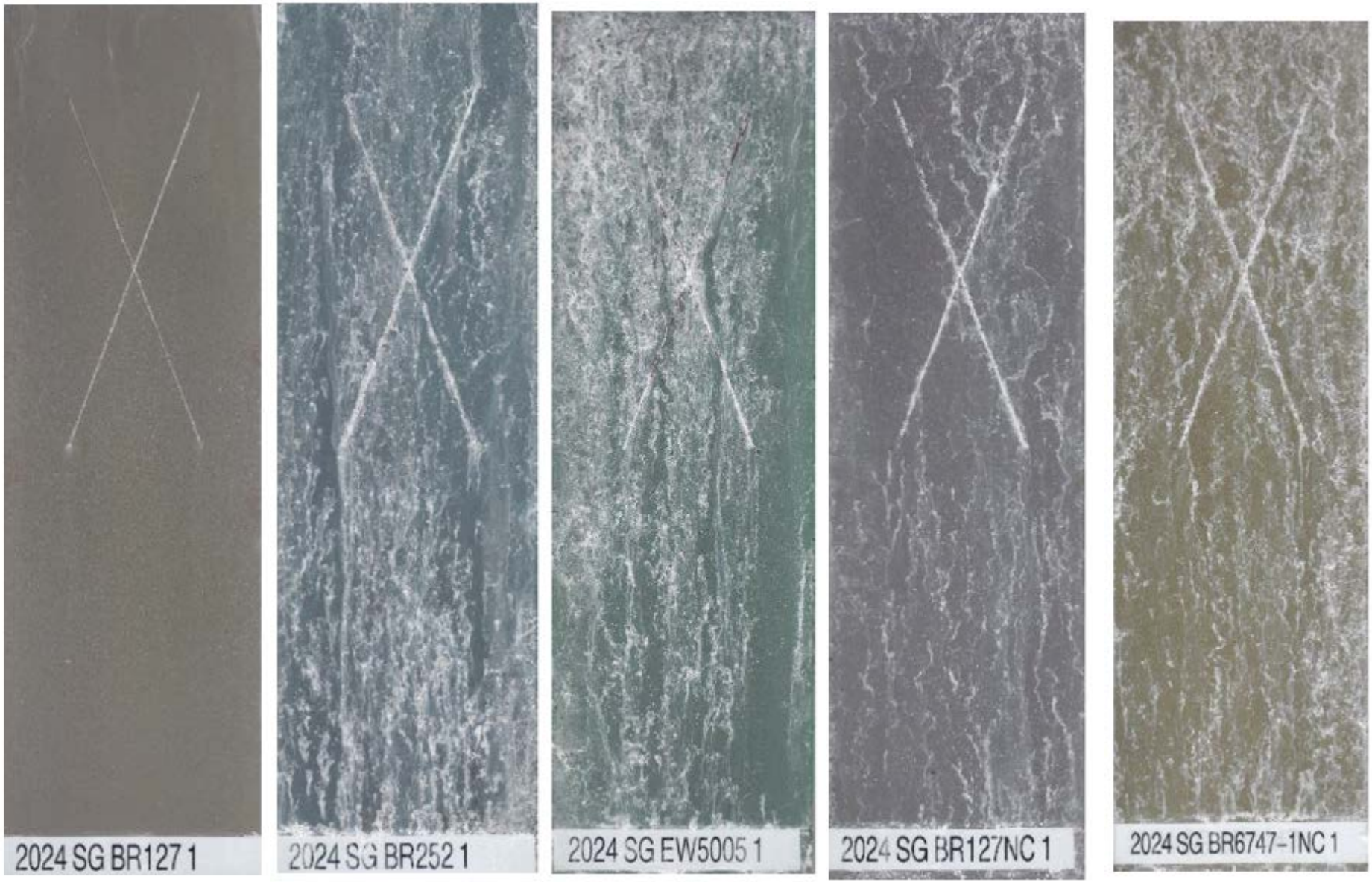

2024 – PAA Surface Prep NSF @ 1008 hours

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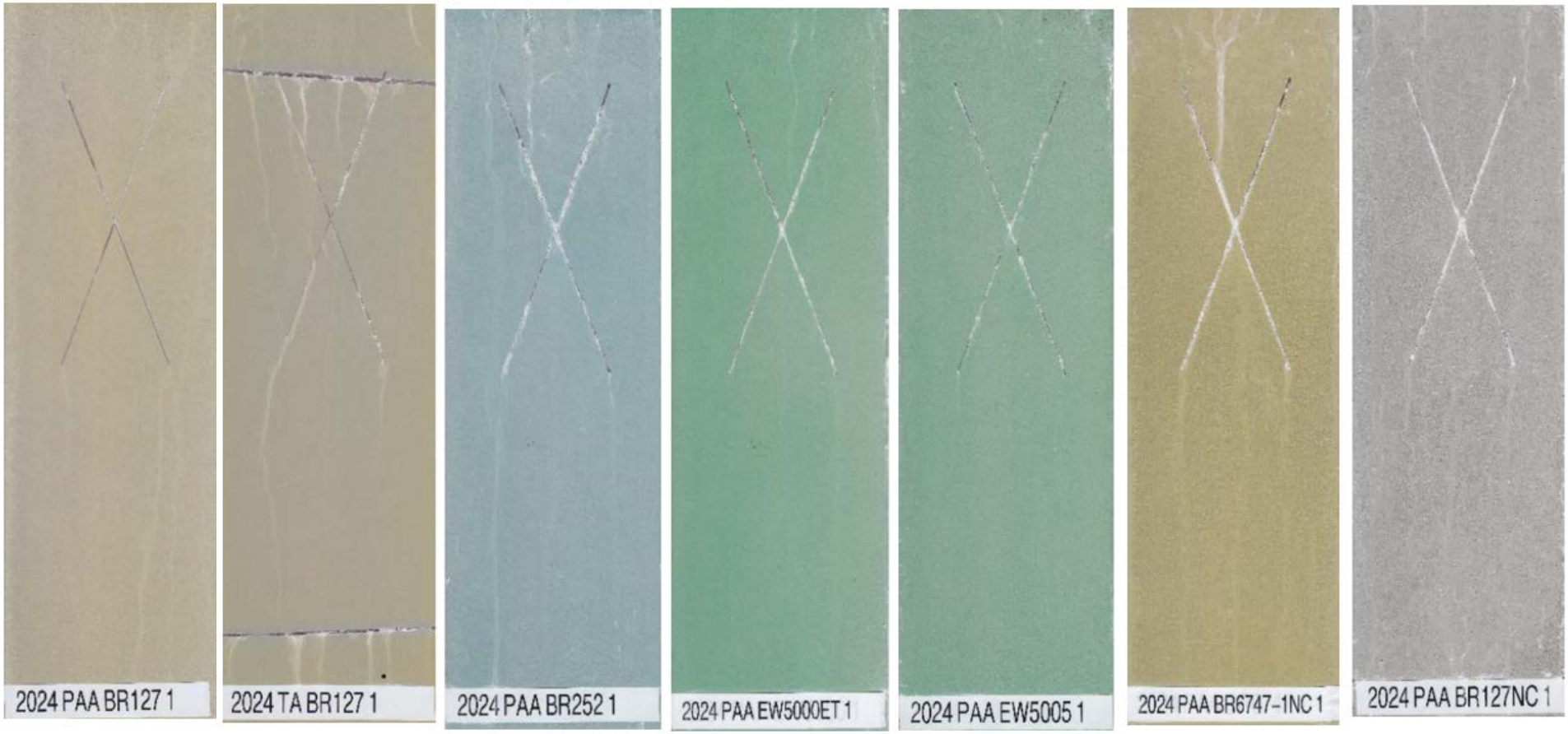

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Salt Fog Summary on 2024 panels

- Grit Blast Only Surface Treatment
  - Corrosion was observed outside the scribe on all alternate primers at 168 hours
  - BR-127 lasted till 504 hour inspection before corrosion outside the scribe was observed
  - No materials passed; therefore grit blast only may not an acceptable surface treatment on 2024 T3 Al with bare BR127

- Grit Blast and AC-130-2 (GB/SG) Surface Treatment
  - Corrosion was observed outside the scribe on all alternate primers at 168 hours
  - BR-127 lasted through the 1000 hour requirement with no corrosion outside the scribe
  - Grit Blast and AC-130-2 surface treatment is an insufficient surface treatment to provide the required 1000 hour neutral salt fog requirement for any of the alternative bond primers tested

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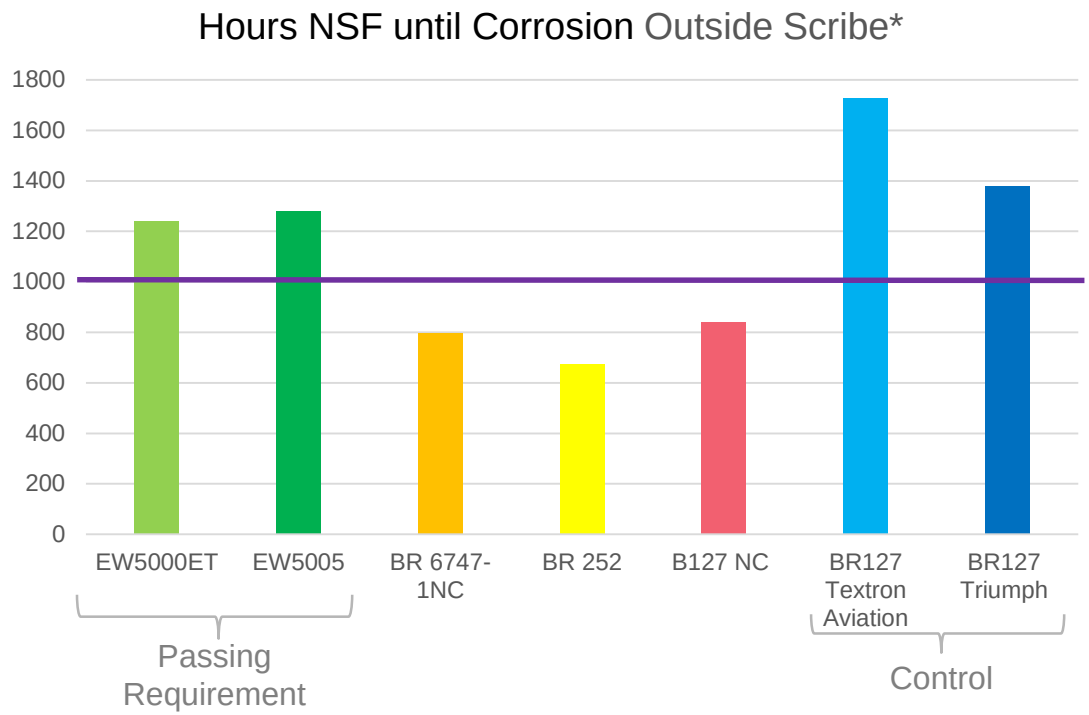
2024 Neutral Salt Fog Testing Summary

- Phosphoric Acid Anodize surface treatment showed the most promising results of all three surface treatments evaluated with the alternative bond primers
- 3M EW 5000-ET and EW5005 showed no corrosion outside the scribe after 1000 hours
- Variability in the samples from Triumph and Textron Aviation on the BR127 control
  - Two panels from Triumph failed at 504 hours, while the remaining two panels passed the 1000 hour requirement and well beyond
  - All four panels from Textron passed the 1000 hour requirement and beyond



*Data plotted based on average time when each of four samples of the group showed any corrosion outside the scribe

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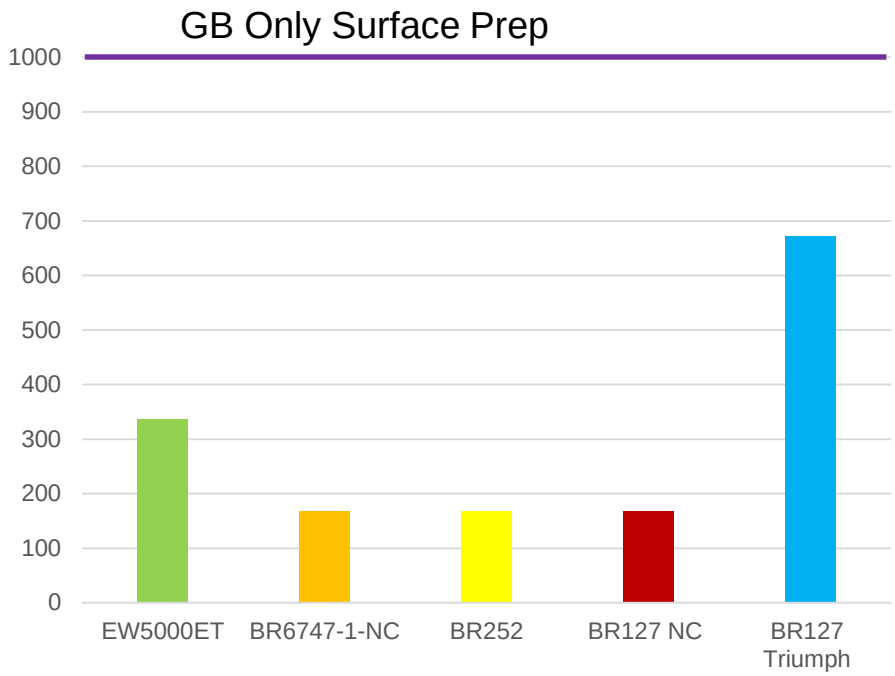
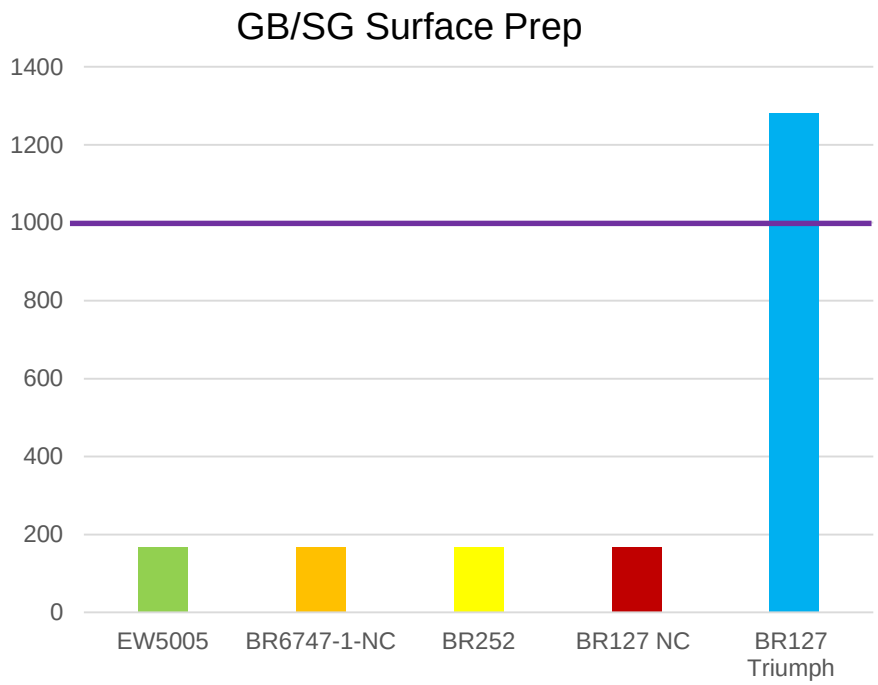
7075 Neutral Salt Fog Testing Summary

- GB only surface preparation
  - No materials passed; therefore grit blast only may not an acceptable surface treatment on 7075 T6 Al with BR127
- GB/SG surface preparation
  - No materials passed; therefore grit blast/sol-gel may not an acceptable surface treatment on 7075 T6 Al with BR127

Hours NSF Exposure until Corrosion Outside the scribe*





*Data plotted based on average time when each of four samples of the group showed any corrosion outside the scribe

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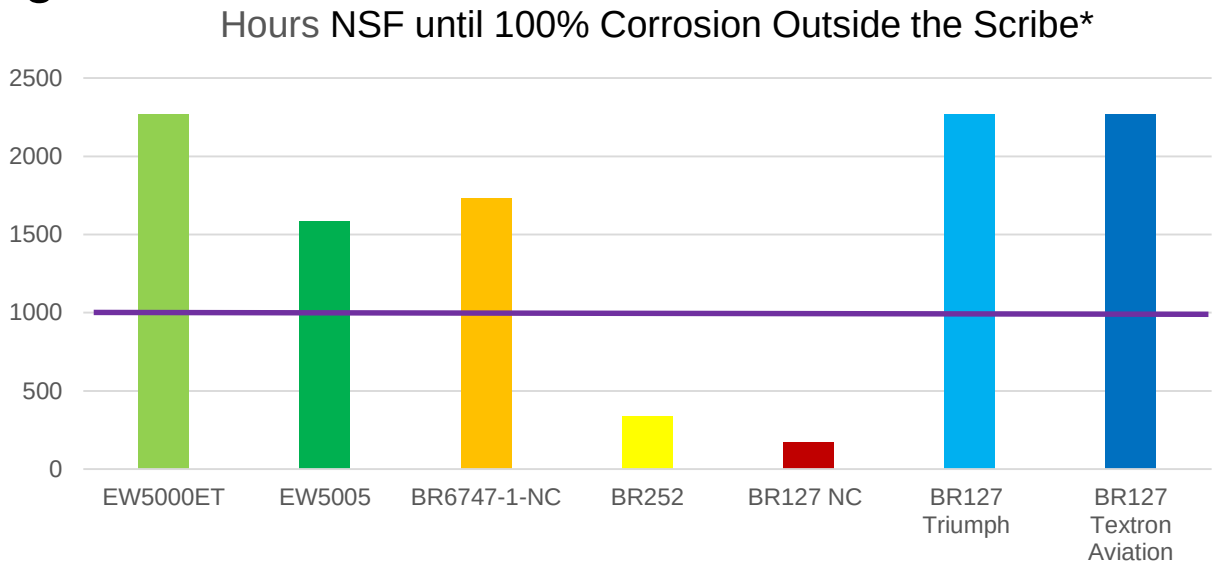
7075 Neutral Salt Fog Testing Summary

- Some alternatives performed better with PAA surface treatment on 7075 than on 2024
- None of the alternative materials achieved the 1000 hour requirement without corrosion inside the scribe
- 3 Candidate materials surpassed the 1000 hour requirement when evaluating corrosion outside the scribe



Bond primers are generally not intended to be left exposed with no other additional corrosion protection; scribe performance impacts shelf life before bonding.

*Data plotted based on average time when each of four samples of the group showed any corrosion outside the scribe

Wedge Crack Extension Testing (ASTM D3762)

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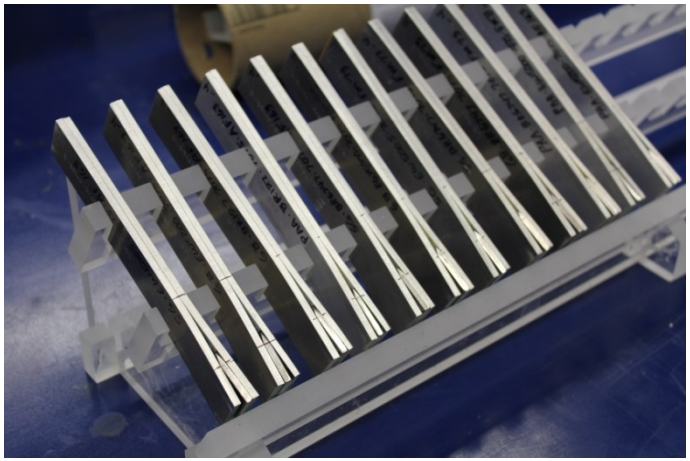
- Over 450 specimens with surface prep/primer/adhesive combinations
  - 3 specimens per condition
  - Two environmental conditions
    - Neutral Salt Fog (ASTM B117)
    - Elevated Temperature and Humidity (ETH) (140°F/95-100%RH)
  - Specimen orientation:
    - NSF exposure oriented ‘bondline up’ and ‘crack down’ at ~30 degrees
    - Elevated Temperature/Humidity (ETW) oriented ‘crack down’ in the chamber
  - Exposure times
    - NSF – 9 weeks
    - ETW – 9 weeks
- 2024 – NSF & ETW
- 7075 – NSF & ETW



POC - Diane Kleinschmidt
Sealants/Adhesives Team Lead
Naval Air Warfare Center - Patuxent River, MD

NSF exposure for GB/SG – 2024 with FM 73

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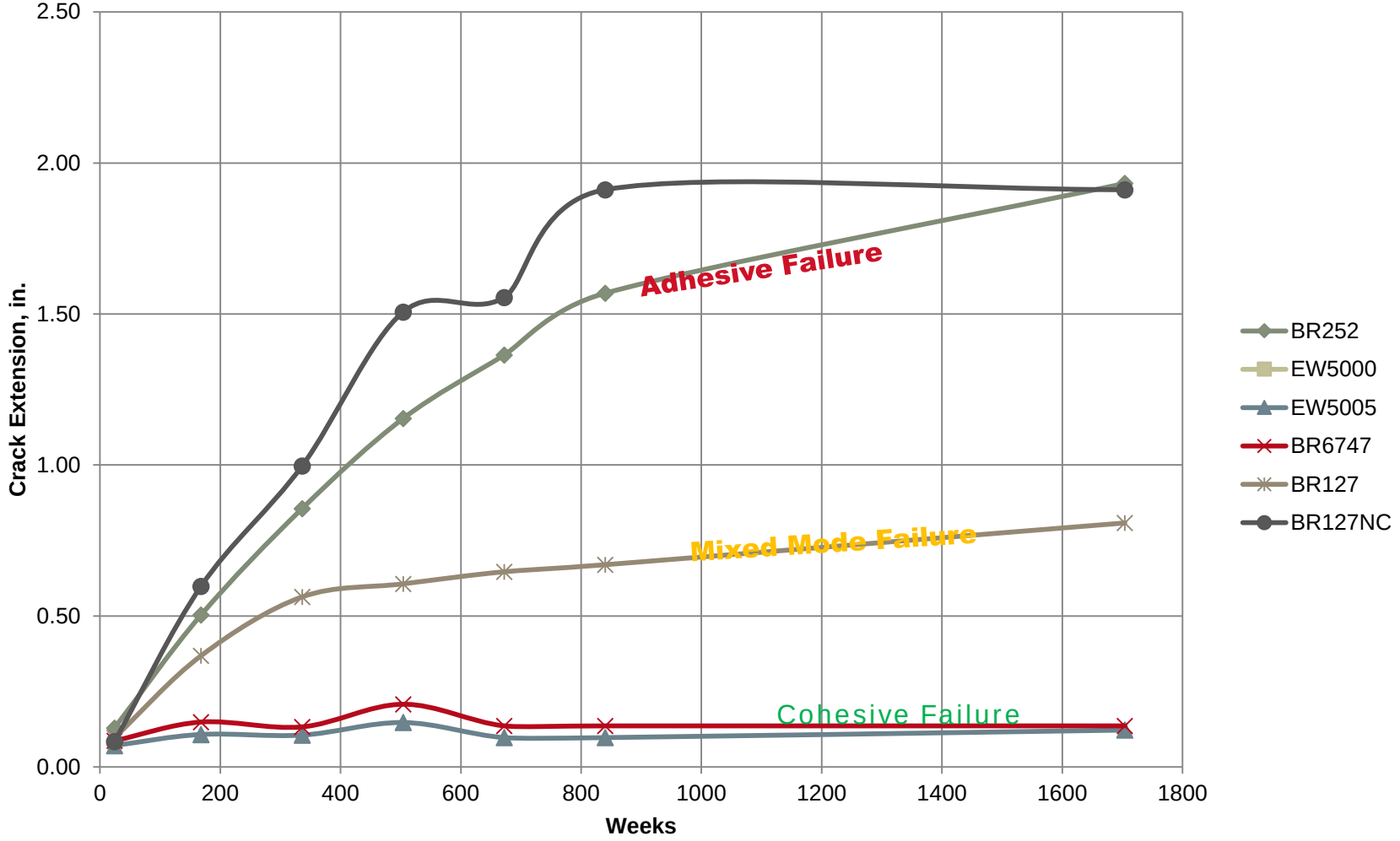

All primers had very similar initial crack growth

EW50005 &BR6747-1NC performed better than control in initial & crack extension

NSF exposure for GB/SG – 2024 with AF 163

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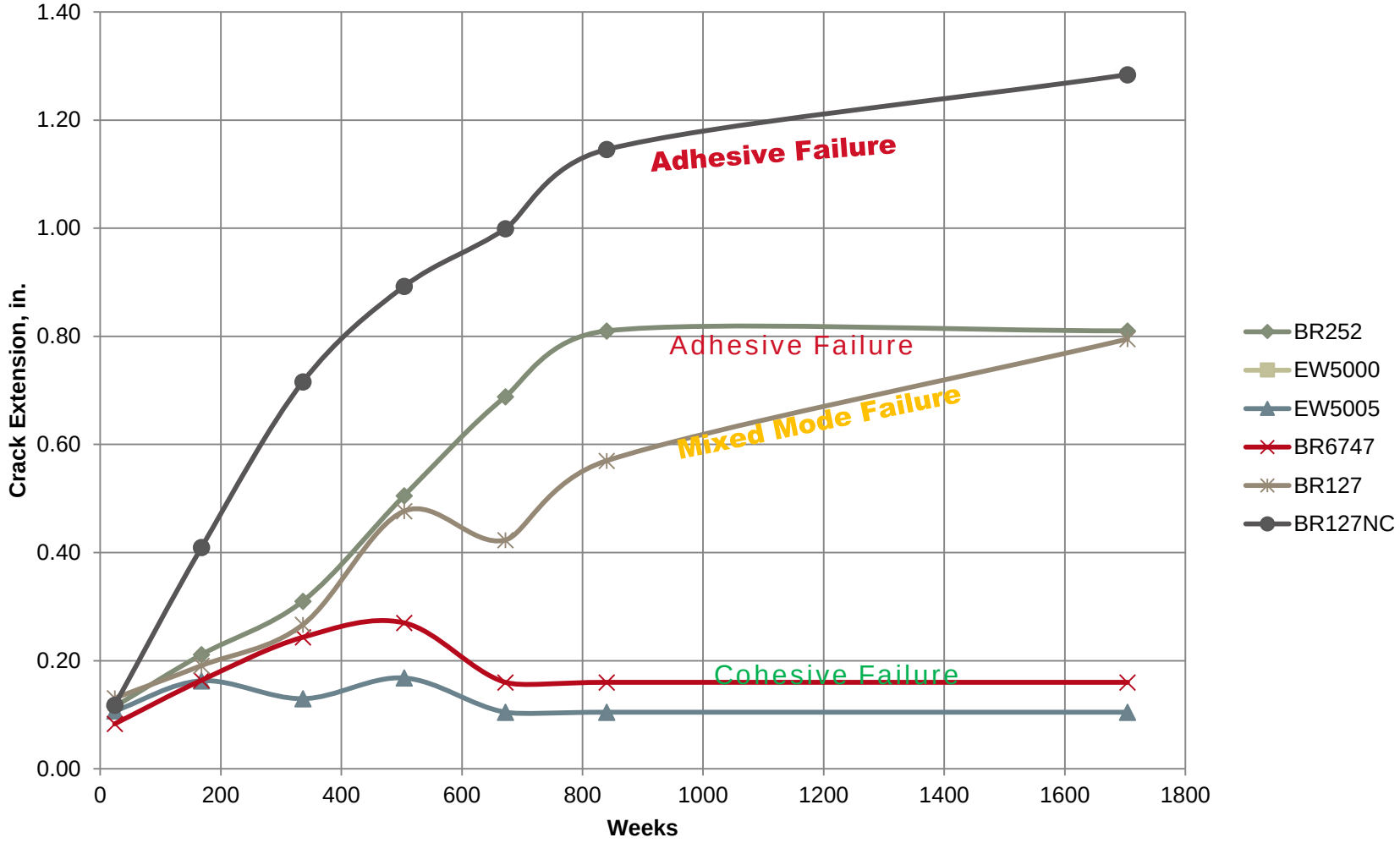

NSF exposure for PAA – 2024 with FM 73

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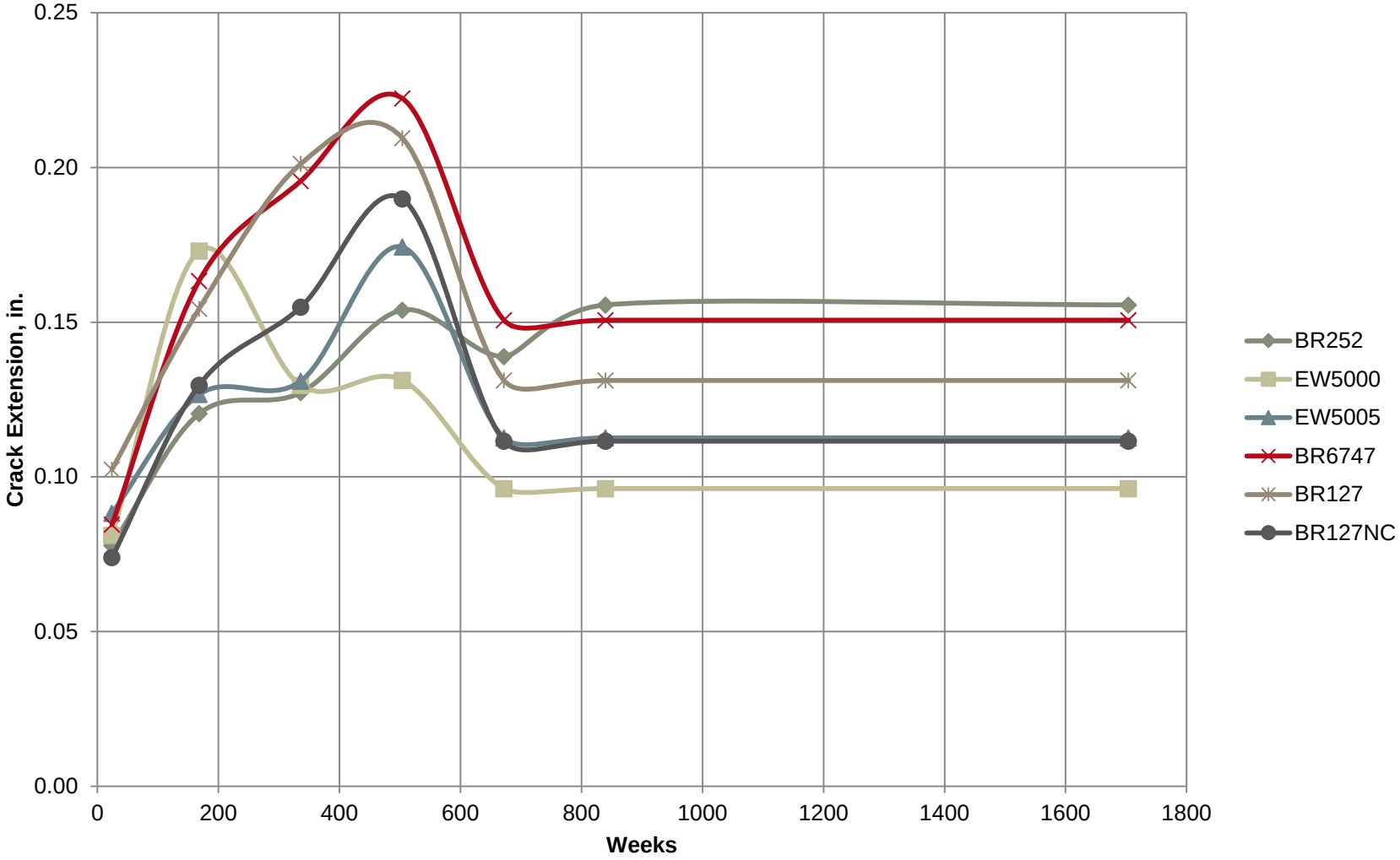

- All alternative bond primers had very similar initial crack and crack extension rates
- Crack extension rate very slow after initial reading
- All PAA samples experienced cohesive failure

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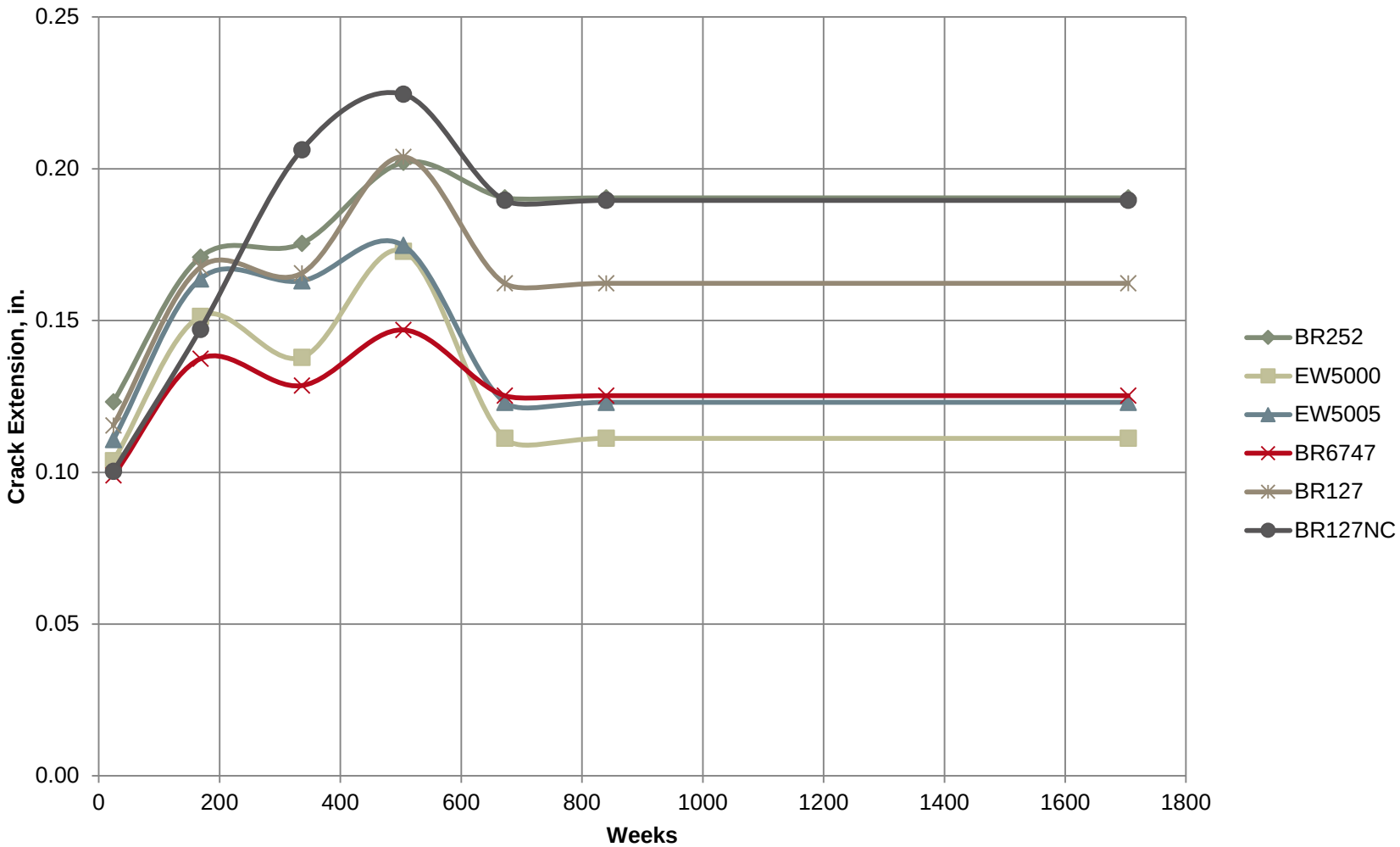
NSF exposure for PAA on 2024 with AF 163



- All alternative bond primers had very similar initial crack and crack extension rates
- Crack extension rate very slow after initial reading
- All PAA samples experienced cohesive failure

ETW exposure for GB/SG – 2024 with FM 73

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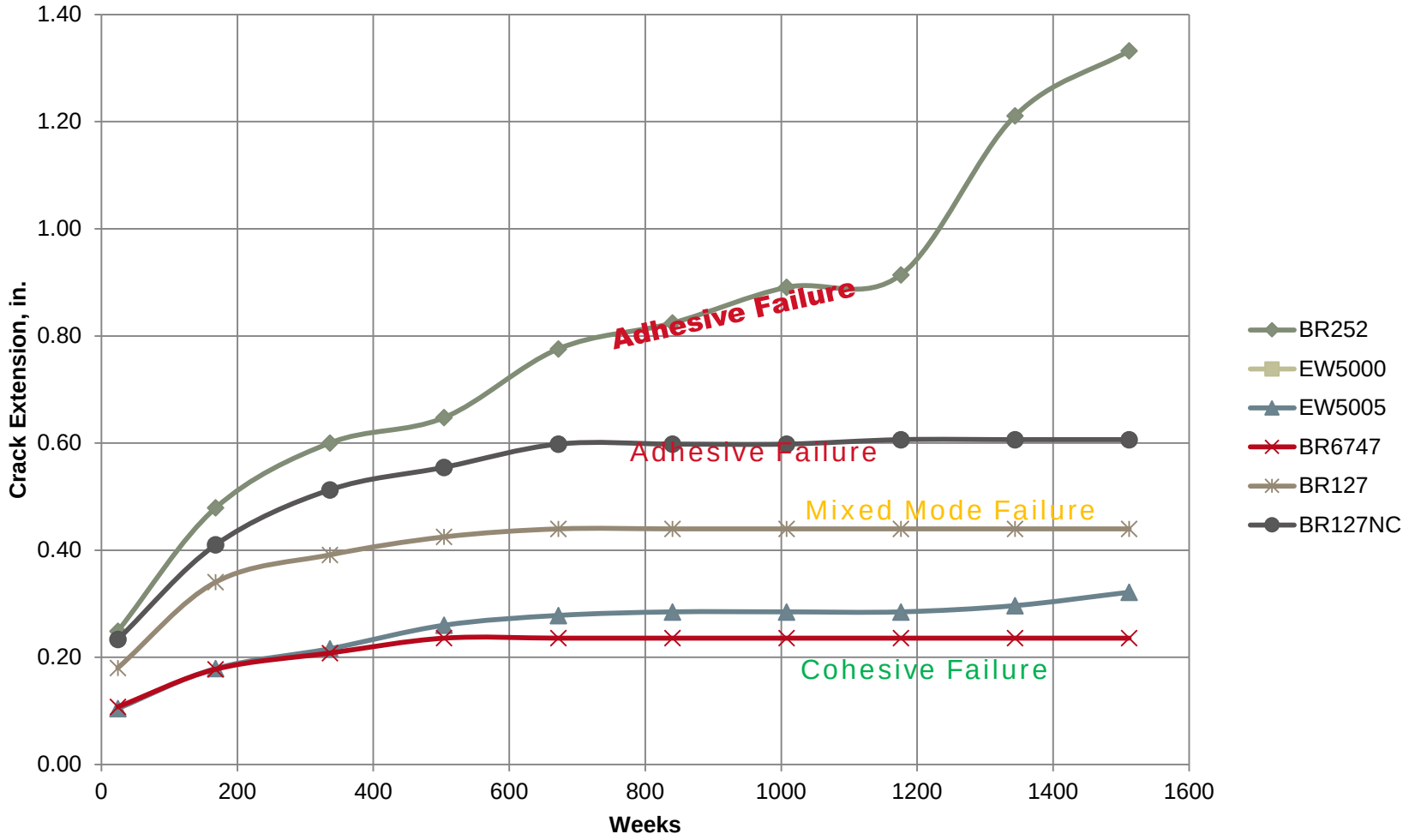

EW50005 and the BR6747-1NC performed better than BR127 control initial crack and crack extension

ETW exposure for GB/SG – 2024 with AF 163

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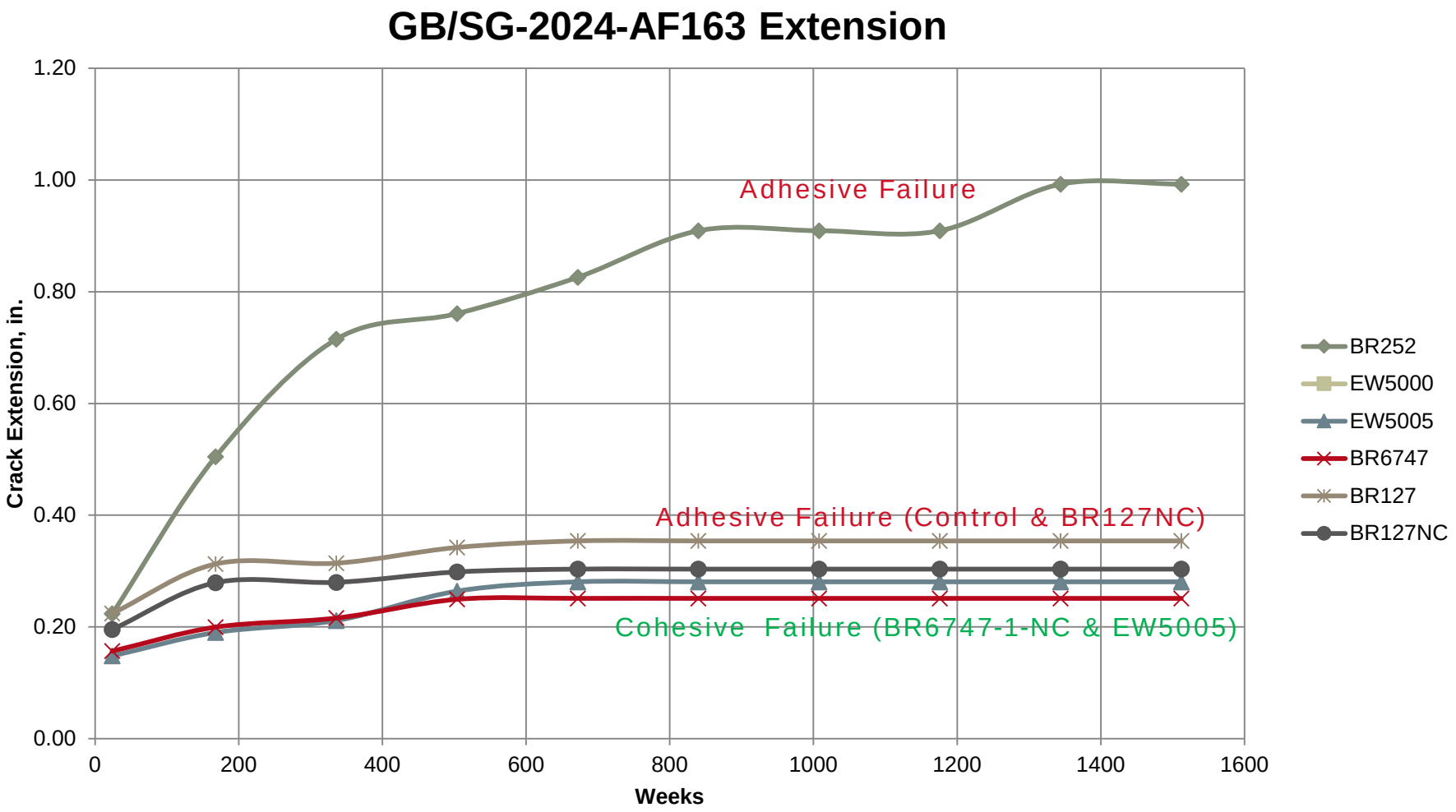

All primers, except BR 252, performed similar to BR127 in initial and crack extension

ETW exposure for PAA – on 2024 with FM 73

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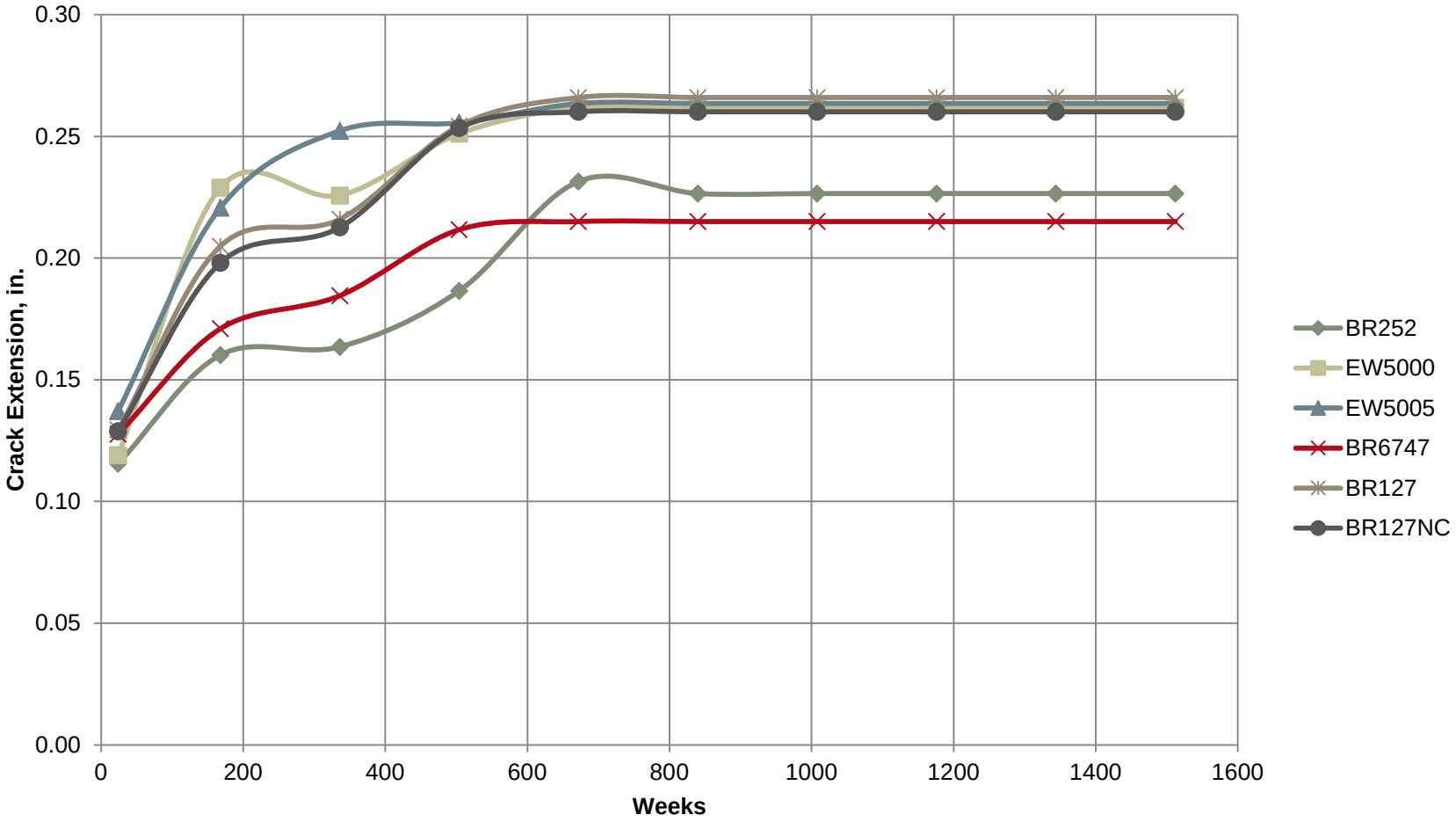

- All alternative bond primers had very similar initial crack and crack extension rates
- Crack extension rate very slow after initial reading
- All PAA samples experienced cohesive failure

ETW exposure for PAA – 2024 with AF 163

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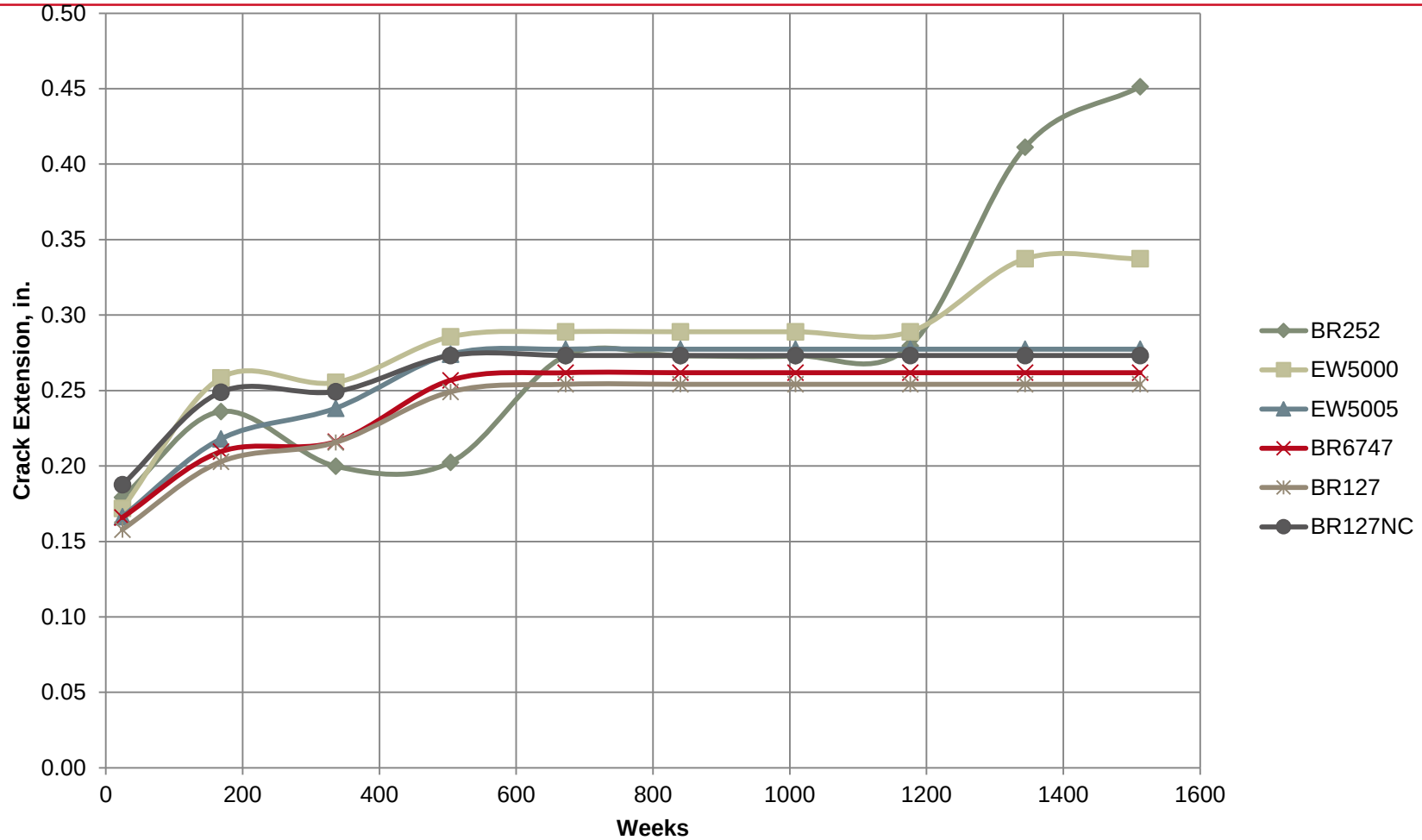

- All alternatives had very similar initial crack extension rates
- Crack extension rate very slow after initial reading
- All PAA WCET samples experienced cohesive failure

NSF exposure for GB/SG on 7075 with FM73

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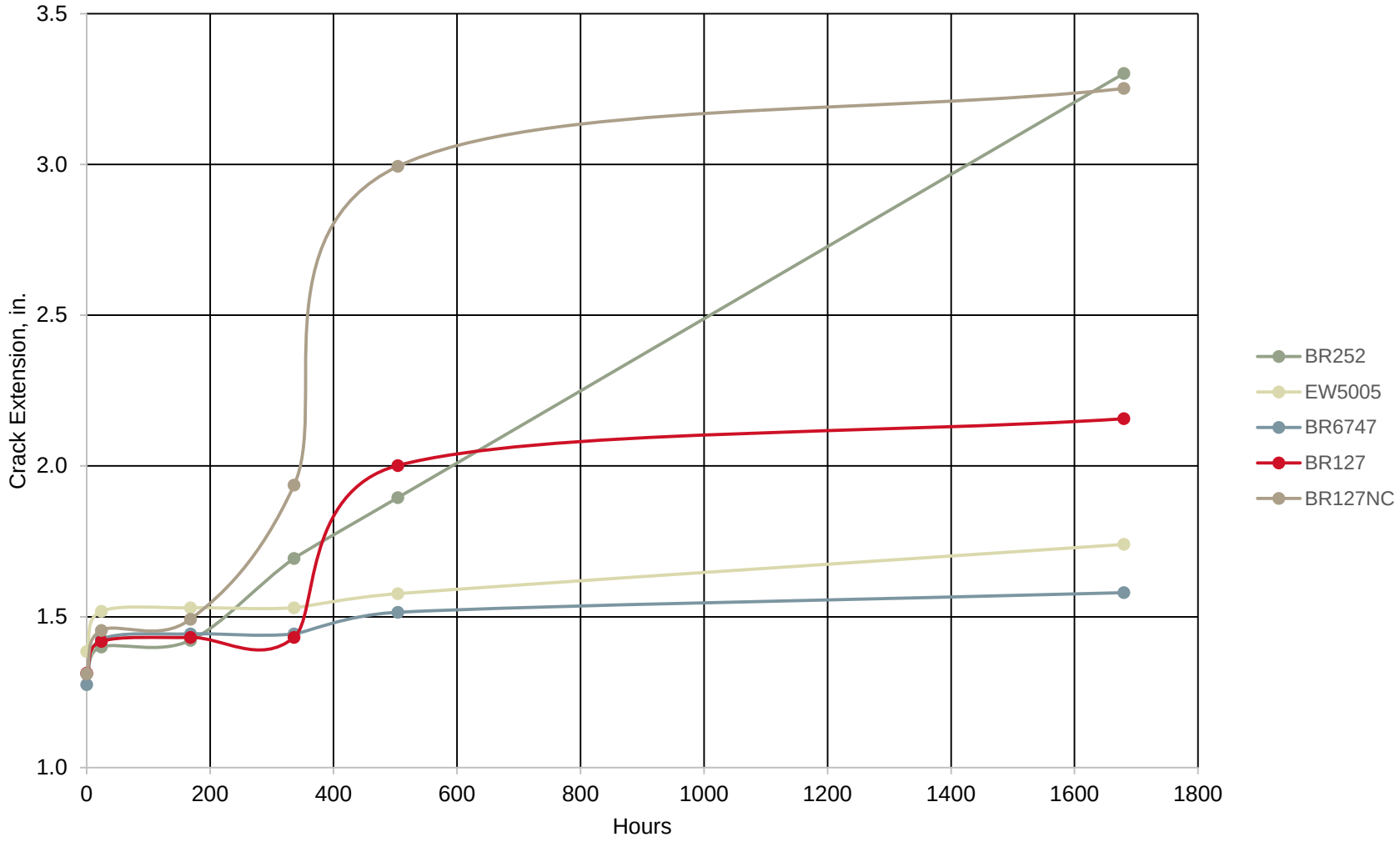

All GB/SG WCET samples experienced adhesive failure

NSF exposure for GB/SG on 7075 with AF163

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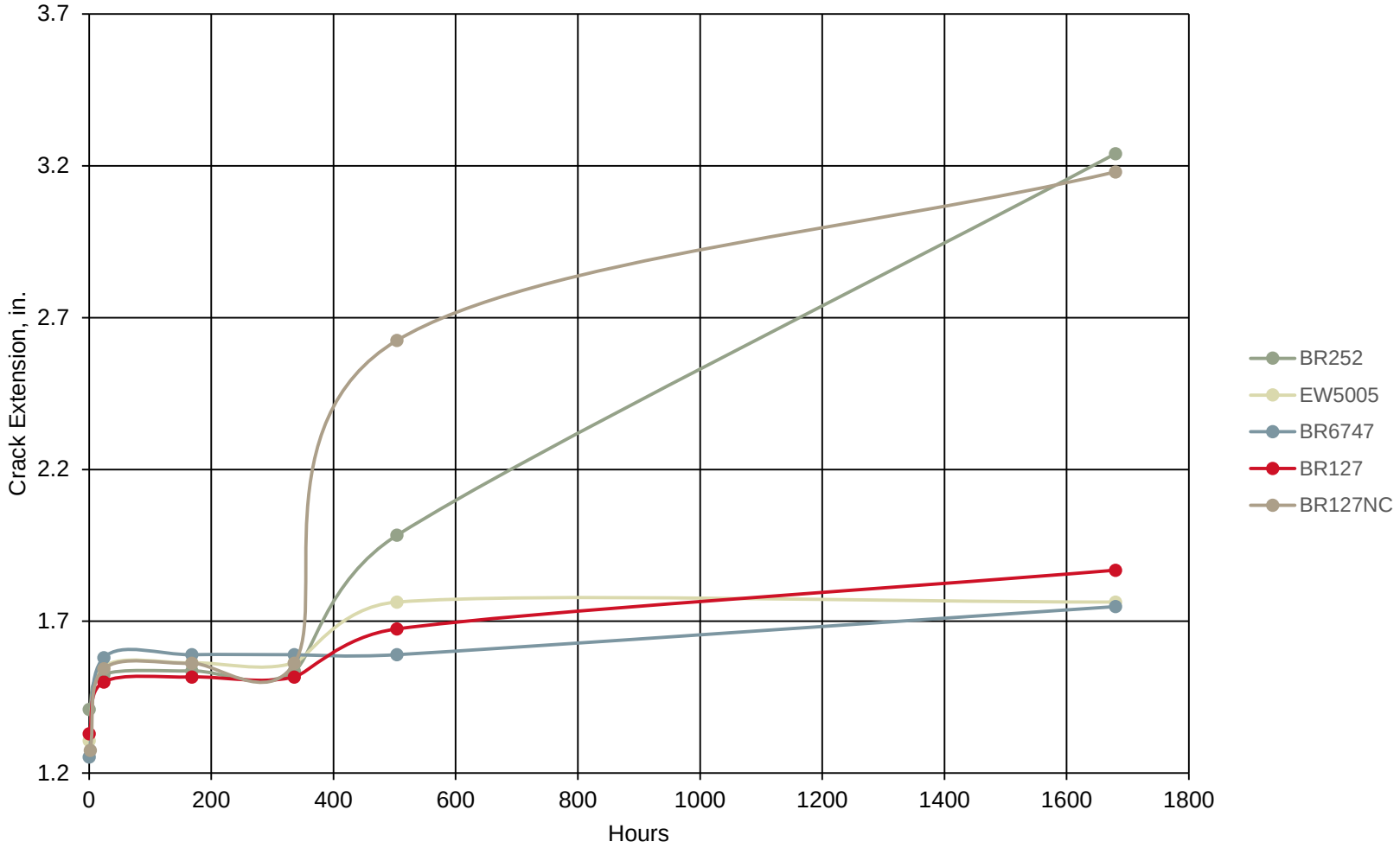

All GB/SG WCET samples experienced adhesive failure except, the EW5005 which was 80% cohesive.

NSF exposure for PAA on 7075 with FM73

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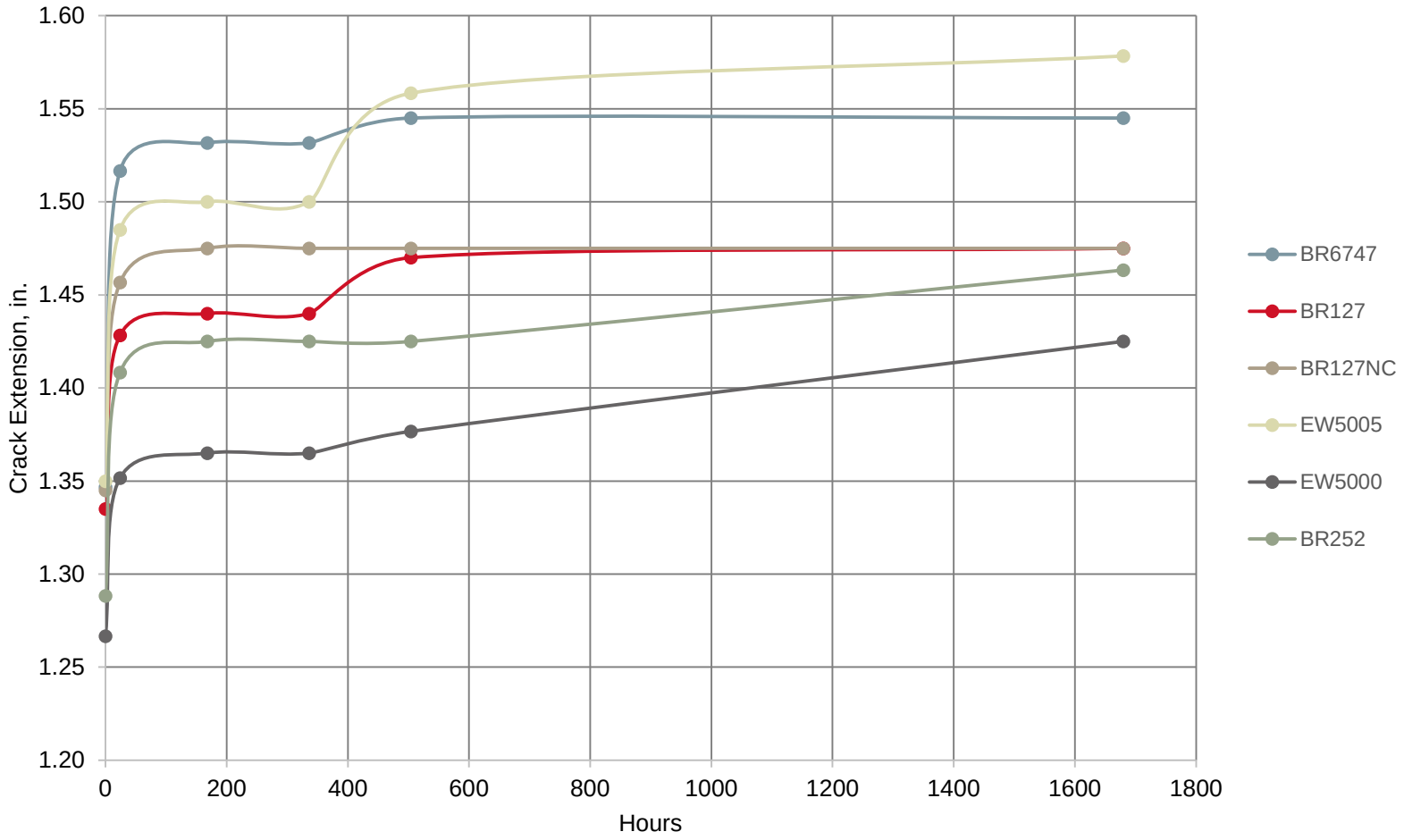

All GB/SG WCET samples experienced cohesive failure

NSF exposure for PAA on 7075 with AF163

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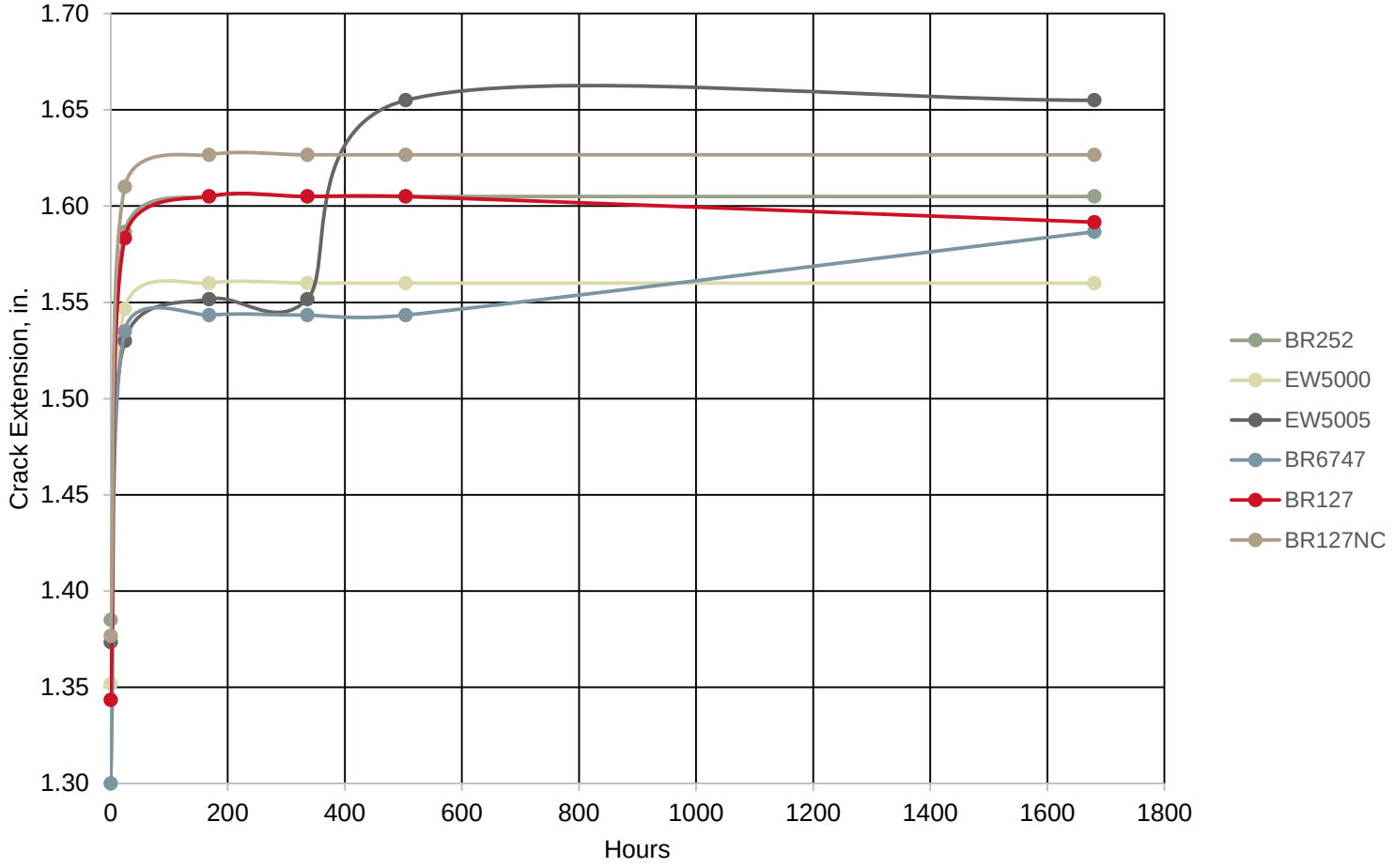

All GB/SG WCET samples experienced cohesive failure except, the BR252 which was adhesive.

ETW exposure for GB/SG on 7075 with FM73

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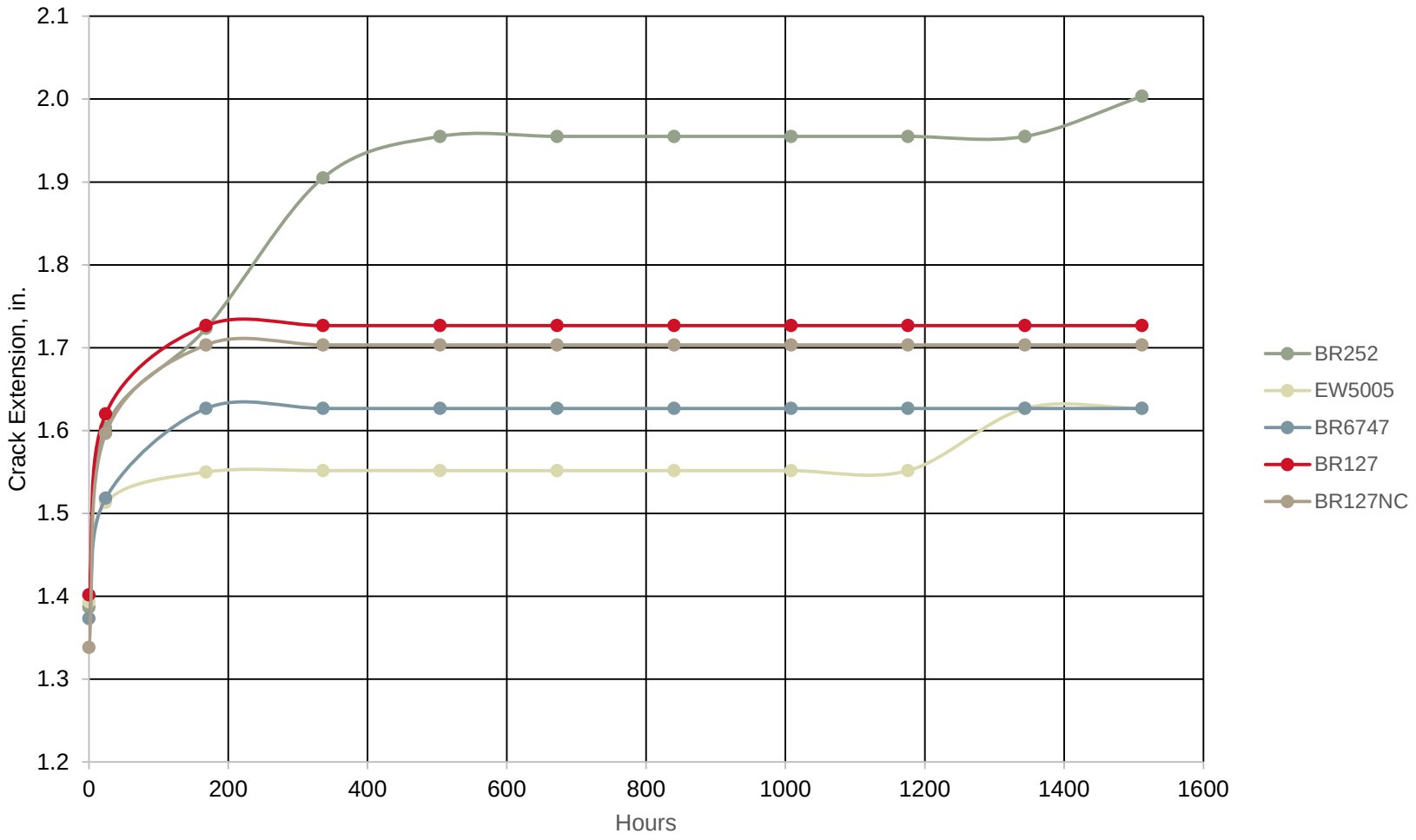

All GB/SG WCET samples experienced adhesive failure except, the BR6747 which was cohesive.

ETW exposure for GB/SG on 7075 with AF163

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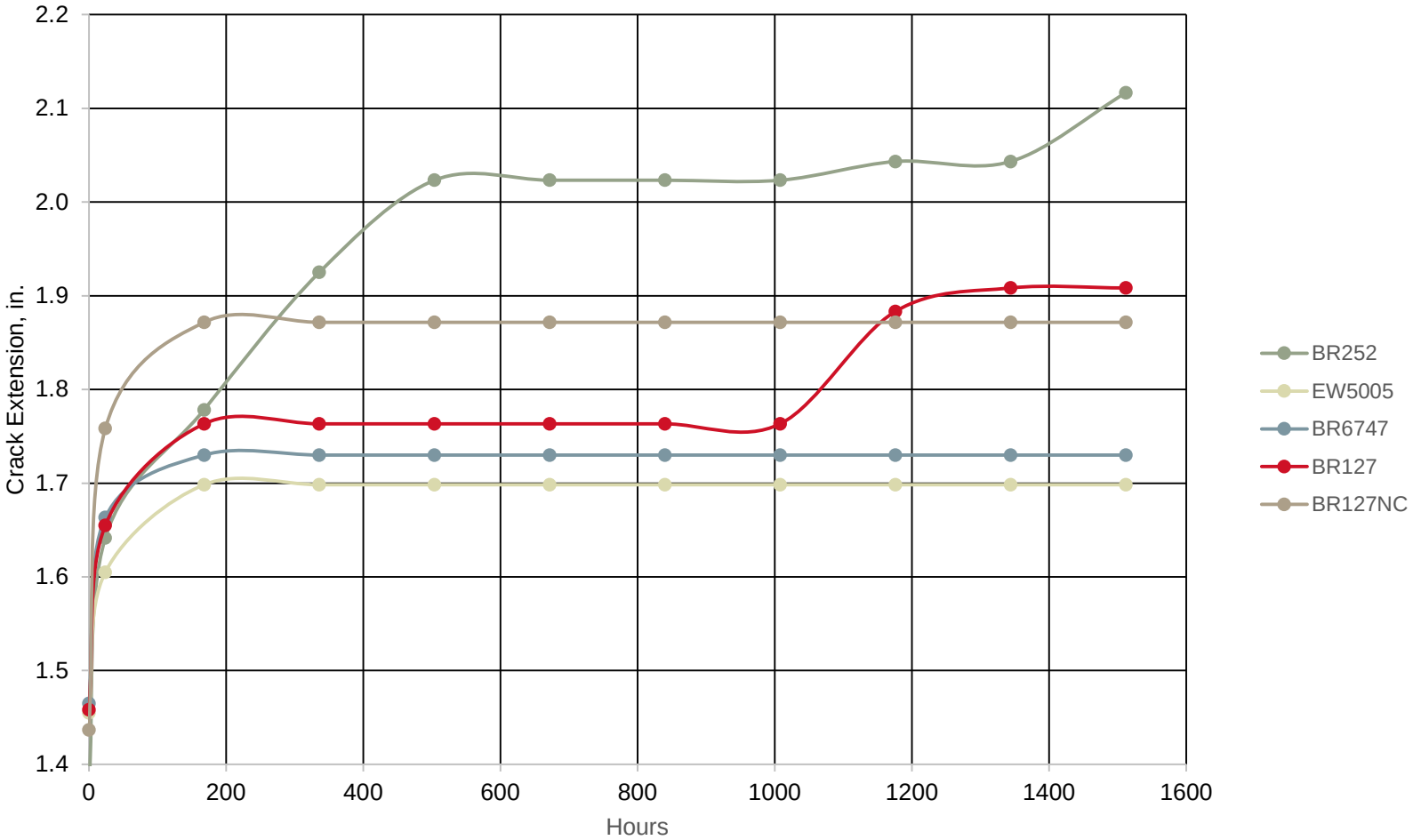

All GB/SG WCET samples experienced adhesive failure except the BR6747 which was cohesive failure and EW5005 was mixed mode failure

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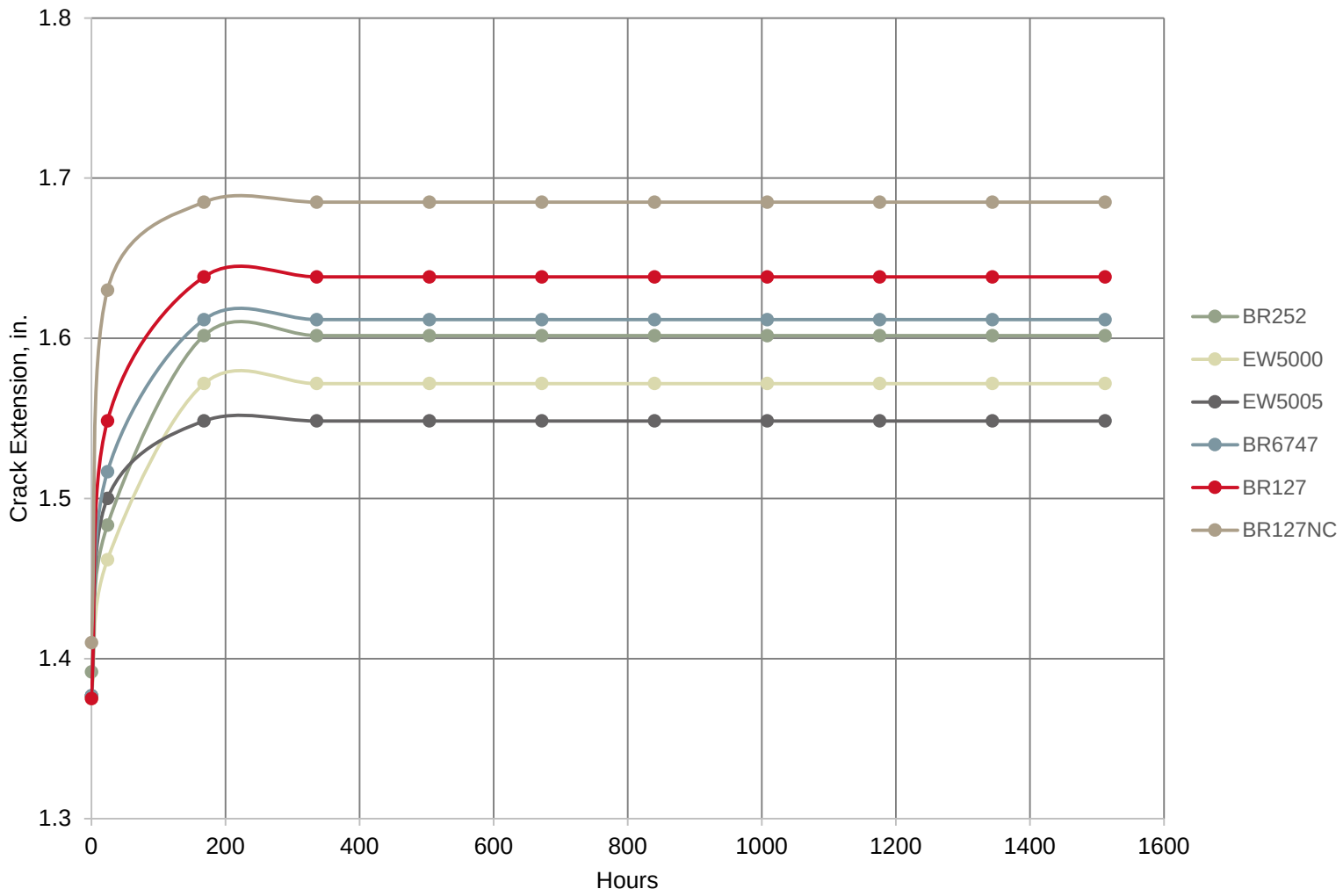
ETW exposure for PAA on 7075 with FM73



All GB/SG WCET samples experienced cohesive failure

ETW exposure for PAA on 7075 with AF 163

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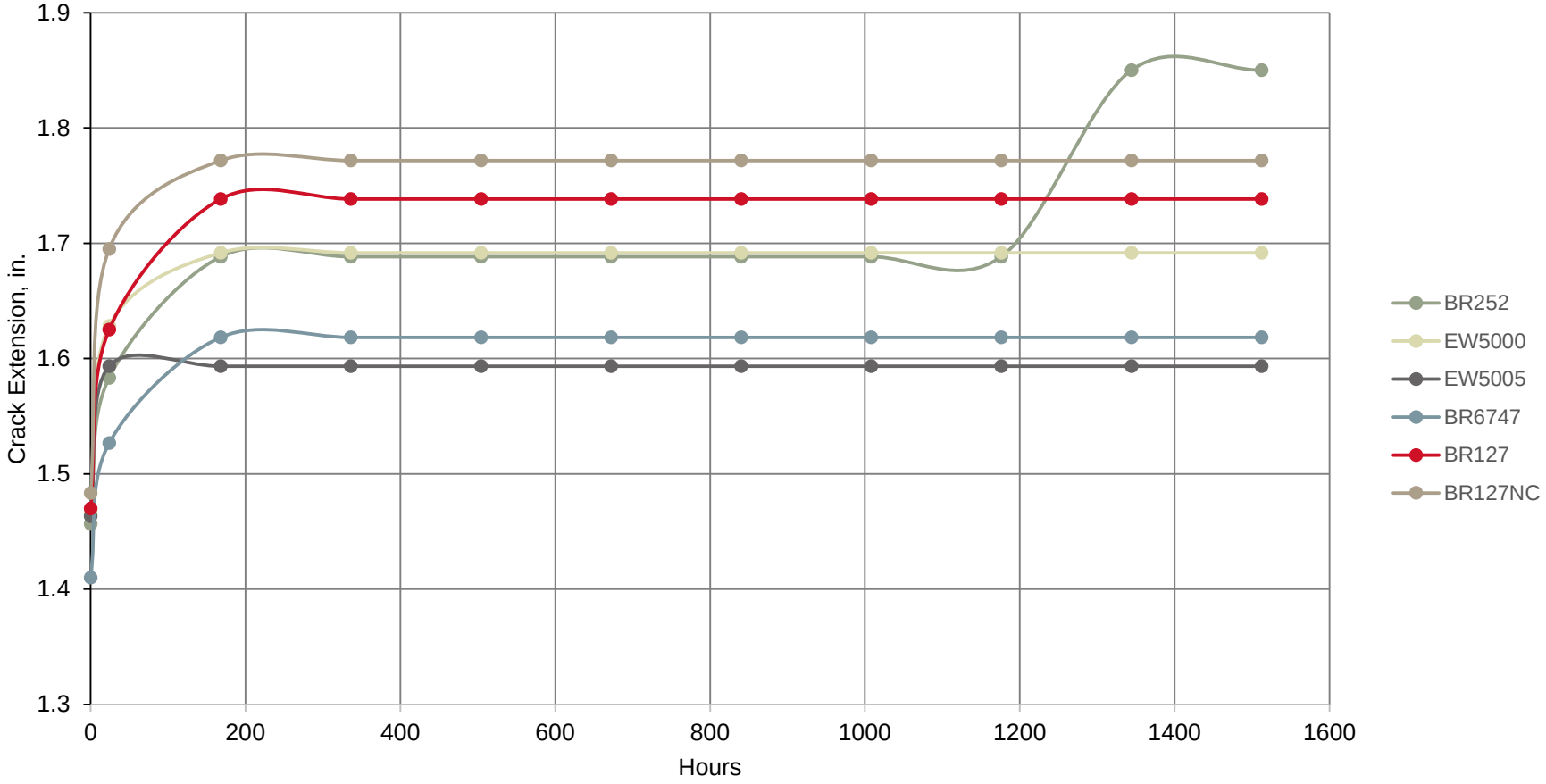

All GB/SG WCET samples experienced cohesive failure

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Overall Summary

- PAA is the best surface treatment for both adhesion and corrosion resistance with both adhesives, both alloys, and in both environments

Surface Treatment is the Overwhelming Discriminator

Wedge Crack Testing

- PAA had the smallest crack growth for 1 day , 1 week, 3 week, and 9 week values as compared to GB and SG
- There was a smaller crack growth than BR127 for 1 day, 3 week, and 9 week values
  - For PAA only - BR6747-1NC, EW 5000-ET, and EW 5005
  - For GB/SG only - BR6747-1NC and EW 5005
  - All combined – BR6747-1NC, EW 5000-ET, and EW 5005
- Crack growth for adhesive was found to be more dependent on surface treatment than environment, alloy or the alternative bond primer
  - AF163 did better on GB and GB/SG while the FM73 did better on the PAA
- Alloy performance was dependent on environment - 7075 alloy had smaller crack growth for ETW and 2024 alloy had smaller crack growth for NSF
- High cohesive failure rates are found similar to low crack growth values for individual factors and in general is also true for all surface treatments.

Overall Summary

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Corrosion Resistance Testing

- Primers exceeding 1000hr NSF requirement outside the scribe with both adhesives on both alloys
  - 3M EW5000ET
  - 3M EW5005
    - BR6767-1-NC exceed the requirement on the 7075 only

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Recommendations

- Overall 3 candidate materials met the screening testing requirements for corrosion resistance and adhesion and are considered viable Cr6+ free bond prier alternatives
  - 1000 hours with no corrosion outside the scribe, cohesive failure and crack growth less than BR127 Control
    - On 2024 & 7075 aluminum alloys
    - In ETW and NSF environments
    - With AF163 and FM 73 adhesives
  - <u>Alternatives</u>
    - 3M EW 5005
    - 3M EW 5000 ET (did not perform better on GB/SG only PAA)
    - Cytec BR6747-1NC (did not exceed 1000 hour SF on 2024)

Every individual company and program need to test and qualify any alternatives for their individual requirements

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Next Steps for NASA TEERM Collaboration

- 2219 panels on hold
- Writing Final Report
  - Publish – Q1 2017
- Phase II – January 2017
  - New members welcome
  - Potential investigations may include
    - Lap shear testing, floating roller peel, etc.
    - High low parameters for processing/manufacturing
    - Larger data sets for smaller sample sizes – validation
    - Different adhesives

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Questions?

Acknowledgements

This project is an team effort and would not be possible without the expertise and hard work of several people at numerous OEMs and DoD agencies. I would personally like to thank Kurt Kessel form NASA TEERM for allowing me the opportunity to present on behalf of the team and Diane Kleinschmidt for her expertise and work with the wedge crack extension test samples, and Greg Morose of TURI for the statistical analysis.

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BACK UP

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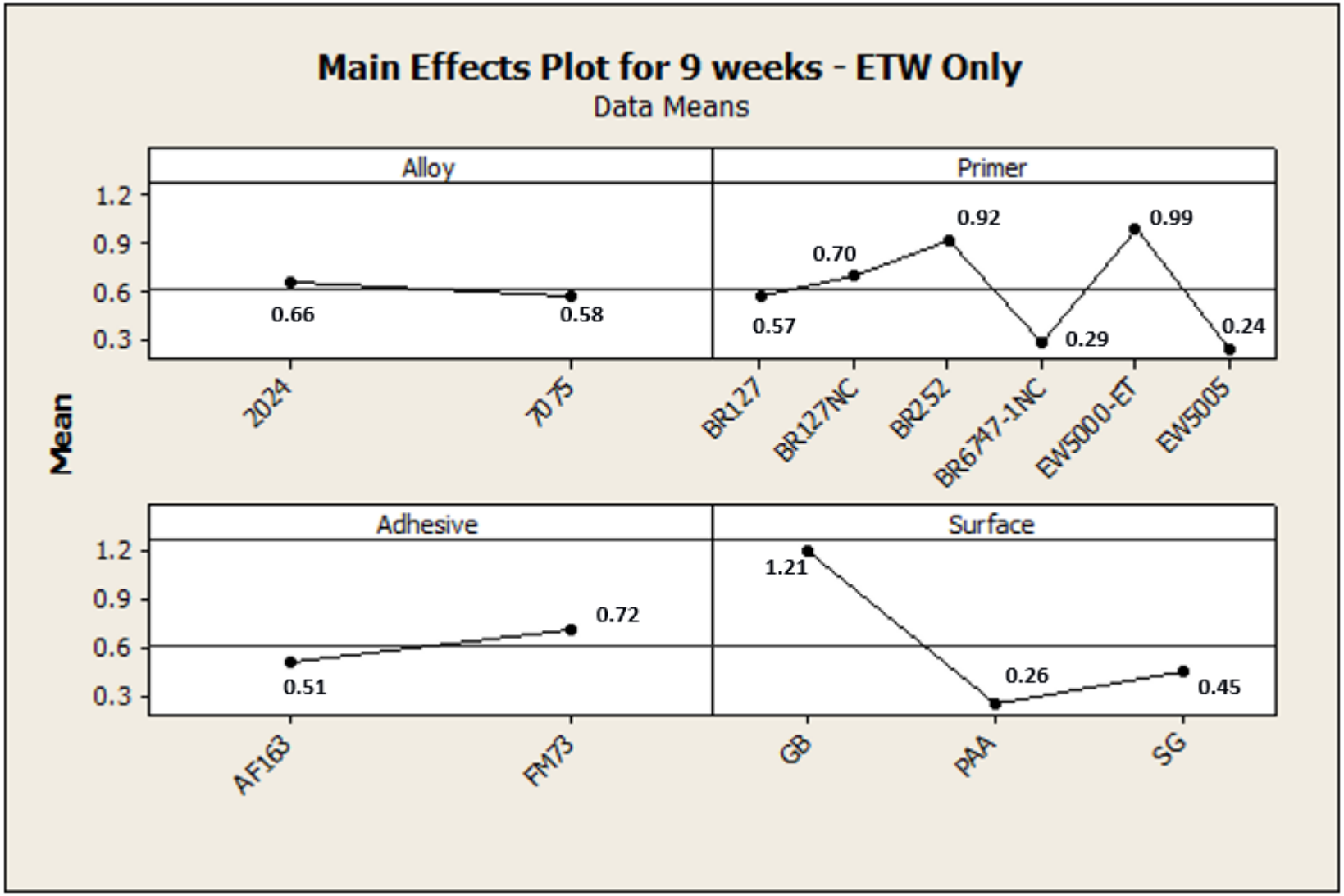

Overall mean: 0.62. Differences for primer, adhesive, and surface are statistically significant.

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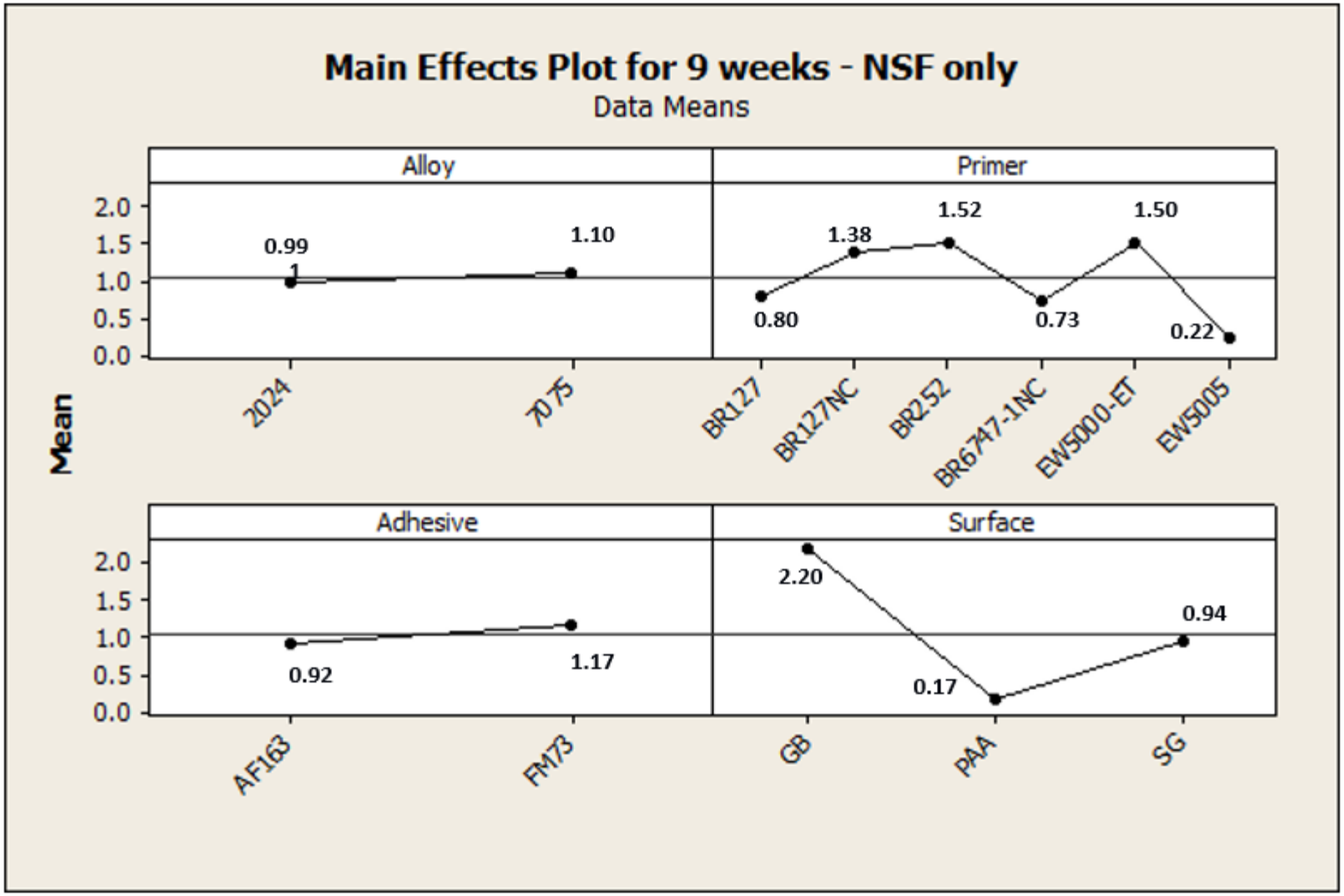
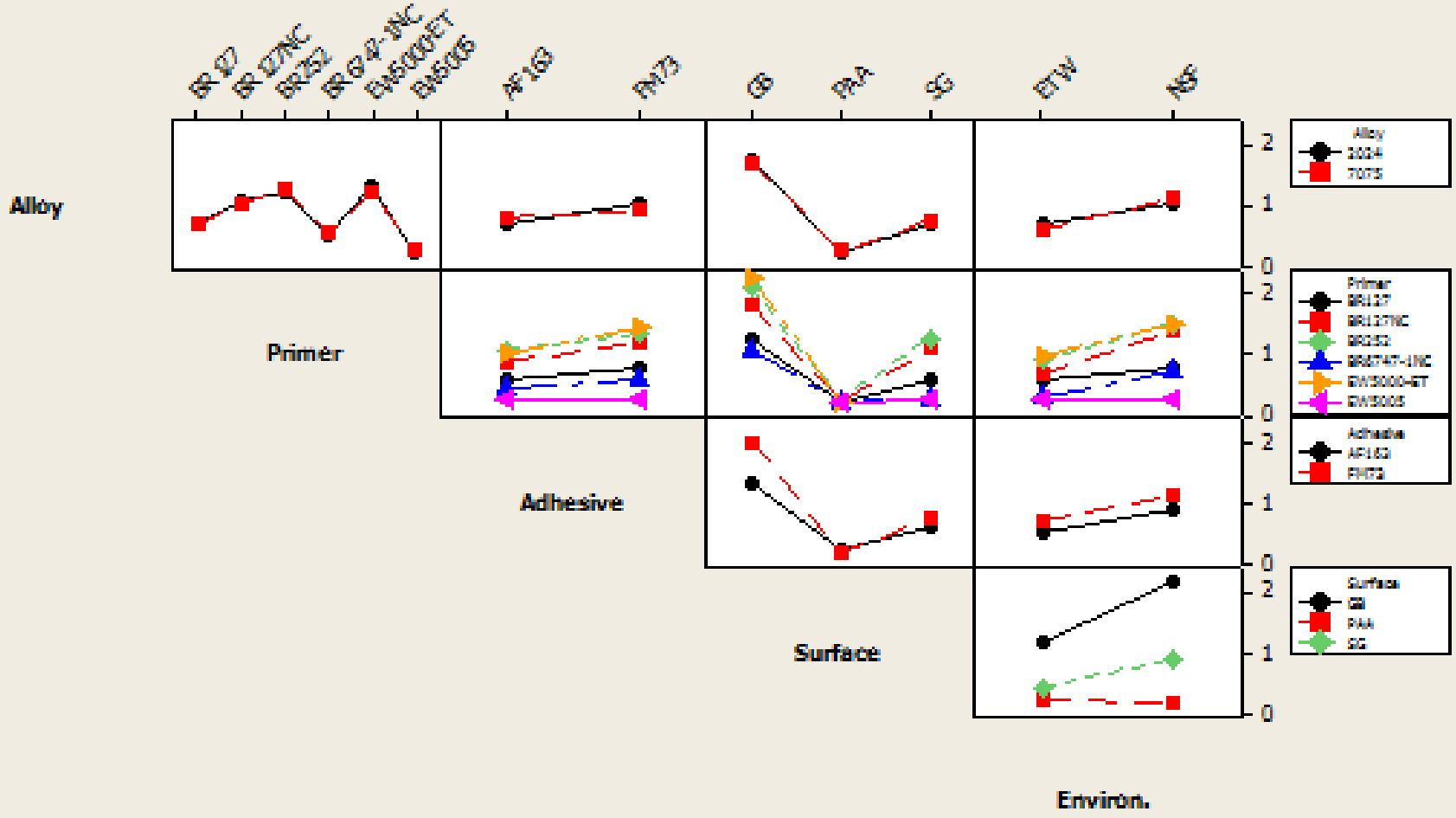


Overall mean: 1.05. Differences for primer, adhesive, and surface are statistically significant.

Interaction Plot for 9 weeks - PAA, GB, and SG

Data Means



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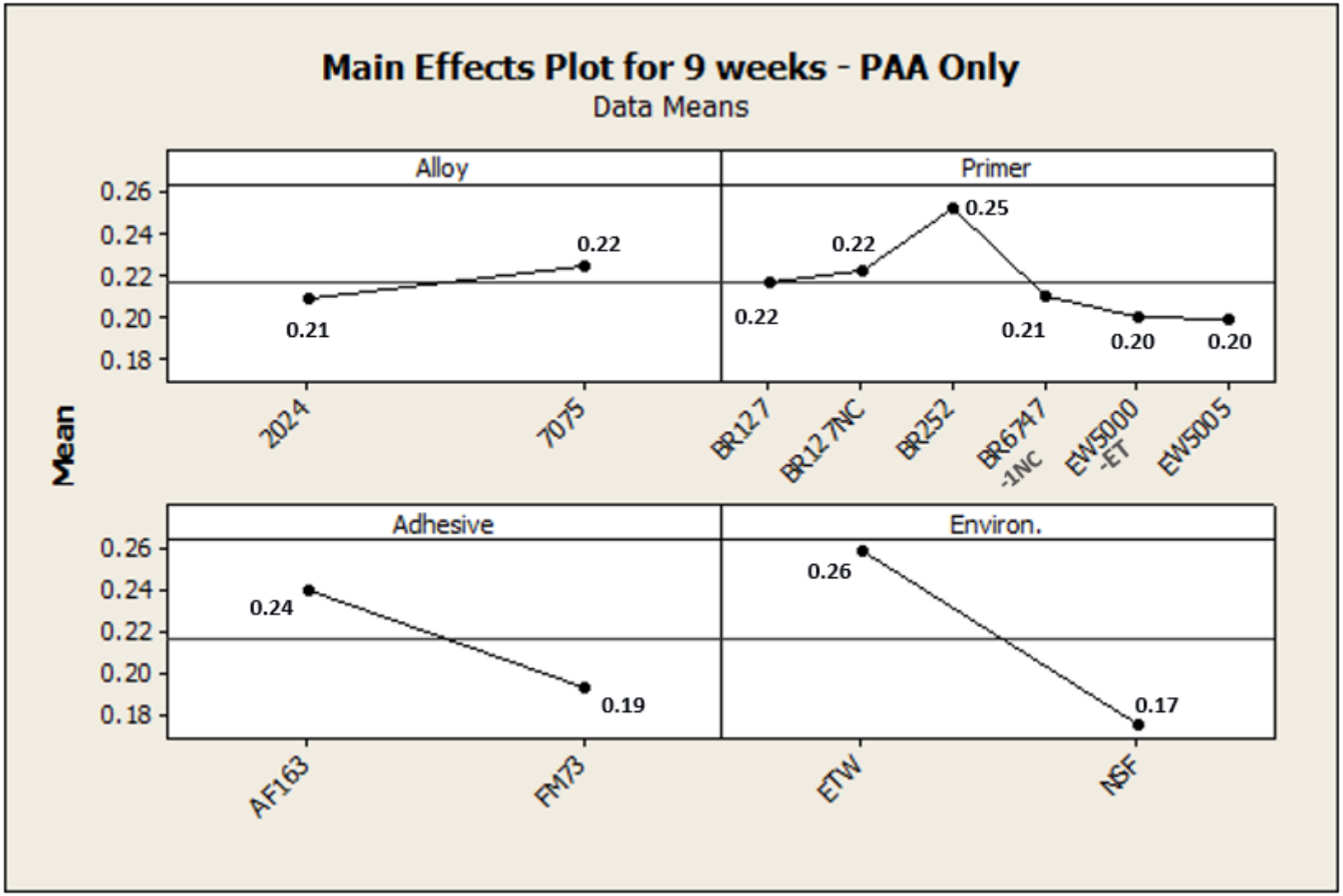

Overall mean: 0.22 inches. Differences for adhesive and environment are statistically significant. Primer values are close with a P value of 5.3%.