SAND2011-2662C

Aging of Adhesive Joints

Spring TCG XIV Review
April 7, 2011
Albuquerque, NM

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

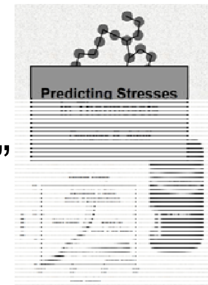
Adhesion Task - Key Personnel

Name	Org	Role
Jamie Kropka, Doug Adolf (jmkropk@sandia.gov; 505-284-0866)	*SNL*	*Task Leader for Aging of Adhesive Joints and mechanical testing*
Mike Bucher (michael.bucher@navy.mil; 301-643-3772)	*NSWC-IH*	*Working Group Leader for Aging of Adhesive Joints*
Scott Spangler (sspangl@sandia.gov; 505-845-3069)	*SNL*	*Polymer properties and mechanical testing*
Bob Chambers (rschamb@sandia.gov; 505-844-0771)	*SNL*	*Finite element analyses*
Dave Dunaj (david.dunaj@navy.mil; 951-204-4933)	*China Lake*	*Navy working group representative*
Alexander Steel (alexander.steel@us.army.mil; 256-876-3867)	*RDECOM*	*Army working group representative*
Jim Mazza (james.mazza@wpafb.af.mil; 937-255-7778)	*AFRL*	*Air Force working group representative*
Aisha Haynes (aisha.s.haynes@us.army.mil, 973-724-9674)	*ARDEC*	*Army working group representative*

Sandia National Laboratories

DoD Interactions

<u>Nien-Hua Chao</u>
Picatinny Arsenal
- delivered copy of “Predicting Stresses in Thermosets”
- advising on joint testing



<u>Timothy Woo</u>
<u>John Osterndorf</u>
Picatinny Arsenal
- discussion of JMP adhesives project
- why do we use the napkin-ring test geometry?

<u>Jennifer Cordes</u>
Picatinny Arsenal
- help with polymer properties determination (http://www.sandia.gov/polymer-properties/Classes_of_Polymers.html) and what can be done with SNL’s predictive tools

NNSA National Nuclear Security Administration

Sandia National Laboratories

Adhesion Task Four-Question Chart

What are you trying to do in this task?

- Measure and predict the critical stresses for adhesive de-bonding
- Measure and predict the change in de-bonding stress when components age in dry and humid environments
- Relate the de-bonding stress to processing history

What makes you think you can do it?

- Leverages previous SNL-funded research on measuring and predicting adhesive strength
- Adhesion working group involves DOE and DoD members to direct goals and share knowledge/experience

What difference will it make?

- Component designs can be more robust if de-bonding stress margins are known
- Knowledge of aging mechanisms improve material selection for given environments
- Processes can be defined to improve adhesive strength

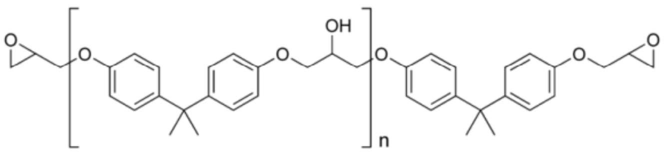
What / When / To Whom Will You Deliver?

- Deliverables are metrics and procedures to measure and predict de-bonding
- Delivery will be staged to provide capability on successively more difficult systems
- Adhesion working group will identify a DoD contact to share capabilities

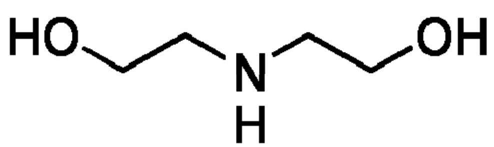
Adhesive Joints

Adhesive: 828/DEA

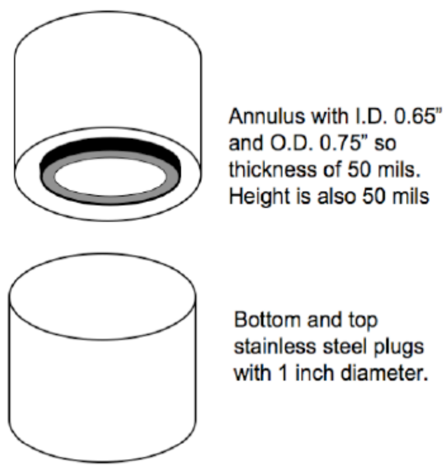
EPON® Resin 828
Diglycidylether of Bisphenol-A

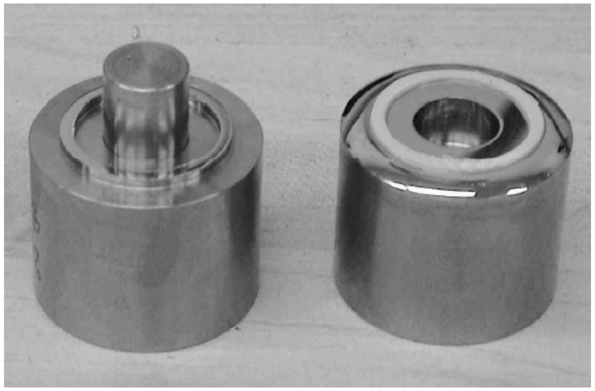


Diethanolamine



Test Geometry: Napkin-Ring





de Bruyne and Houwink (eds) *Adhesion and Adhesives*, Elsevier, London p.92 (1951)

http://www.sandia.gov/polymer-properties/828_DEA.html

Discussion Topics

1. **Adhesive joint geometry and stress states**

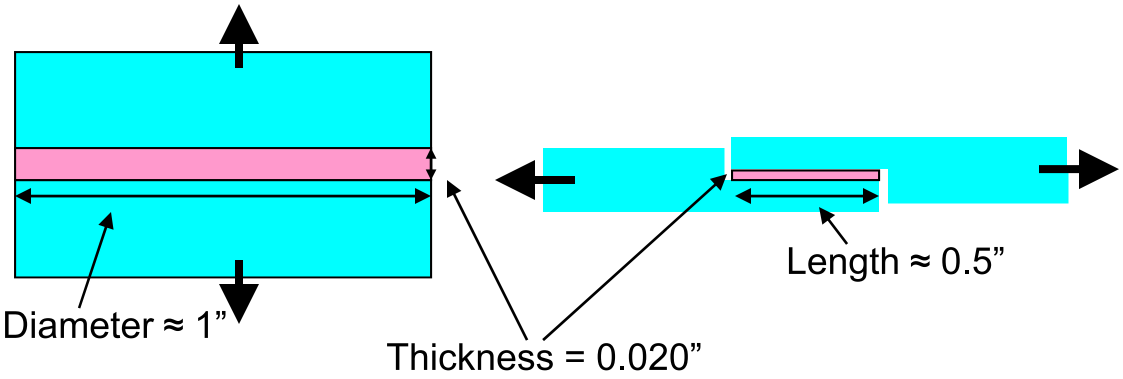
2. **Measuring and predicting the critical stress for debonding and how this changes with age in a humid environment**

Review of Test Geometry: Why the Napkin-Ring?

Stress State of Adhesive During Cure and Cool-down

ASTM Standards:

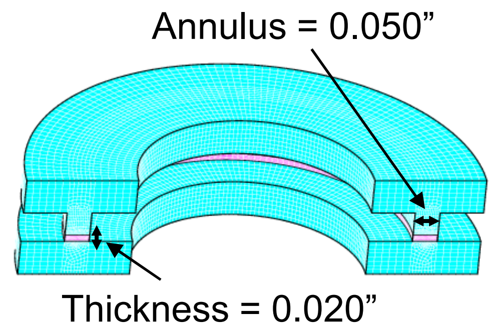
Butt Tension | Lap Shear



Large diameter(length)-to-thickness ratio: ~25-50

- large aspect ratio in epoxy bondline leaves little free surface to relieve shrinkage strains
- constrained volume generates significant residual stresses during cure and cooling before any load is applied

Napkin-Ring



Relatively small annulus-to-thickness ratio: ~2

- more free surface and less volume constraint
- minimal cure and thermal stress build-up in adhesive before test loading

If residual stresses are high, then epoxy is closer to failure load

NNSA National Nuclear Security Administration

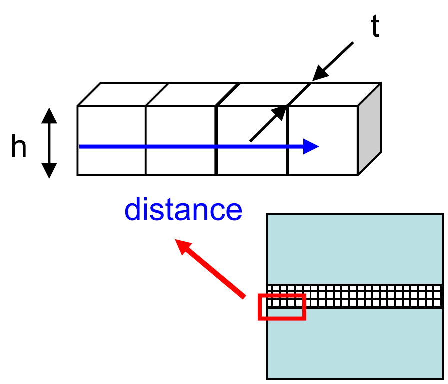
Sandia National Laboratories

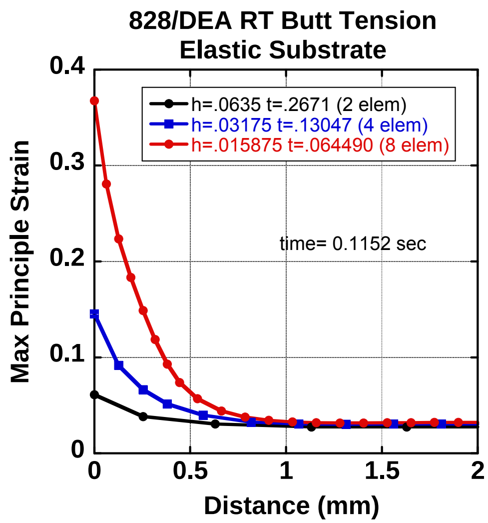
Review of Test Geometry: Why the Napkin-Ring?

Stress State of Adhesive During Load

ASTM Standards:

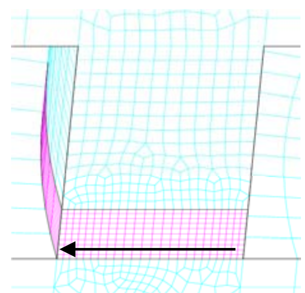
Butt Tension

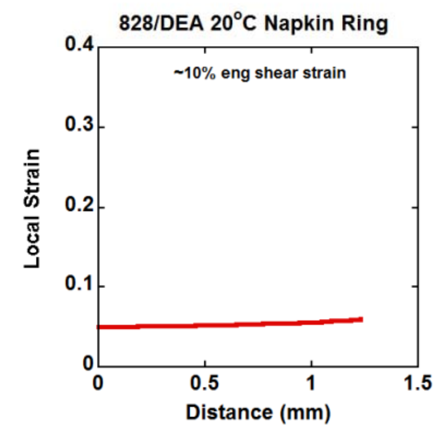


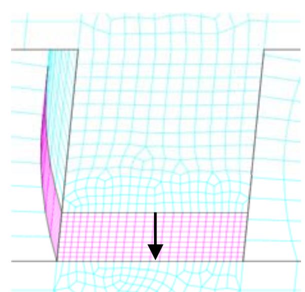


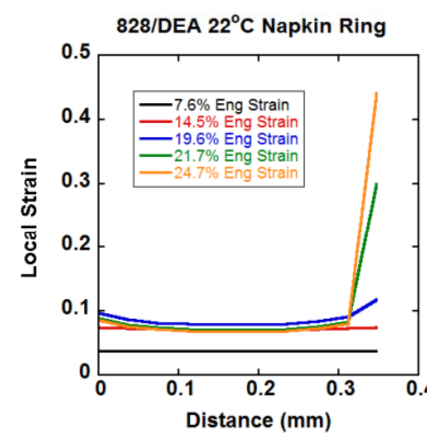
•Sample has high stress/strain concentration at triple interface
•Model results are sensitive to mesh refinement at that point

Napkin-Ring









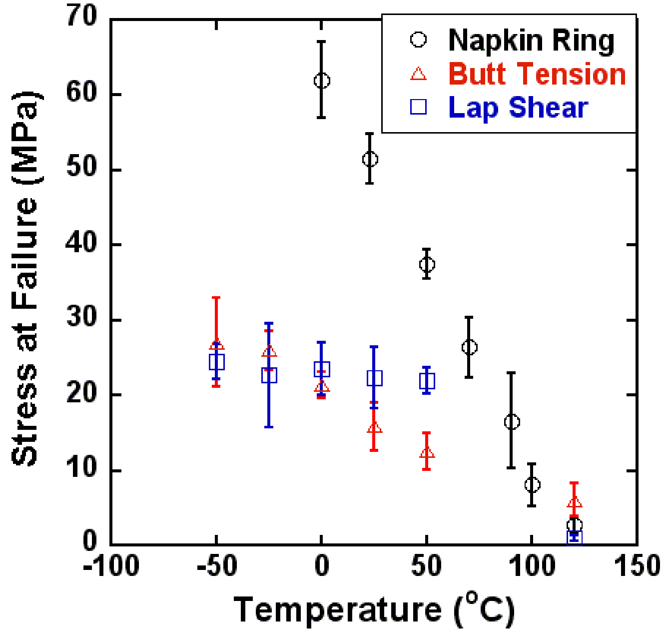
Relatively uniform stress/strain distribution across entire bond

NNSA National Nuclear Security Administration

Sandia National Laboratories

Review of Test Geometry: Why the Napkin-Ring?

Assume: Stress = (Applied Load)/Area



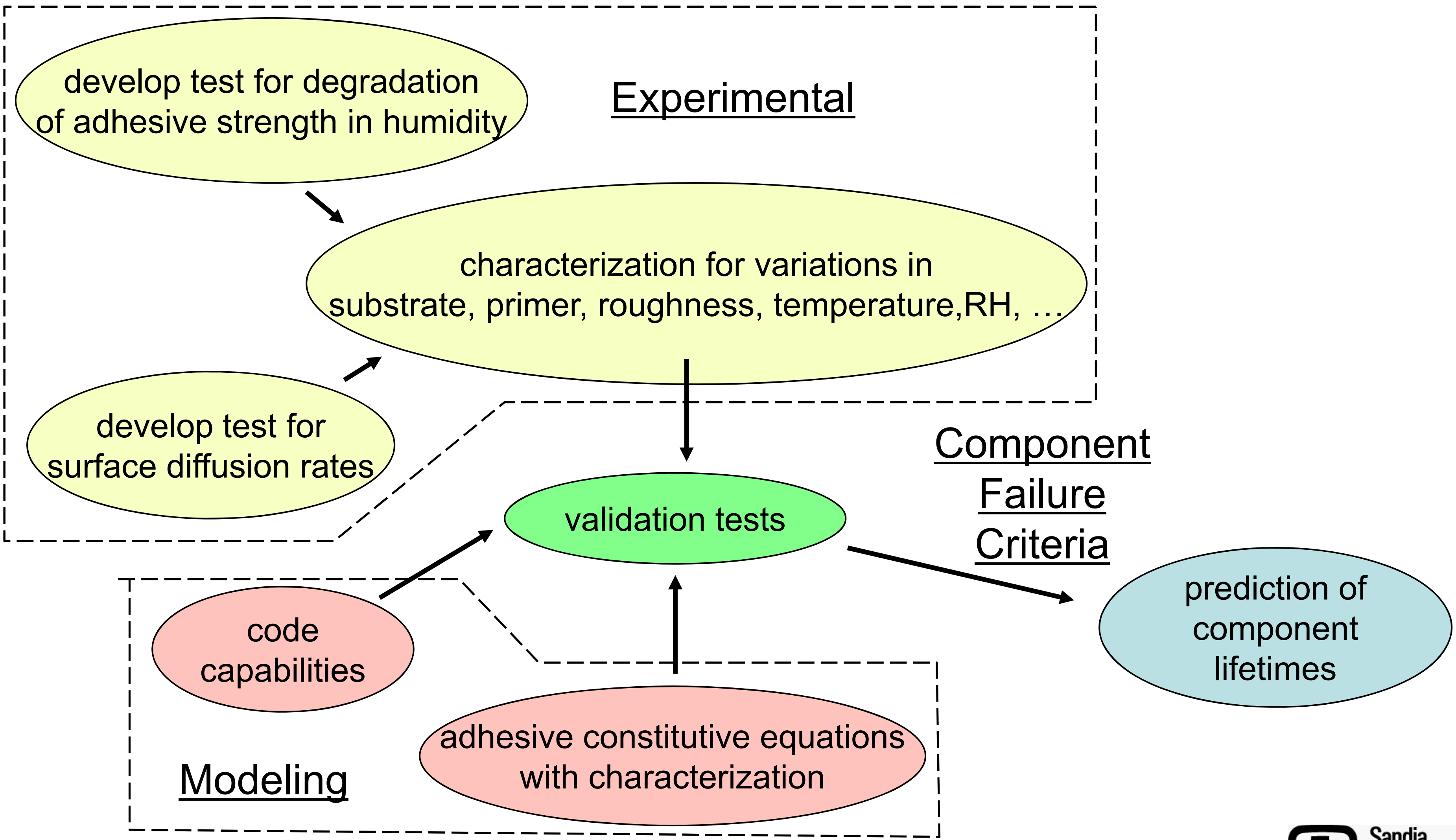
- Cure/Thermal residual stresses in BT/LS are much higher than in napkin-ring, so epoxy is closer to failure point before additional mechanical load
- On loading BT/LS strains are concentrated at the triple interface rather than being distributed more uniformly like napkin ring
- BT/LS samples are more susceptible to edge defects

Discussion Topics

1. **Adhesive joint geometry and stress states**

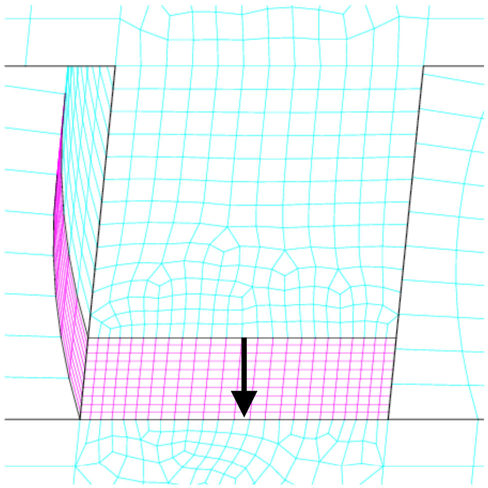
2. **Measuring and predicting the critical stress for debonding and how this changes with age in a humid environment**

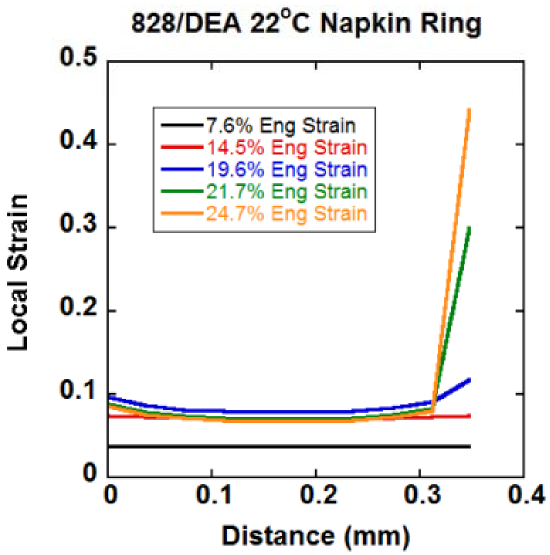
Adhesive Joint Aging in Humid Environments



Dry Adhesive Failure on Napkin-Rings

Predicting the Critical Stress/Strain for Debonding





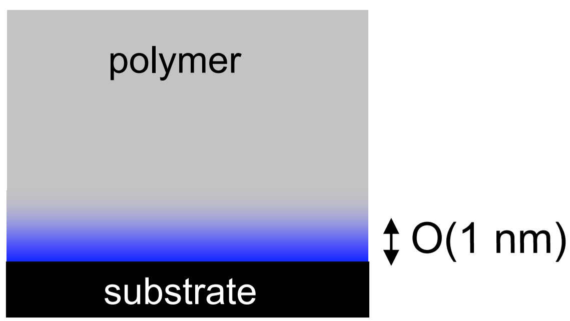
<u>Failure Mechanism:</u>

- Highest stress regions at bonding interfaces
- Highest adhesive confinement at lower interface
- Polymer in interfacial region shows highest strains and yields prior to bulk polymer
- Premature yield concentrates strain in the interfacial region
- High strain concentrations further increase relaxation rates until strain levels are no longer sustainable

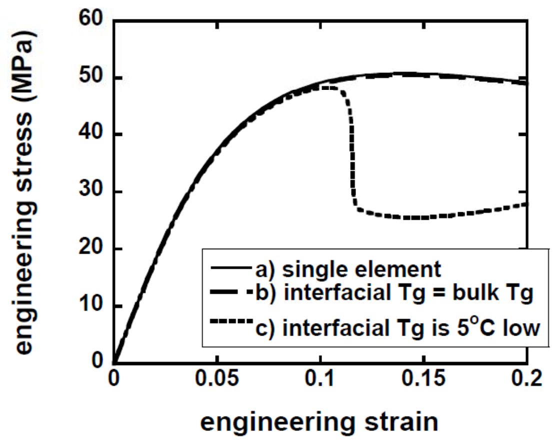
Failure is cohesive, although it visually appears adhesive

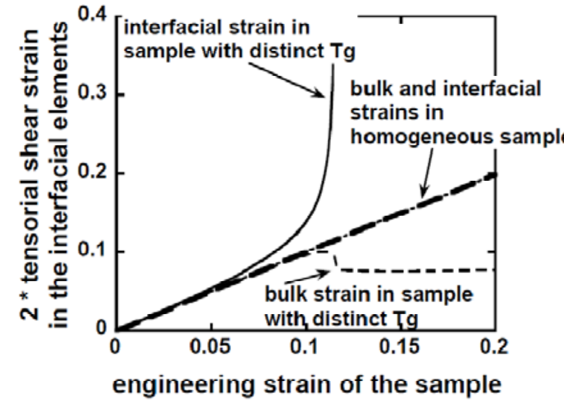
Dry Adhesive Failure on Napkin-Rings

A “Weak” Interfacial Layer will further Promote Failure at the Interface



Entropic, $\Delta T_g \sim 5^oC$





Same failure mechanism, exacerbated by reduced polymer T_g at interface

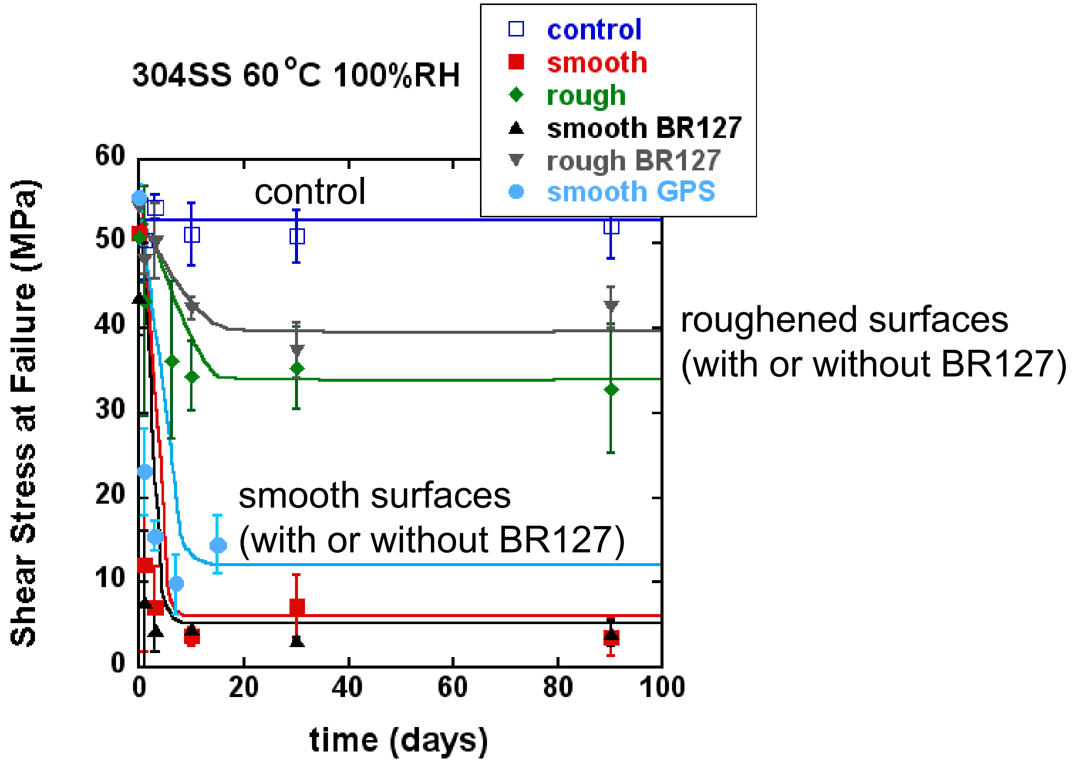
<u>Failure Mechanism:</u>

- Highest stress regions at bonding interfaces
- Highest adhesive confinement at lower interface
- Polymer in interfacial region shows highest strains and yields prior to bulk polymer
- Premature yield concentrates strain in the interfacial region
- High strain concentrations further increase relaxation rates until strain levels are no longer sustainable

Failure is cohesive, although it visually appears adhesive

Wet Adhesive Failure on Napkin-Rings

828/DEA bonding 304SS of varied surface preparations



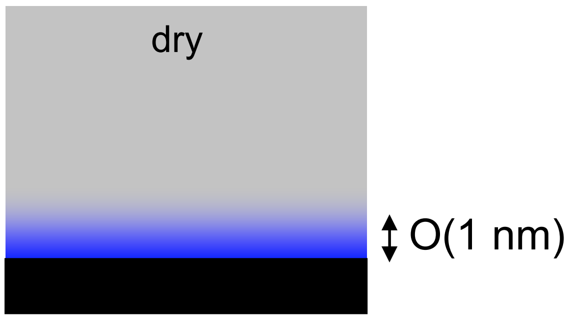
Effects of humidity can be measured:

- Equilibrium effect of water on bond strength reached in days
- Surface roughness critical in determining magnitude of water effect on bond strength

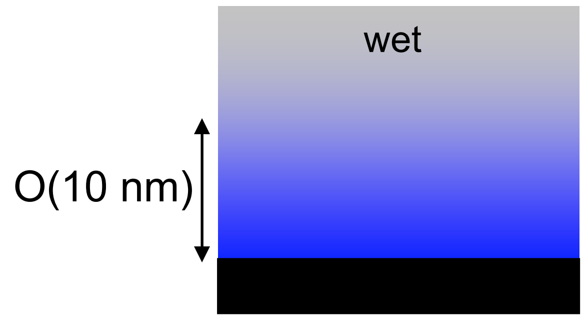
Adolf, D. B., *Predicting Stresses in Thermosets*, Sandia National Laboratories, Albuquerque, NM, 2010.

Wet Adhesive Failure Mechanism

Reduced T_g: wet vs. dry

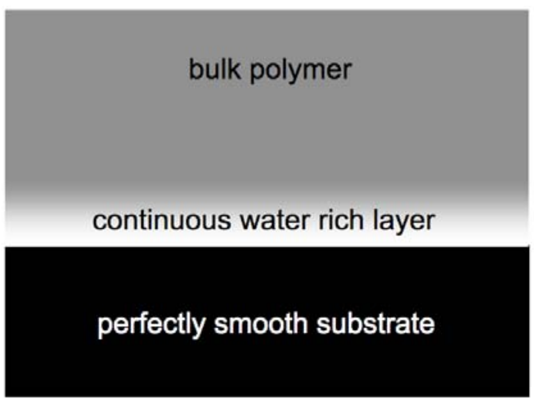


Entropic, $\Delta T_g \sim 5^oC$

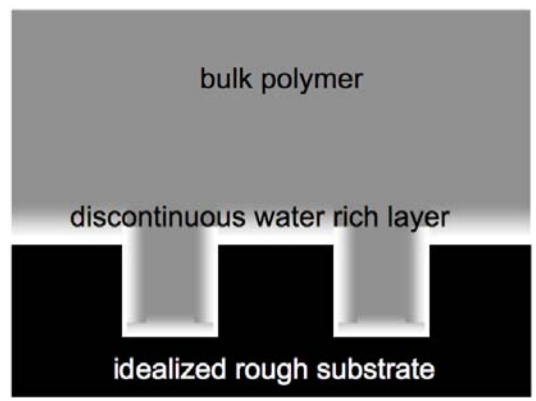


Plasticization, $\Delta T_g \sim 50^oC$

Moisture Effects on Bond Strength: smooth vs. rough surface



Clean break across reduced T_g interface

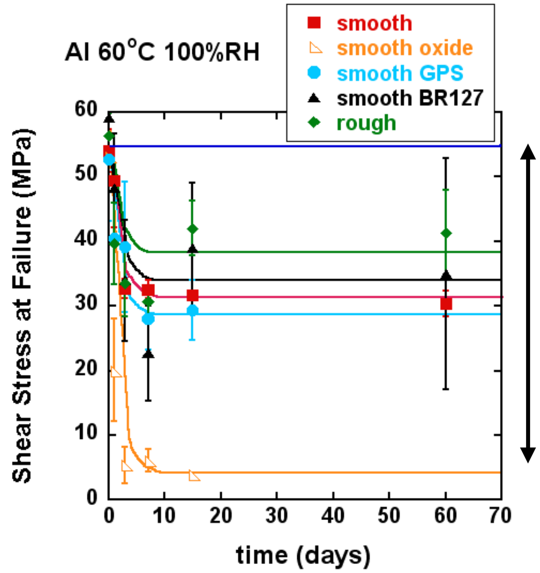


Bulk polymer must be traversed

NNSA National Nuclear Security Administration

Sandia National Laboratories

Wet Adhesive Failure: Adherend Composition



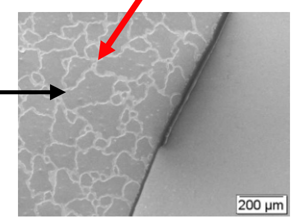
decrease on rough aluminum

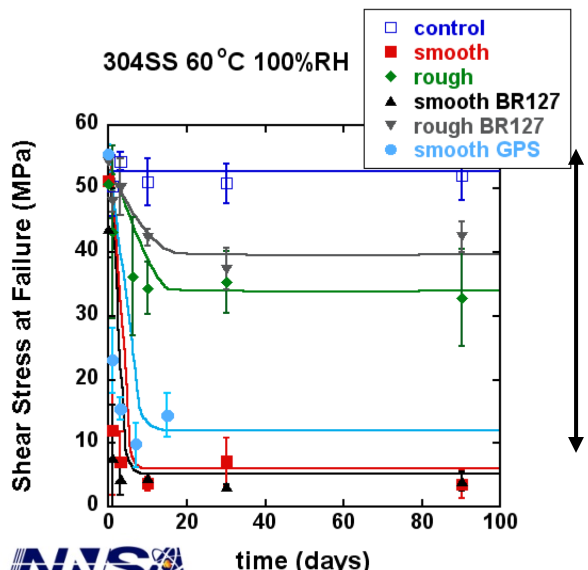
decrease on smooth aluminum (with or without GPS or BR127)

decrease on smooth oxide

unbonded area

bonded area





decrease on rough steel (with or without BR127)

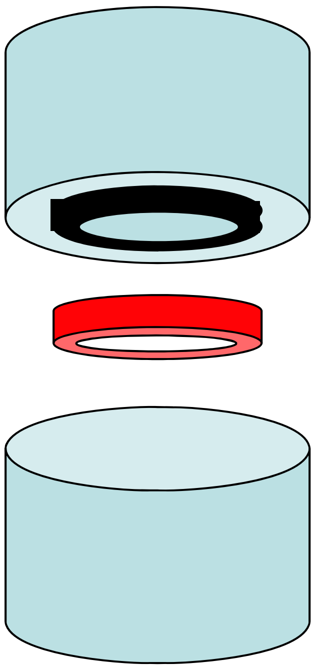
decrease on smooth steel (with or without GPS)

- decrease in strength on smooth surfaces is less for Al than steel
- GPS does not minimize loss of adhesive strength
- oxide layer on Al significantly decreases wet strength

NNSA National Nuclear Security Administration

Sandia National Laboratories

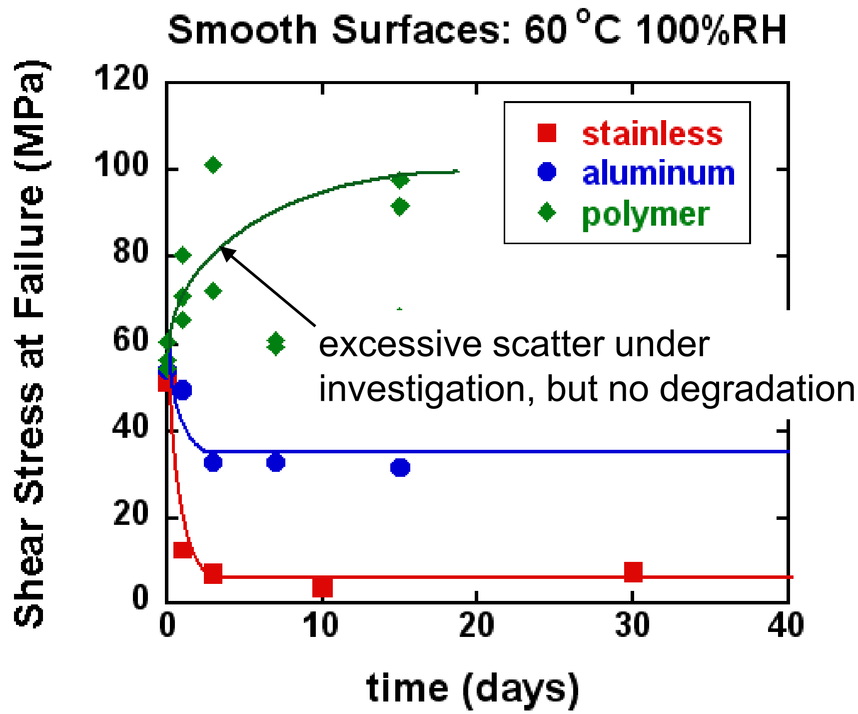
Wet Adhesive Failure: Adherend Composition



upper plug with annulus
alumina-filled epoxy (T_g~160°C)

bonded adhesive
unfilled epoxy (T_g~70°C)

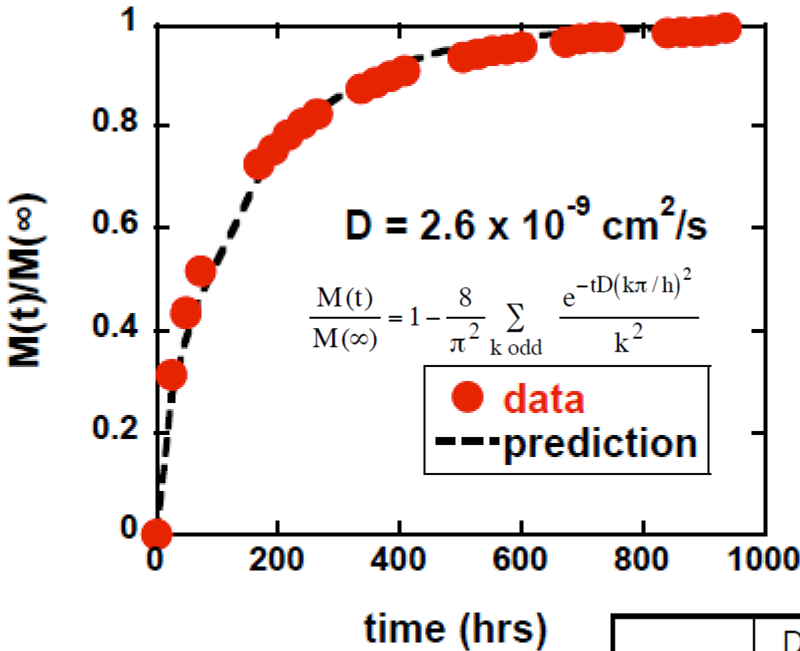
lower plug
alumina-filled epoxy (T_g~160°C)



polymer-polymer interfaces (e.g., adhesive to composite) show no degradation
- no thermodynamic driving force for water to migrate to interface

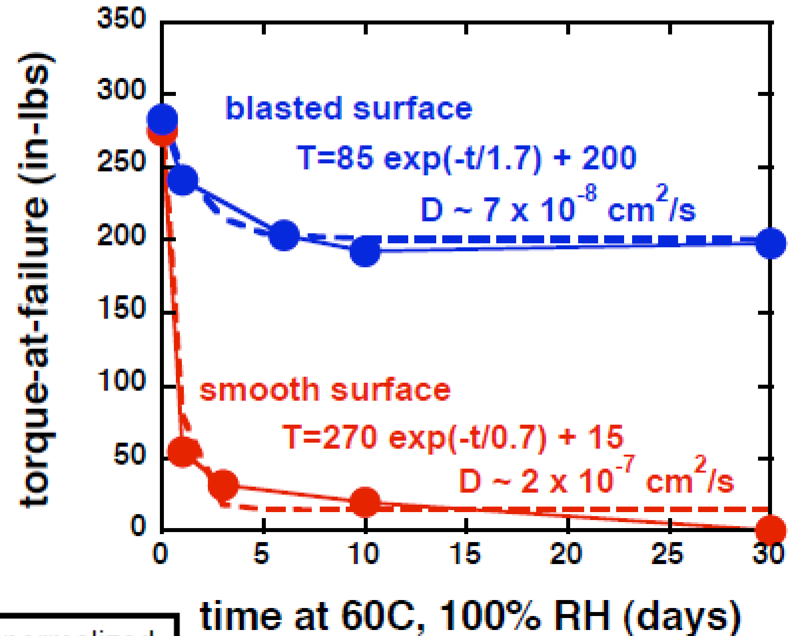
Predicting Humid Joint Aging: Water Diffusion

Mass Gain: 60°C 100% RH



$$\frac{M(t)}{M(\infty)} = 1 - \frac{8}{\pi^2}\sum_{k\ odd}\frac{e^{-tD(k\pi/h)^2}}{k^2}$$

Napkin Ring Adhesion: 60°C 100% RH

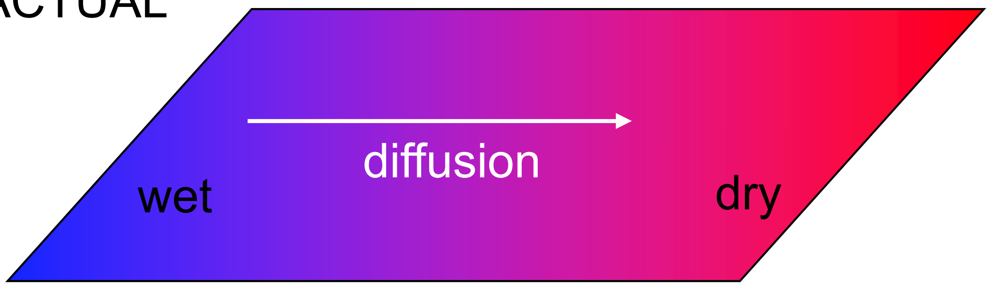


	D (cm^2/s)	normalized to bulk D
smooth	1.6×10^{-7}	62
rough	6.8×10^{-8}	26
bulk	2.6×10^{-9}	1

Interfacial diffusion ~50 times faster than bulk diffusion

Predicting Humid Joint Aging: Simplest Scheme

ACTUAL

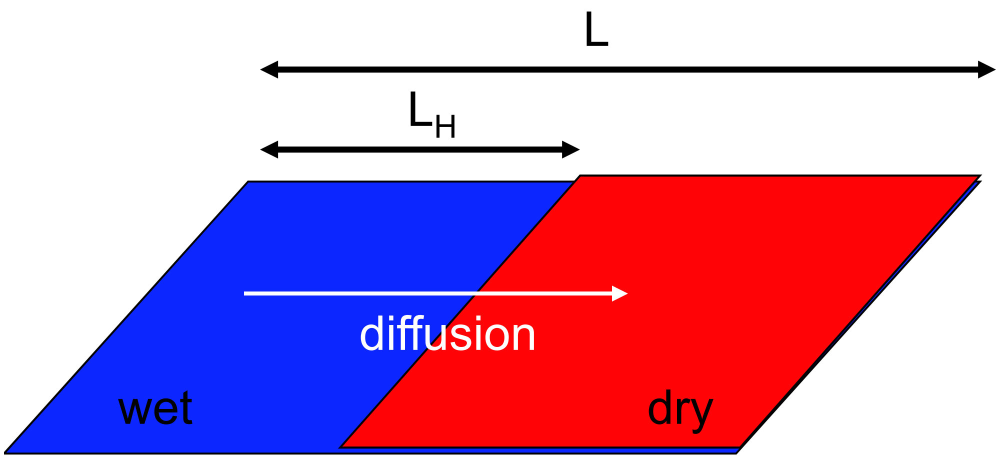


EXAMPLE CALCULATION

$$\text{total strength} = H\left(\frac{L_H}{L}\right) + V\left(\frac{L - L_H}{L}\right)$$

where $L_H = (Dt)^{1/2}$

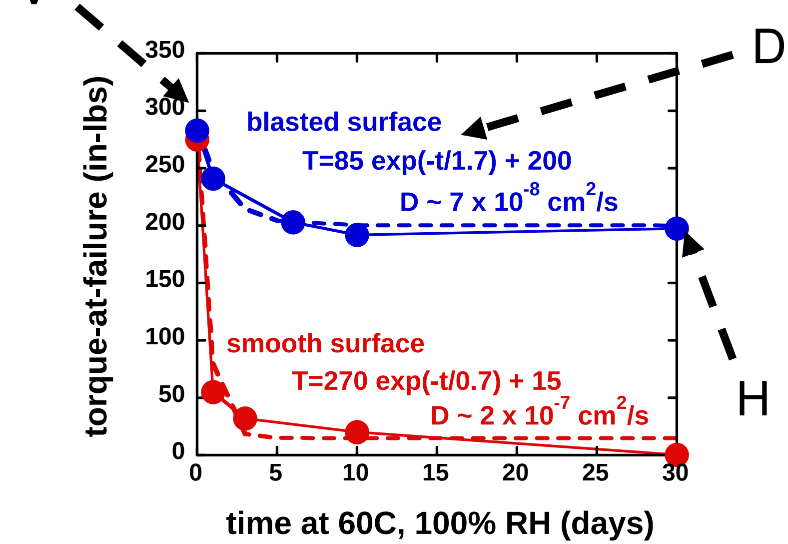
IDEALIZED



“humid” strength = H

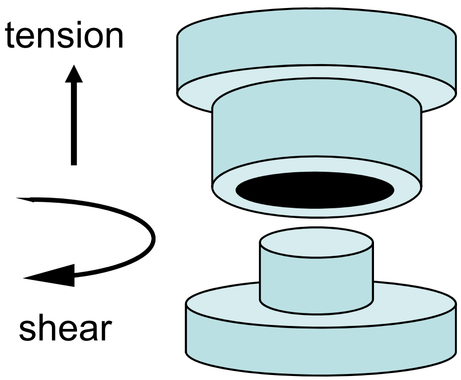
“virgin” strength = V

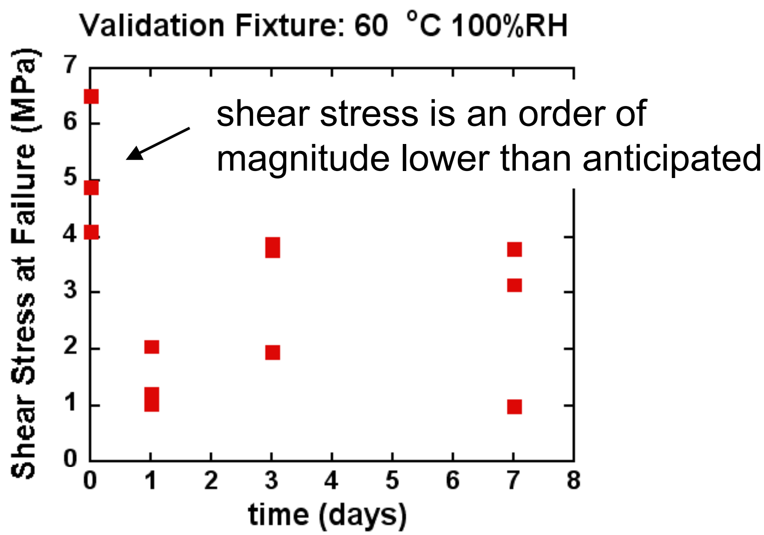
from napkin ring adhesion tests at 60°C in 100% RH



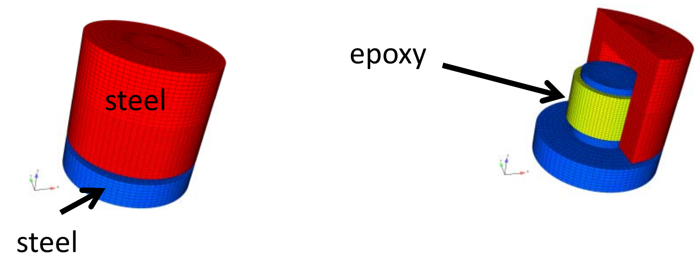
Testing Predictions: Validation Geometry

Experimental

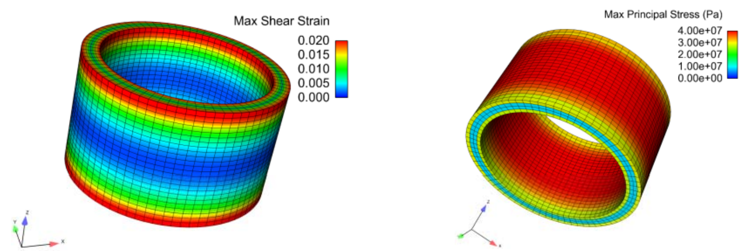




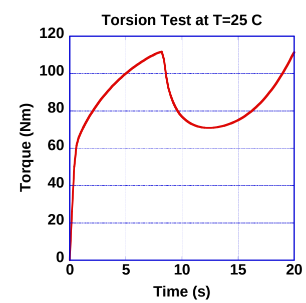
Stress Analysis

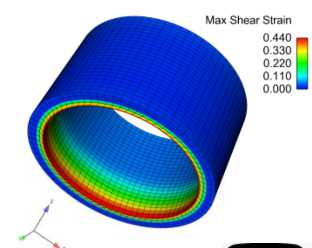


Thermal Stress/Strain

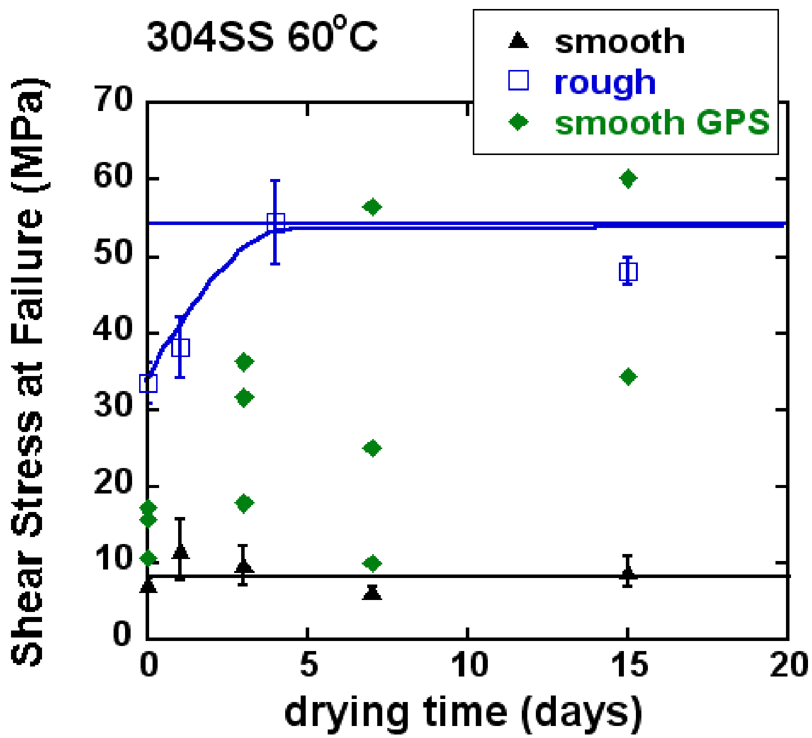


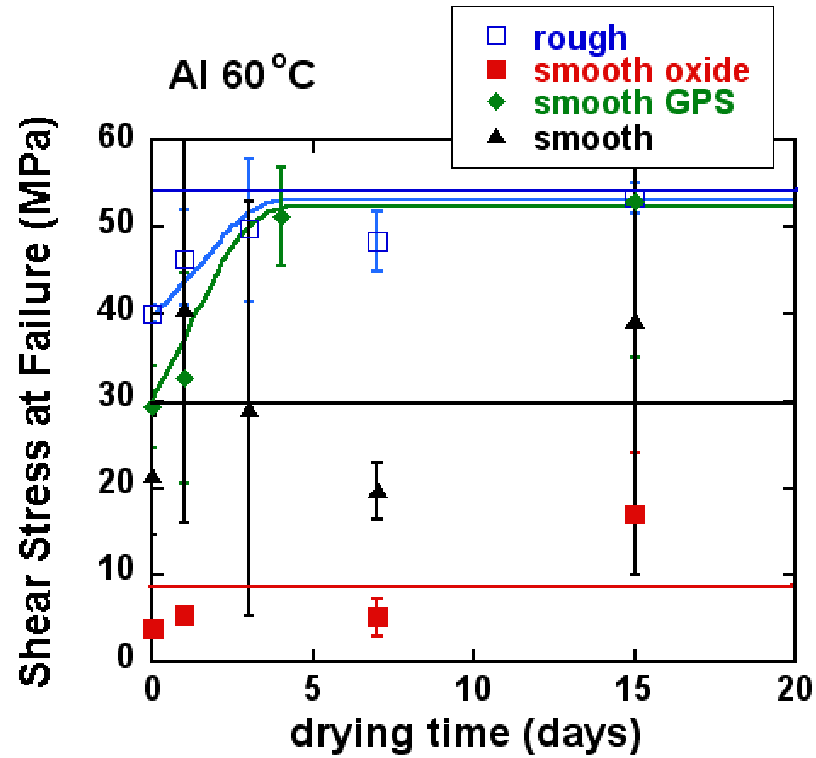
Rotational Loading Strain





Can Adhesive Joints be "Healed"





- Original strength is regained on rough surfaces
- No regaining of strength on smooth, unprimed surfaces
- GPS allows regaining of original strength on smooth Al but scattered results on steel

NNSA National Nuclear Security Administration

Sandia National Laboratories

Summary

- Failure isn't truly adhesive failure, typically the polymer fails cohesively and this can occur in a weak interfacial layer
- Loads to adhesive failure do depend on the joint geometry…choose carefully
- Napkin-Ring geometry is an excellent tool to characterize wet adhesive failure: fast (~2 weeks to equil.), directly yields stress-to-failure, simplicity allows mechanistic interpretation
- Bonding materials and surface preparation significantly affect the role of moisture on adhesive strength
- Degradation effects of moisture can be healed in some cases

Adhesion Task: Major Results to Date

1. Napkin ring test is an excellent metric for monitoring adhesion aging
   a. Simple and fast (~2 weeks to equilibrate)
   b. Directly yields stress at failure for predictive capability
   c. Simplicity allows mechanistic interpretation

2. Developed mechanism and predictive tool for dry environments

3. Developed mechanism and predictive tool for humid aging without corrosion or silane primers
   a. Swelling of epoxy at interface due to preferential water absorption
   b. Depressed yield stress of swollen polymer leads to reduced strength

4. Bonding materials and surface preparation significantly affect role of moisture on adhesion
   a. Al surfaces (without corrosion) less susceptible to adhesive degradation than SS
   b. Rough surfaces less susceptible to adhesive degradation than smooth surfaces
   c. Polymer-polymer interfaces show no adhesive degradation

5. Degradation effect of moisture on adhesion can be “healed” by drying in some cases

Adhesion Task Milestones/Deliverables for FY12-16

Task #	Milestones/Deliverables	Date
1	*Prove adhesive degradation validation geometry: FEA stress analysis of bonding geometry and experimental evaluation of virgin stress at failure*	***FY12***
2	*Validate predictions of adhesive degradation in humid environments: smooth stainless steel surfaces*	***FY13***
3	*Present results to DoD interested parties (Picattiny? Redstone?). Gather feedback and learn history of adhesive issues*	***FY14***
4	*Refine predictions of adhesive failure: napkin ring tests to identify additional parameters necessary for predictive model (e.g., critical humidity levels, environmental effects on degradation rate, resin cure stresses, thermal stresses, and/or dynamic loadings)*	***FY14-15***
5	*Validate refined prediction of adhesive failure*	***FY16***

Back Up Slides

Adhesion Task GOTChA

Goal: ---

Predict de-bonding of adhesively bonded components

Objective: ---

Develop a straightforward experimental test, unravel the underlying mechanisms, develop a predictive approach, and implement it in a computational procedure

Challenges: --

experimental	mechanism	theory	computational	validation

Approach: --

napkin ring test	NLVE polymer model	finite element stress prediction

Tasks: ---

develop experimental path	assess sensitivities	develop computational approach

Adhesion Task
JMP Five Year Plan for FY12-16

Performing Organization: **Sandia National Laboratories**

Principal Investigator: **Jamie Kropka, SNL-ABQ, 505-284-0866, 505-844-2894, jmkropk@sandia.gov**

Customer	Collaboration
Tom Erickson US Army Redstone 256.876.0218 Tom.Erickson@us.army.mil	Adhesive degradation in munitions. Transition: present summary of work completed to characterize adhesive degradation (FY14)
Sergio Gonzalez Sandia National Labs 505.845.2393 slgonza@sandia.gov	Adhesion of UV-cured coatings to PWBs and degradation of the adhesion in humid environments
Barbara Wells Sandia National Labs 505.844.4642 bjwells@sandia.go	Adhesion and adhesive failure of thermosets

FYP Presentation Template

Project *'Name'* Schedule
(Example)

	FY11 Q1 Q2 Q3 Q4	FY12 Q1 Q2 Q3 Q4	FY13 Q1 Q2 Q3 Q4	FY14 Q1 Q2 Q3 Q4	FY15 Q1 Q2 Q3 Q4
Project Milestones			Deliverable A	Deliverable B	
Task 1		Accomp1			
Subtask 1.1					
Subtask 1.2					
Sub-Sub Task 1.2.1					
Task 2			Accomp 2		Accomp 3
Subtask 2.1					
Subtask 2.2					
Task X					Accomp X
Subtask X.1					
Subtask X.2					

Include this slide the Back Up Slides for ongoing projects with updated out year

Project ‘*Name*’ Funding and T

I will generate this slide. You do not need to present this info in your talk.

Planned:

FY12	FY13	FY14	FY15	FY16
$K	$K	$K	$K	$K

Historical:

prior FYs	FY06	FY08	FY09	FY10	FY11
$K	$K	$K	$K	$K	$K

Tasks *	Funding**
1. Task Title	
2. Task Title	

X. Task Title	
Total FY12 Project Funding	

Indicate a new task by an "" next to title, **Indicate any previous-year task that was terminated as $ 0K

Values include the total of both DoD and DOE $s

Project *'x-short title'* - Key Personnel

I will generate this slide. You do not need to present this info in your talk.

Name	Org	Role
Jane/John Doe ***(e-mail & phone number)***	***DOE Lab***	***Task Leader for Task X***
	DOE Lab	***Task Leader for Task Y***
	DoD Lab	***(Define area of responsibility or interest: Tasks X, Y, Z)***
	University	
	Etc.	

Instructions:

- **Explicitly identify the 'Task Leader', even if that person is also the Project Leader**
- **Include key collaborators even if they are not at a DOE lab or not directly funded by the JMP**
- **Examples only shown above – not all orgs will apply to each task**
- <u>**Treat as your acknowledgement slide, do not speak to at length!**</u>

Project ‘*Name*’ – Major Results to Date

Each PI should fill out this slide. I will compile the info into one or two slides.

FY10

- **Bonding materials and surface preparation significantly affect the role of moisture on adhesion**
  - **Corrosion on Al surfaces significantly decreases wet adhesive strength**
  - **Al surfaces (without corrosion) are less susceptible to adhesive degradation than SS**
  - **Rough surfaces are less susceptible to adhesive degradation than smooth surfaces**
  - **Polymer-polymer interfaces show no adhesive degradation**
- **Degradation effects of moisture on adhesion can be “healed” by drying in some cases**
  - **Original adhesion strength is regained on rough surfaces**
  - **GPS (silane coupling agent) allows regaining of original strength on smooth Al**

Project ‘*Name*’ Schedule

(Example)

	FY12 Q1 Q2 Q3 Q4	FY13 Q1 Q2 Q3 Q4	FY14 Q1 Q2 Q3 Q4	FY15 Q1 Q2 Q3 Q4	FY16 Q1 Q2 Q3 Q4
Project Milestones			Deliverable A	Deliverable B	
Task 1		Accomp1			
Subtask 1.1					
Subtask 1.2					
Sub-Sub Task 1.2.1					
Task 2			Accomp 2		Accomp 3
Subtask 2.1					
Subtask 2.2					
Task X					Accomp X
Subtask X.1					
Subtask X.2					

Include this slide in presentation only for proposed new start projects or tasks, or if project has changed significantly from previous year. Otherwise include previously completed Schedule in the Back-Up Slides

Project '*Name*' - Issues

Each PI should fill out this slide. I will compile the info into one slide.

None