SAND2010-7492P

Aging of Adhesive Joints

Fall TCG XIV Review
November 2, 2010
Panama City, FL

Introductions

Doug Adolf

"The New Doug Adolf"

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Education:
Ph.D. , Chemical Engineering
The University of Texas at Austin

Industrial Experience:
Product Development, Applied Science Fiction 1999-2002
Research and Process Engineering, Dow Chemical and Hoechst Celanese 1996-1998

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*

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 with component 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

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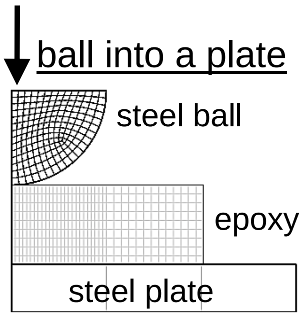
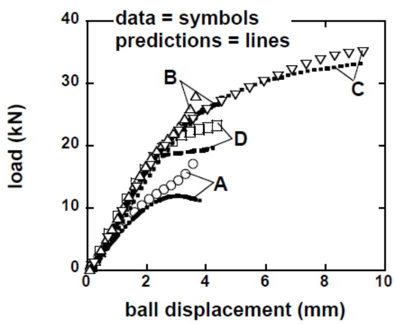
Review of SNL Failure Predictions in Thermosets: Cohesive Failure

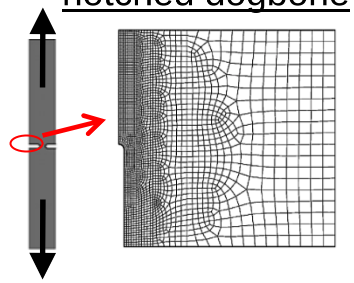
Ramp Tests

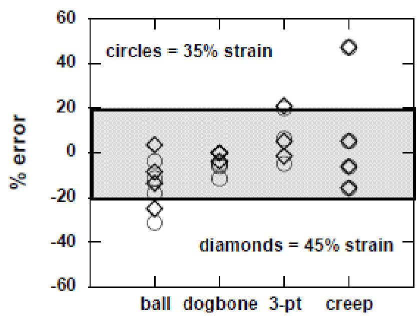
ball into a plate



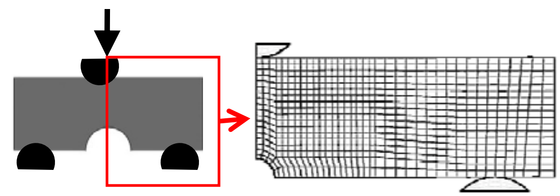


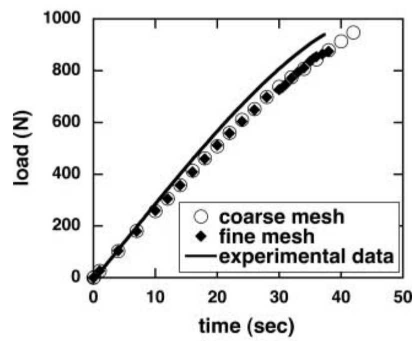
notched dogbone





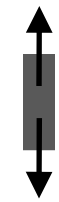
notched 3-point bend

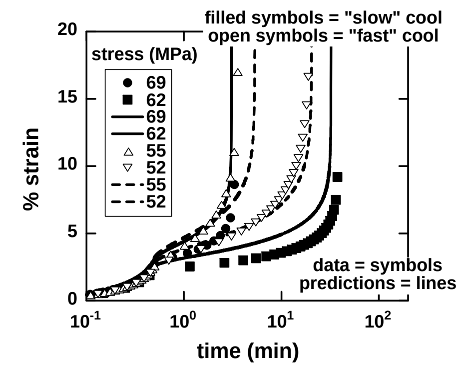




Creep Tests

un-notched dogbone



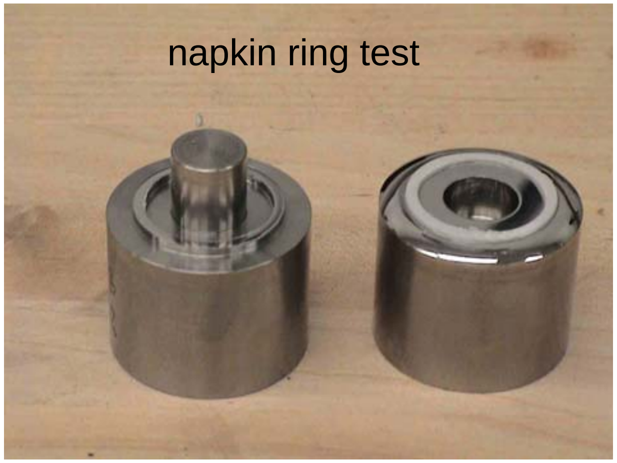


Loads and times to fail can be predicted quantitatively by:

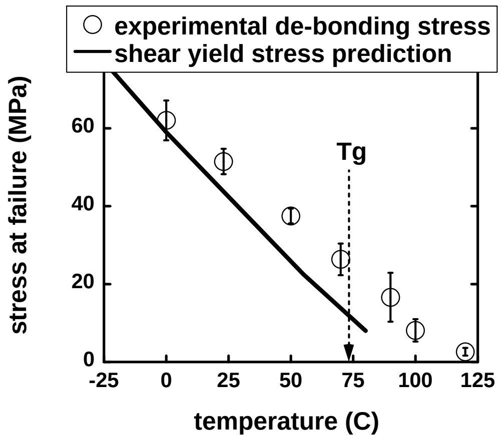
- simulating the actual test performed
- calculating stresses and strains in the epoxy using the SPEC nonlinear viscoelastic model
- using a maximum principal strain of ~40% as a failure metric

Adolf, D. B., Chambers, R. S., Elisberg, B., Stavig, M. and Ruff, M.
Journal of Applied Polymer Science, 2010

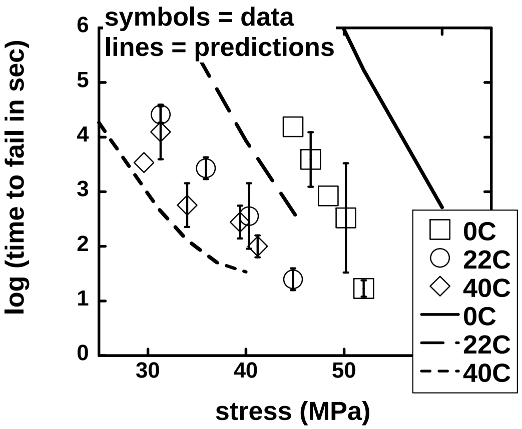
Review of SNL Failure Predictions in Thermosets: Adhesive Failure



ramp tests



creep tests

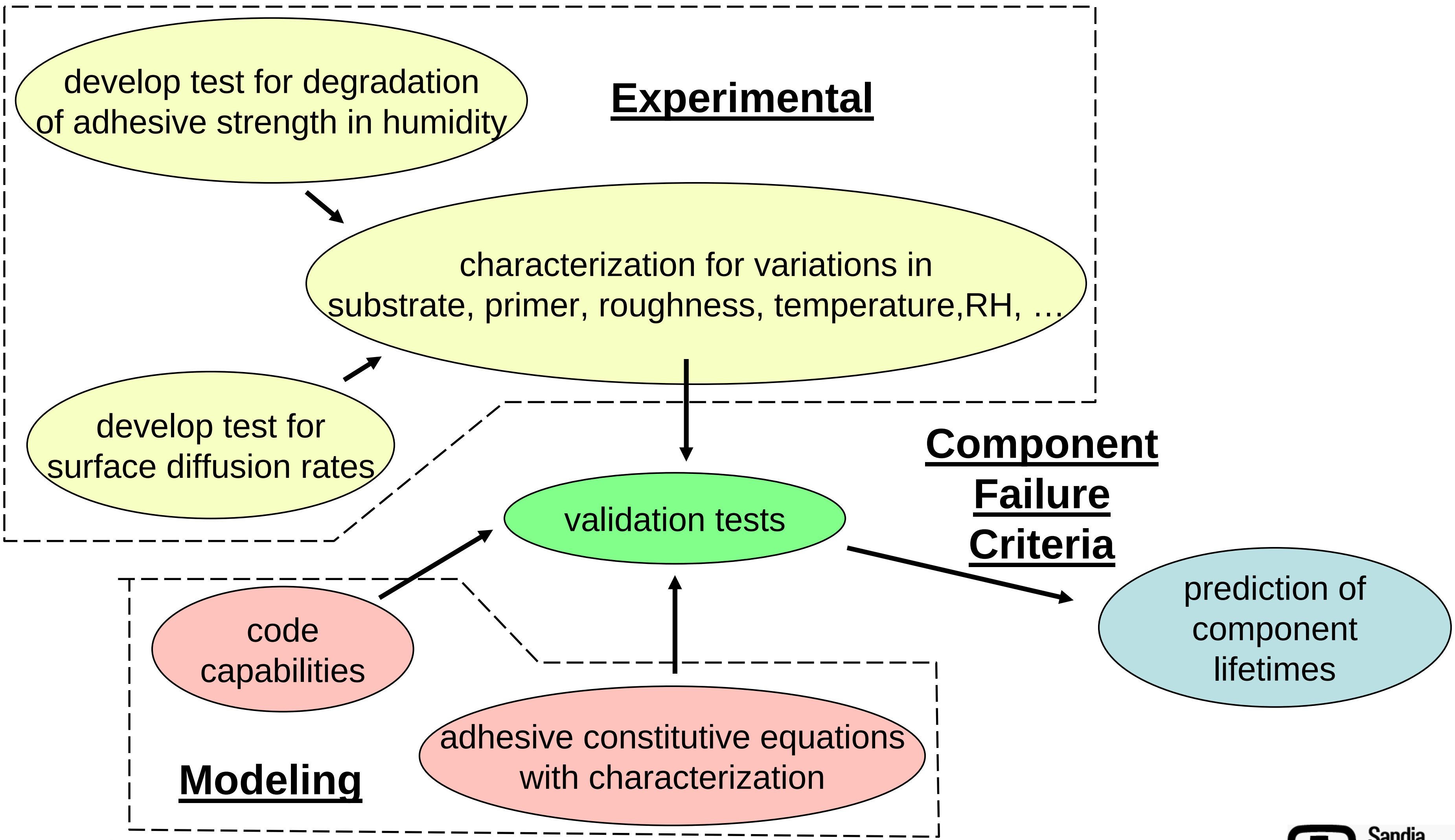


Loads (times) to fail can be predicted quantitatively (qualitatively) by:

- simulating the actual test performed
- calculating stresses and strains in the epoxy using the SPEC nonlinear viscoelastic model
- acknowledging that the polymer very near the metal interface has a slightly lower glass transition temperature
- using a maximum principal strain of ~40% as a failure metric

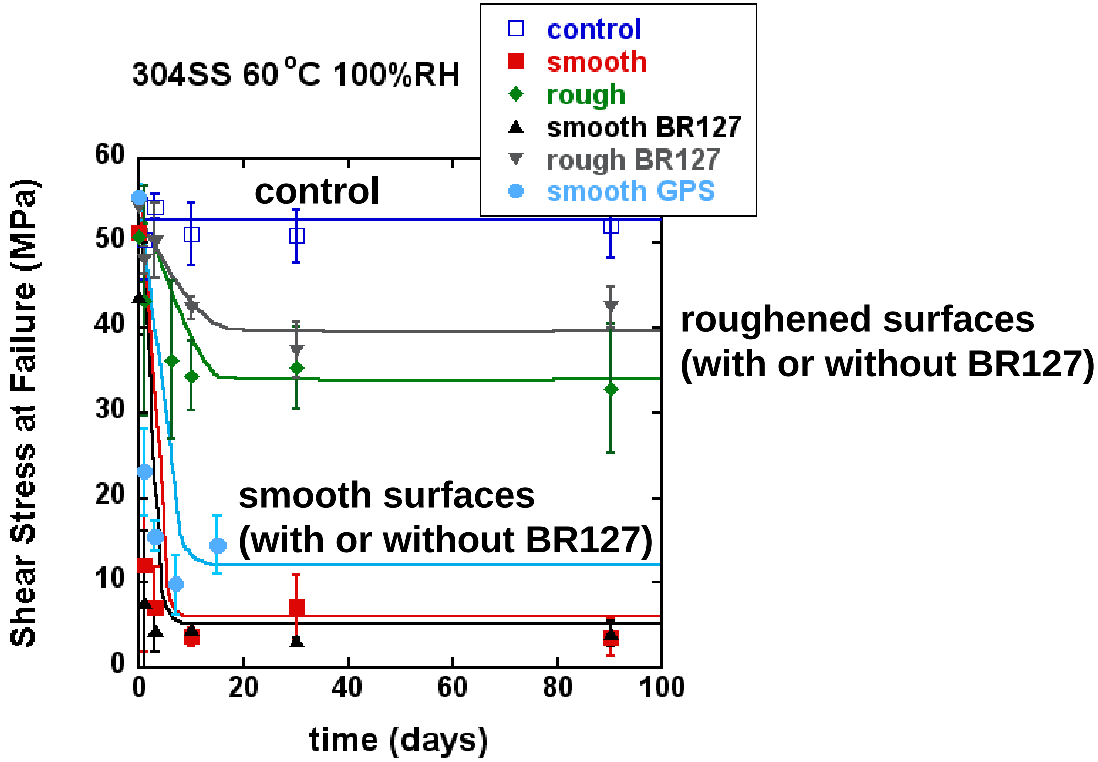
Adolf, D. B., Chambers, R. S., Hance, B. and Elisberg, B. *Journal of Adhesion*, 2010

Review of SNL TCG XIV Adhesive Task Approach



Review of Previous Results: Wet Adhesive Failure on Napkin Rings

<u>Epoxy bonding 304SS of varied surface preparations</u>

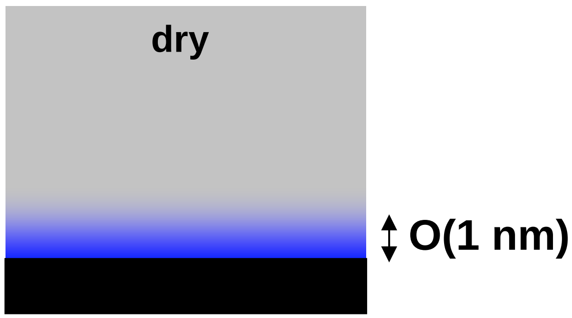


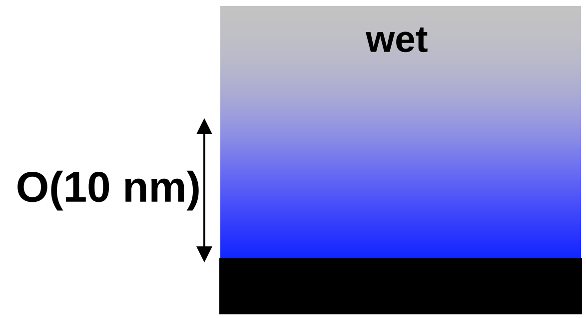
Effects of humidity can be measured:
- Equilibrium effect of water on bond strength reached in days
- Surface roughness critical in determining magnitude of water effect on bond strength

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

Review of Previous Results: Wet Adhesive Failure Mechanism

Reduced T_g: wet vs. dry

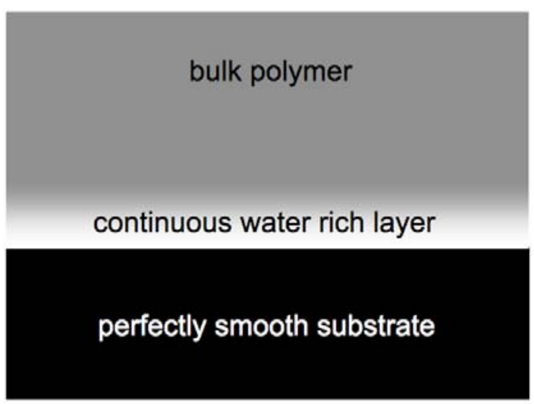


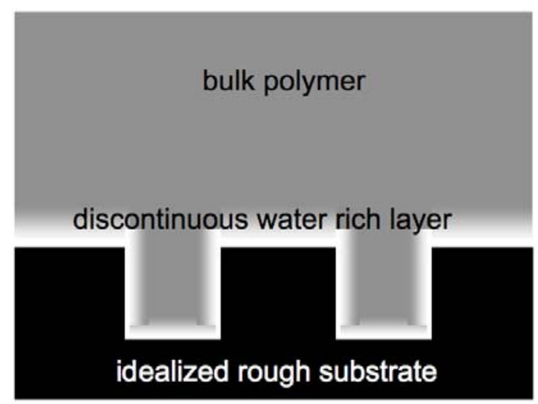


Entropic, ΔT_g ~ 5ºC

Plasticization, ΔT_g ~ 50ºC

Moisture Effects on Bond Strength: smooth vs. rough surface



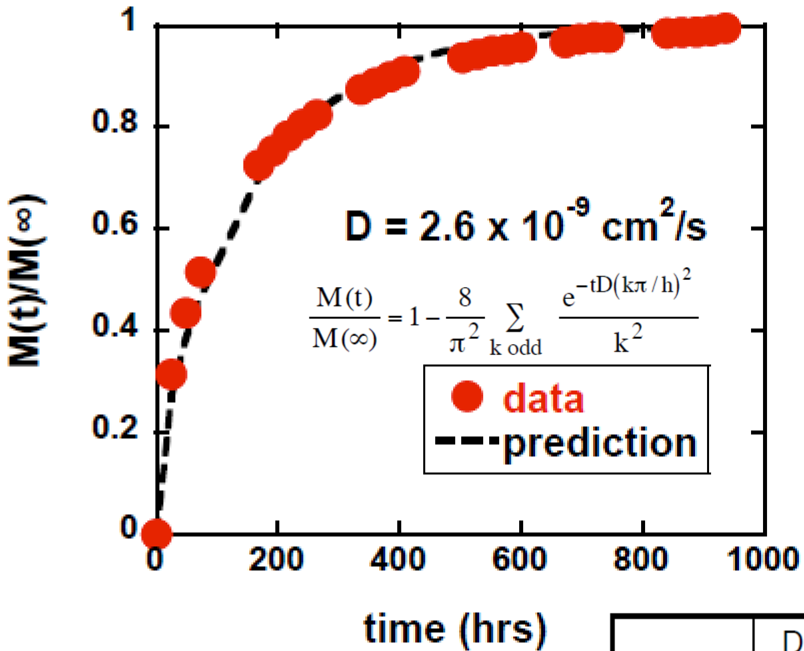


Clean break across reduced T_g interface

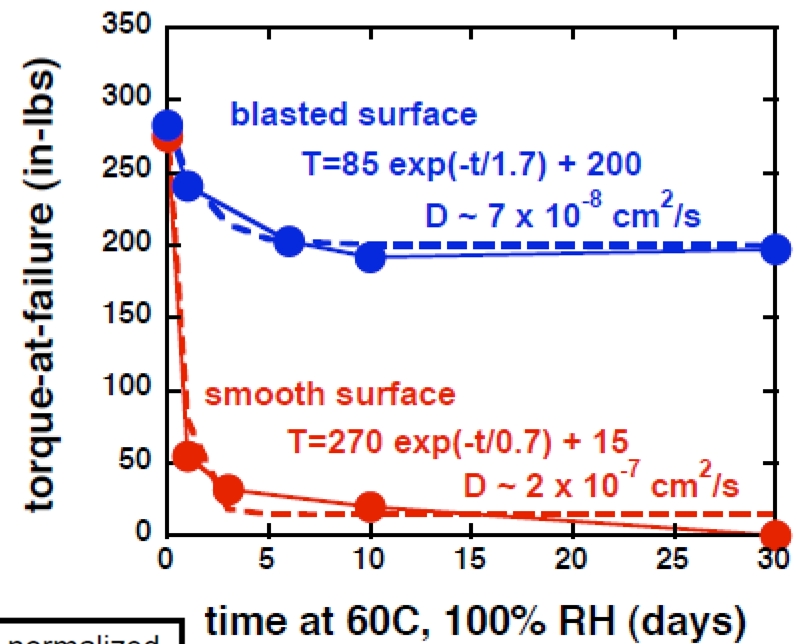
Bulk polymer must be traversed

Review of Previous Results: Water Diffusion Rates

Mass Gain: 60°C 100% RH



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

FY10 Budget and Tasks

FY10 Proposed Tasks and Budget:

1. Characterize adhesive strength sensitivities to substrate and environmental variables using napkin ring geometry
2. Develop test geometry that enables validation of proposed models for predicting degradation of adhesive strength

	budget	task 1	task 2	meetings
DoD	125	65	50	5
DOE P&EM	50 ÷2	25		
DOE C6	85 ÷2	42		
DOE NG	120÷2		55	5

FY10 Results:

1. Aluminum surfaces
2. Silane coupling agent primers (GPS)
3. Drying wet interfaces
4. Epoxy-epoxy bonding
5. Developing validation test geometry

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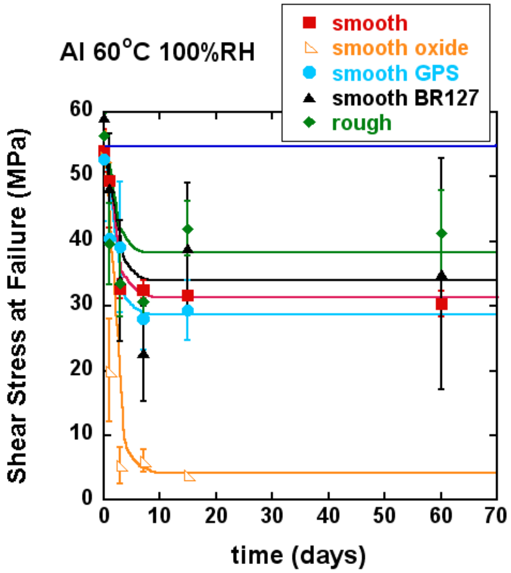
Aluminum Surfaces - 100%RH at 60C



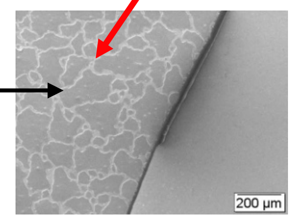
decrease on rough aluminum

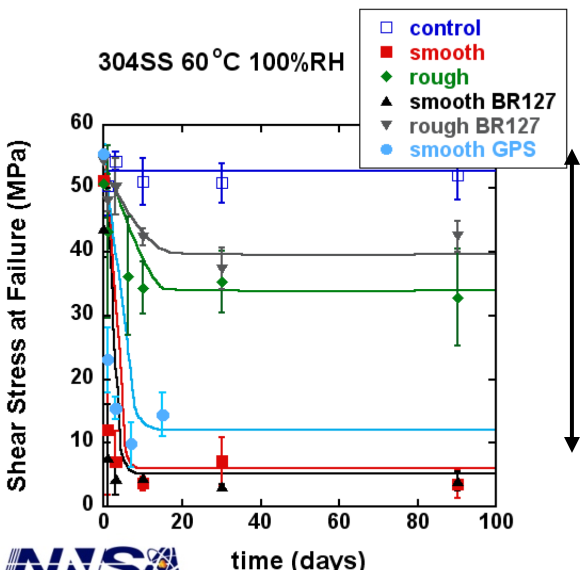
decrease on smooth aluminum (with or without GPS or BR127)

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

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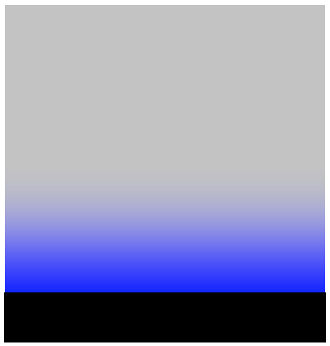
Possible Explanation of Results



Proposed Mechanism

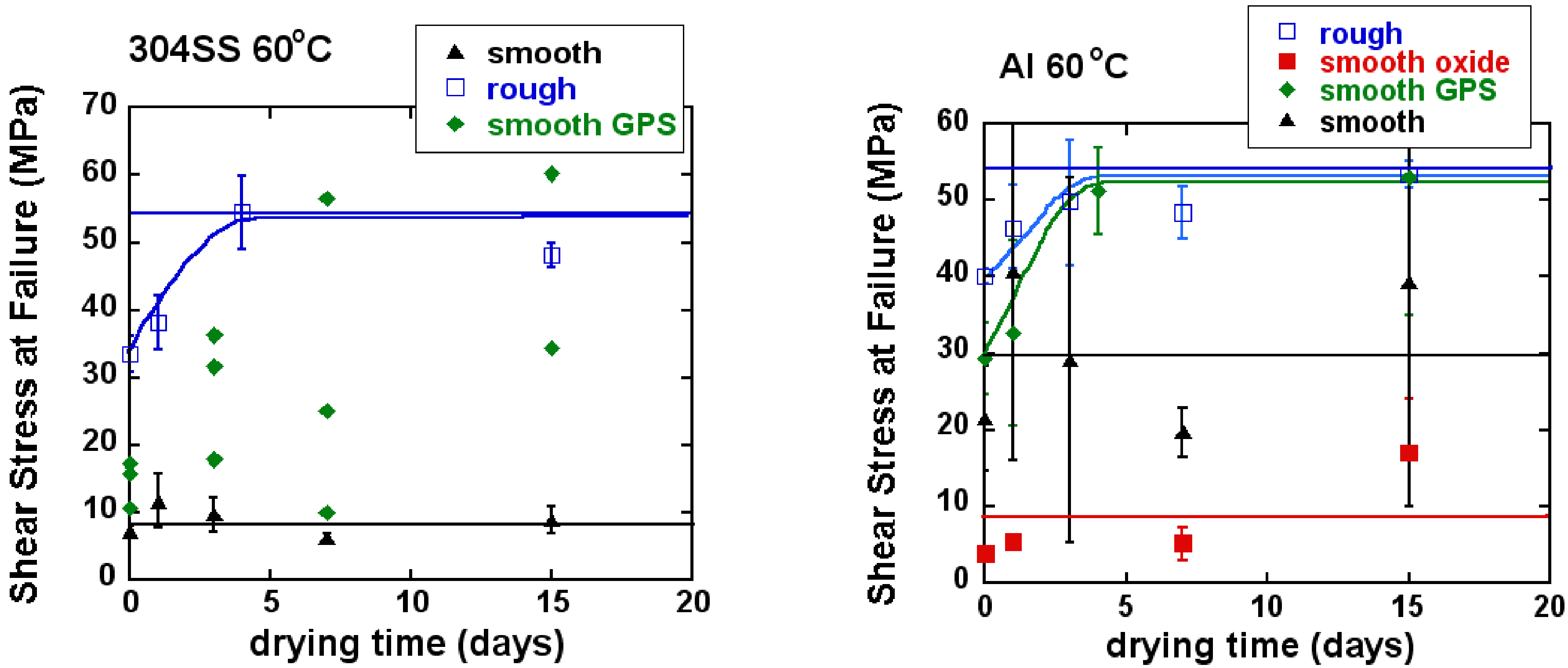
- water accumulates preferentially at the interface
- water plasticizes the polymer reducing the T_g
- a lower T_g implies a lower yield stress
- de-bonding is concurrent with interphase yielding

Substrate Effect

- the amount of water at the interface depends on:
  1. the thermodynamic driver and
  2. the attraction of the epoxy to the surface
- both are dependent on the specifics of the substrate

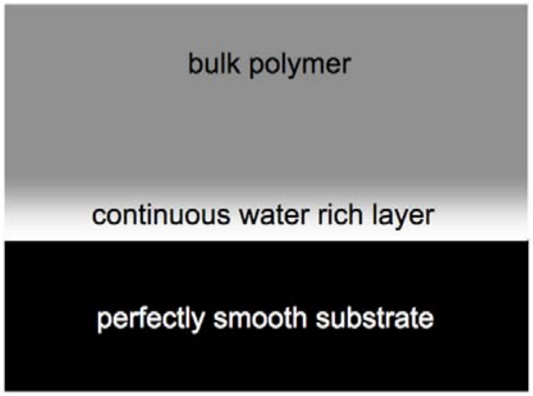
It appears that the attraction of the polymer to aluminum is greater than to steel (not unexpected) such that the polymer cannot be as easily “pushed away” from the interface

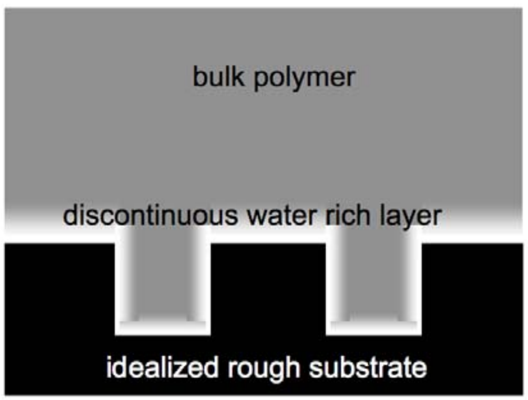
Effect of Drying



- 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

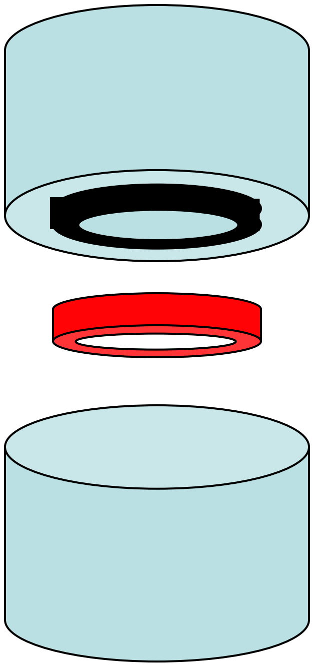
Possible Explanation of Results





- Roughened surface may not allow polymer to “drift away” from the interface as water accumulates.
- During drying, re-wetting is not needed.
- GPS results on Al may invoke specifics of silane chemistry.

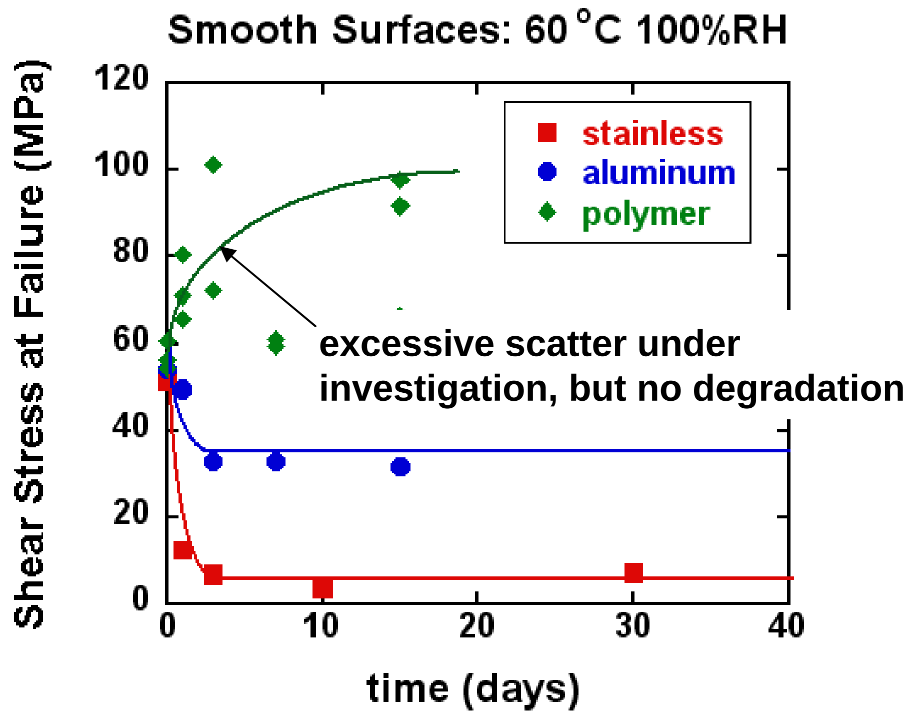
Epoxy Substrate



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

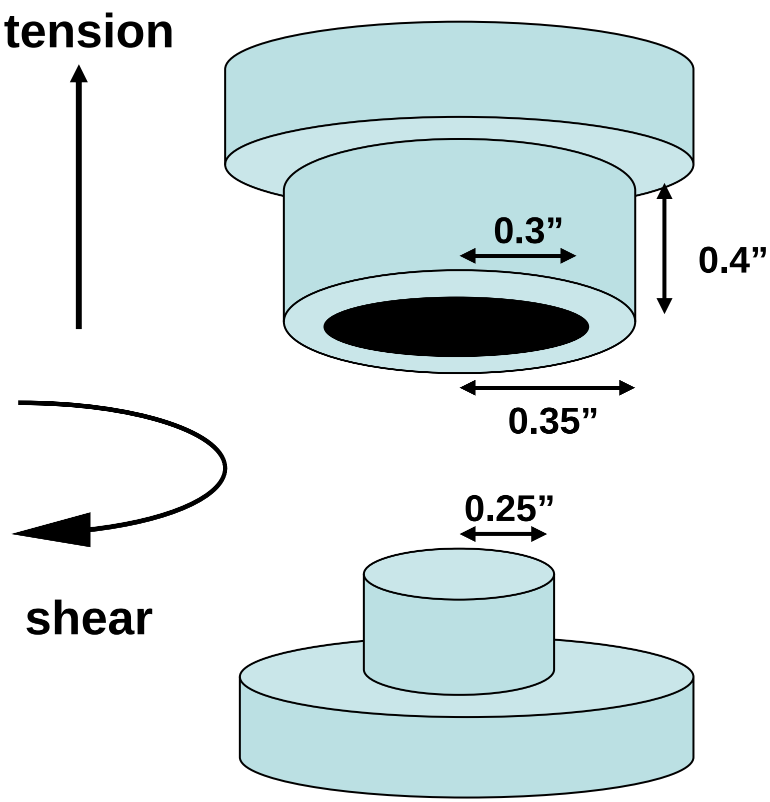
bonded adhesive
unfilled epoxy (T_g~70°C)

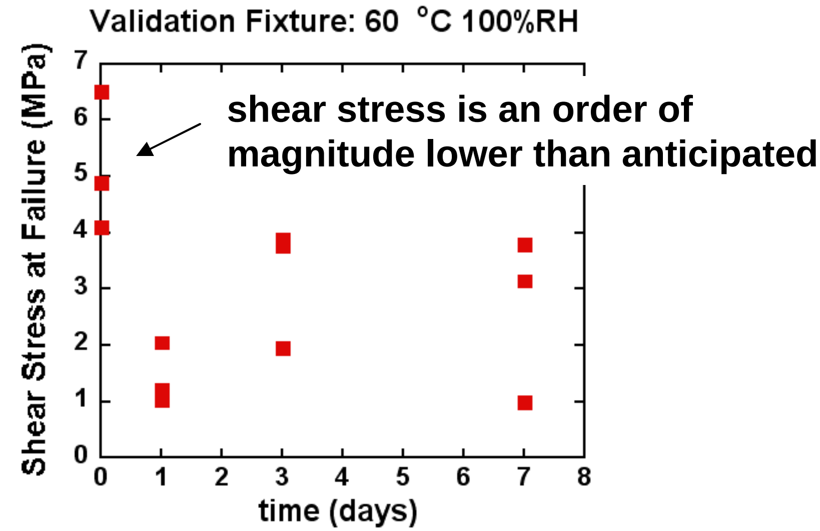
lower plug
alumina-filled epoxy (T_g~160°C)



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

Validation Geometry Tests





- Stress-at-failure less than expected
- Analysis of virgin stress-at-failure proceeding under TCGX funding

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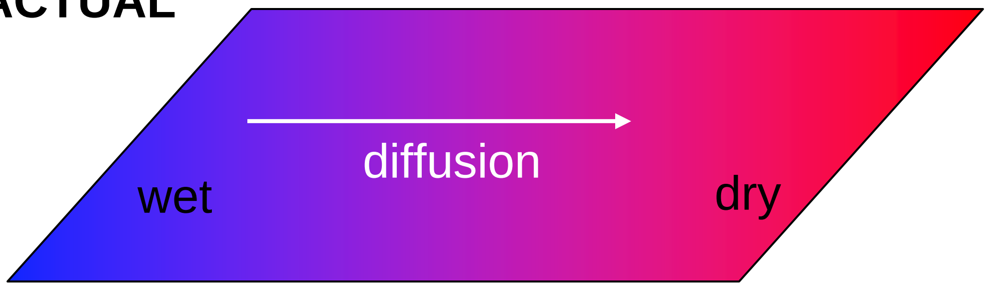
Modeling Adhesive Degradation: Simplest Possible Scheme

ACTUAL

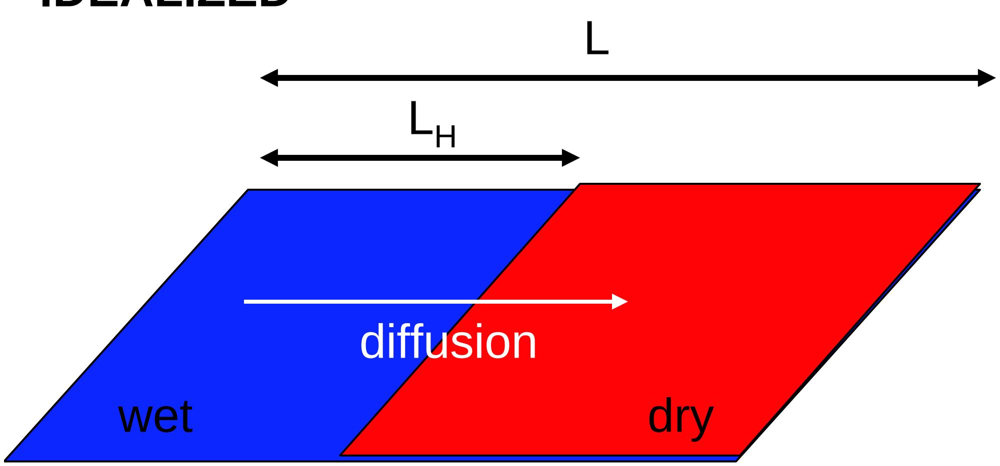


EXAMPLE CALCULATION

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

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

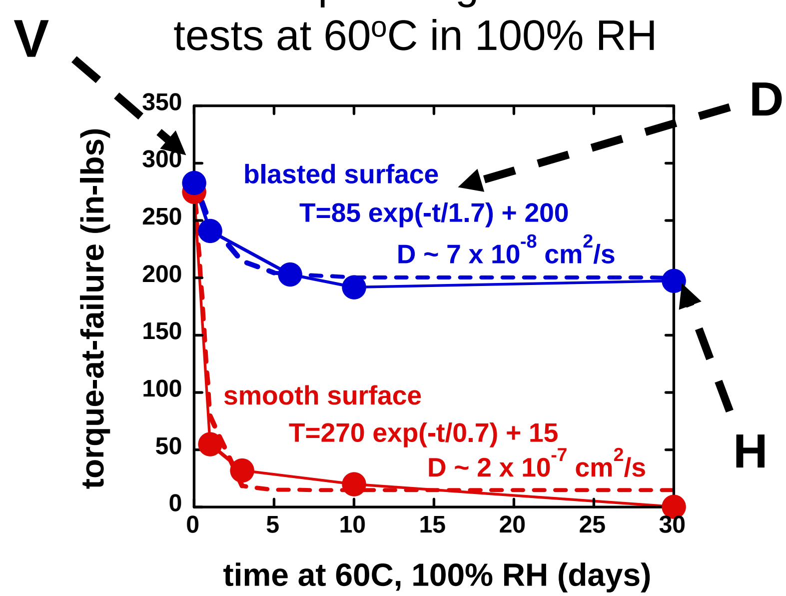
IDEALIZED



"humid" strength = H

"virgin" strength = V

from napkin ring adhesion tests at 60ºC in 100% RH



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

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

Adhesion Task: Remaining Questions

1. How does adhesion degradation change with aging environment?
   a. Temperature (deep glass to rubber adhesives)
   b. RH

2. What other conditions might effect adhesion aging?
   a. Water freezing at bond-line

3. Can napkin ring metrics be validated in an independent geometry?
   a. Adhesion strength degradation
   b. Water ingress rate

4. Why are epoxy-composite bonds so strong?

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Transitions

ABAQUS user sub-routine for the "SPEC" nonlinear viscoelastic material model is complete

- accurately predicts stresses in thermosets
- used to define failure metrics in dry environments
- transitioning mechanism proposed through TCG10

review book written on the nonlinear viscoelastic polymer model with applications to wet adhesion

FY11 Tasks & Budget

Proposed project goals for FY11

1. More permutations on napkin ring tests: vary aging conditions and thermal history
2. Determine validation geometry shear bond strength

	budget	task 1	task 2	meetings
DoD	120	60	55	5
DOE NG	120	60	55	5

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 Schedule

	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					
Task 1: Degradation of Adhesive Strength in Humidity		Deliv1			
Subtask 1.1: Degradation of Adhesive Strength in Humidity:30, 100ºC; 100%RH					
Subtask 1.2: Degradation of Adhesive Strength in Humidity: Freezing					
Task 3: Bond Healing Metric for Drying of Water from Bond-line				Deliv2	
Task 4: Validation of Metrics in More Realistic Geometry					