SAND2007-2459C

Silanated Alumina for Novel Epoxy Composites

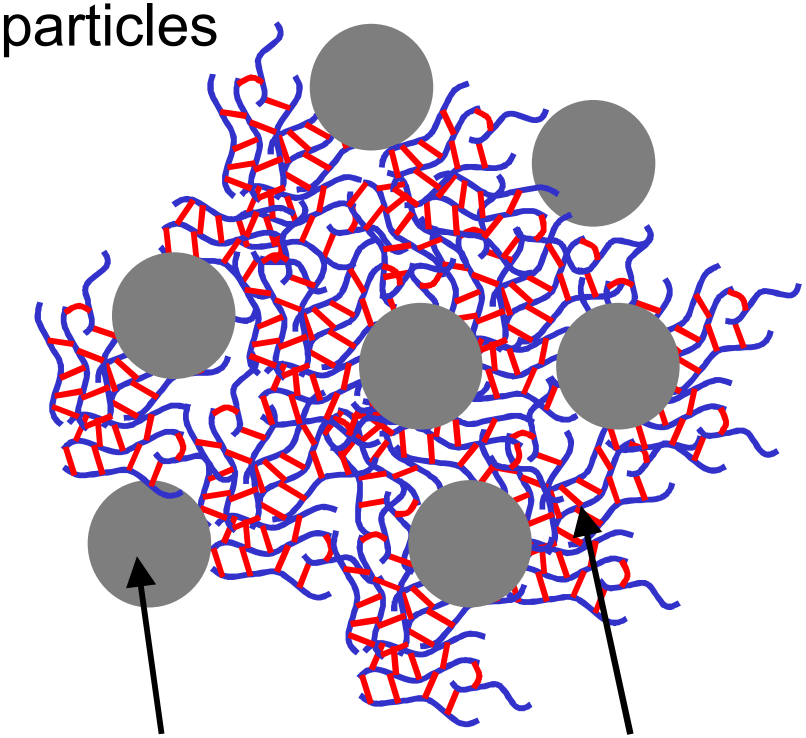
Laura M. McGrath[1,2], Joseph L. Lenhart[2] and Richard S. Parnas[1]

[1]University of Connecticut, Institute of Material Science: Polymer Program, Storrs, CT
[2]Sandia National Laboratories, Materials Science and Technology Division, Albuquerque, NM

This work was performed at Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Safety Administration under contract DE-AC04-94AL85000.

Particulate Filled Composites

- Inclusion of a particle in a polymer matrix:
  - Continuous matrix phase: polymer
  - Discontinuous filler phase: discrete particles
- Alumina[1]
  - Micron-sized particles
  - E (Elastic Modulus) ~416 GPa
- Cross-linked epoxy resin (thermoset)
  - E ~ 3GPa



[1]http://www.ceramics.nist.gov/srd/summary/scdaos.htm

Final Objectives and Approach

- Determine which, if any, Al_2O_3 variables: particle shape, size, size distribution, and surface chemistry affects composite properties and processibility
- Determine which, if any epoxy variables: T_g, crosslink density affects composite properties and processibility
- Establish the critical composite properties for processability and performance
- Resolve performance sensitivity to those properties and variables

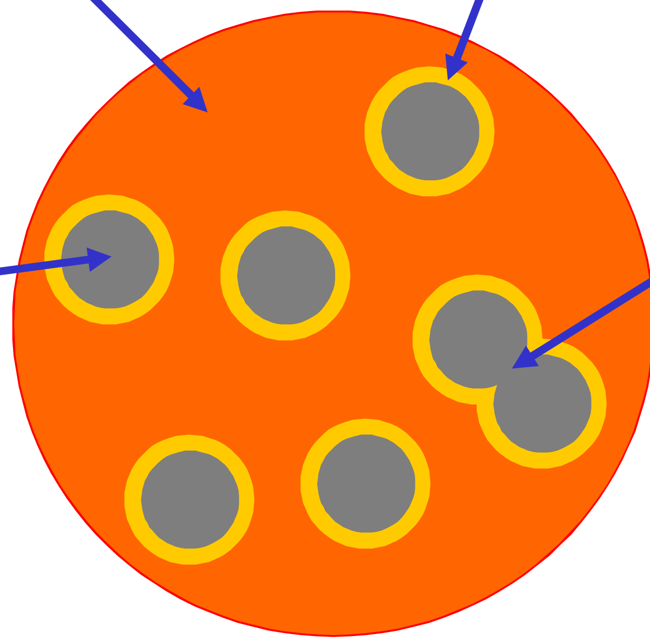
Final Objectives:

1) Set characterization tools for incoming material specifications
2) Understand structure-property relationships in filled epoxy composites

A Simple Picture of the Composite

3) Polymer / filler interface region
- Surface chemistry / morphology
- Surface cleaning / modification
- Surface coupling agents

2) Bulk polymer
- Vary cross-link density
- Vary hardener type/ curing agent
- Chemistry/Functionality



4) Filler / filler interactions

1) Filler – Al_2O_3
- Shape
- Size
- Size Distribution

- How do the system variables influence the composite properties?
- When and why are these factors important?

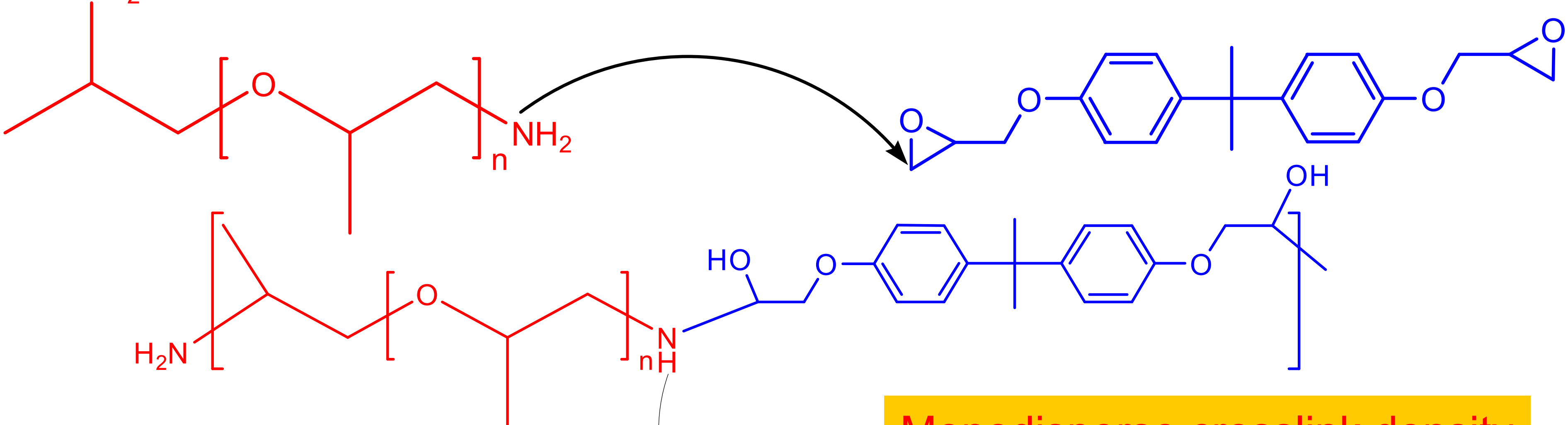
Mc Impact on Crosslinked Polymers

Polypropyleneoxide diamine: D230, D400, and D2000

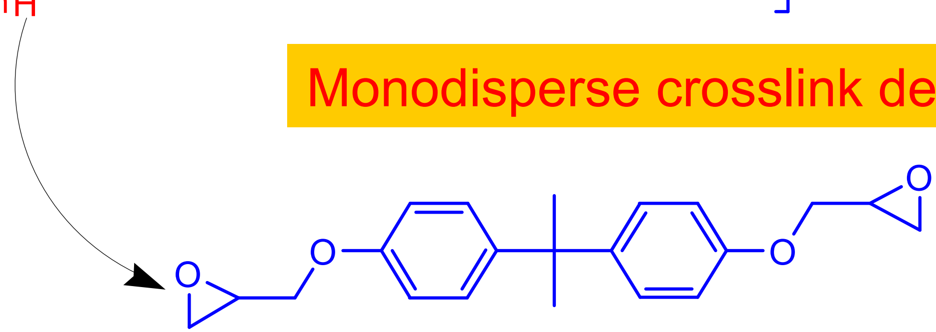
Diglycidyl ether of bisphenol A (DGEBA) Mw=348g/mol

f = 4

f = 2

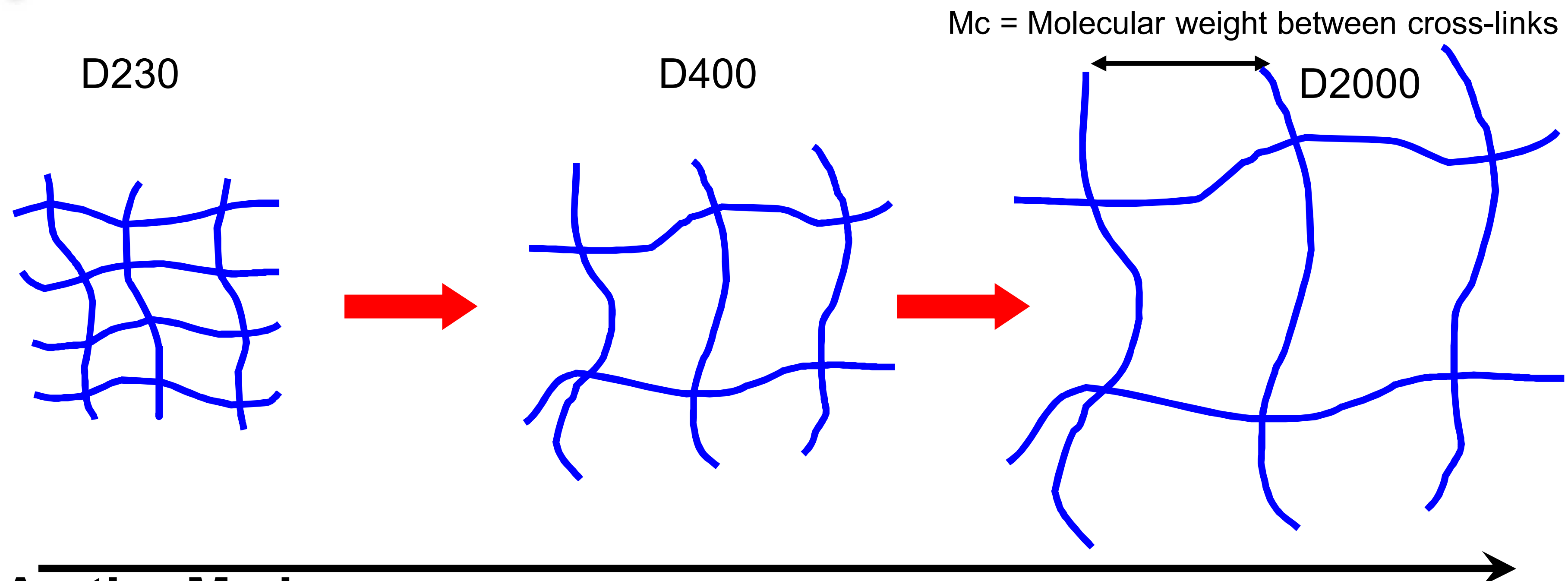


Monodisperse crosslink density



	n	MW
D230	2-3	230
D400	5-6	400
D2000	33 (Avg.)	2000

Mc Impact on Cross-linked Polymers: Qualitative Look



As the Mc increases:

- Tg decreases
- Rubbery modulus decreases
- CTE increases
- Diffusion constants increase

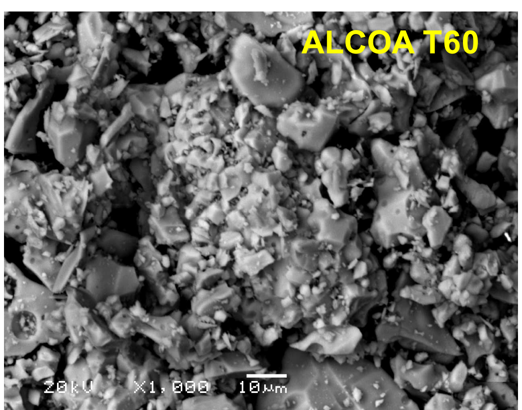
- Energy dissipation increases
- Viscosity changes with Mw of monomers

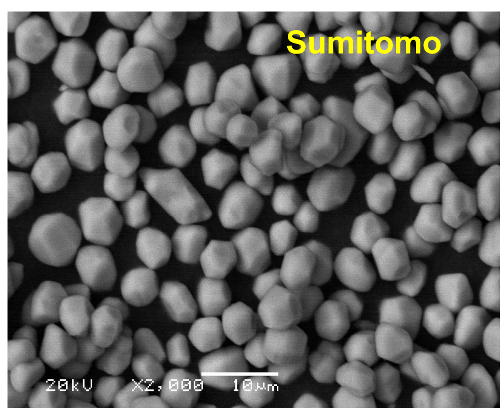
Mc and network homogeneity is critical

Alumina (α-Al_2O_3)

- White powder
- Natural rhombohedral shape
- Low density: 3.93 g/cc
- 0-50% by volume loading
- Two different size distributions
  - Sumitomo
    - AA2
    - AA5
    - AA10
    - AA18
  - Alcoa
    - T60
- Beckman Coulter LS particle size analyzer

	Sumitomo				Alcoa
Particle Size (µm)	AA2	AA5	AA10	AA18	T60
Mean	3.683	5.064	8.083	16.700	18.81
Mode	3.359	5.064	8.536	18.000	26.14
Standard Dev.	1.589	4.878	2.614	4.713	

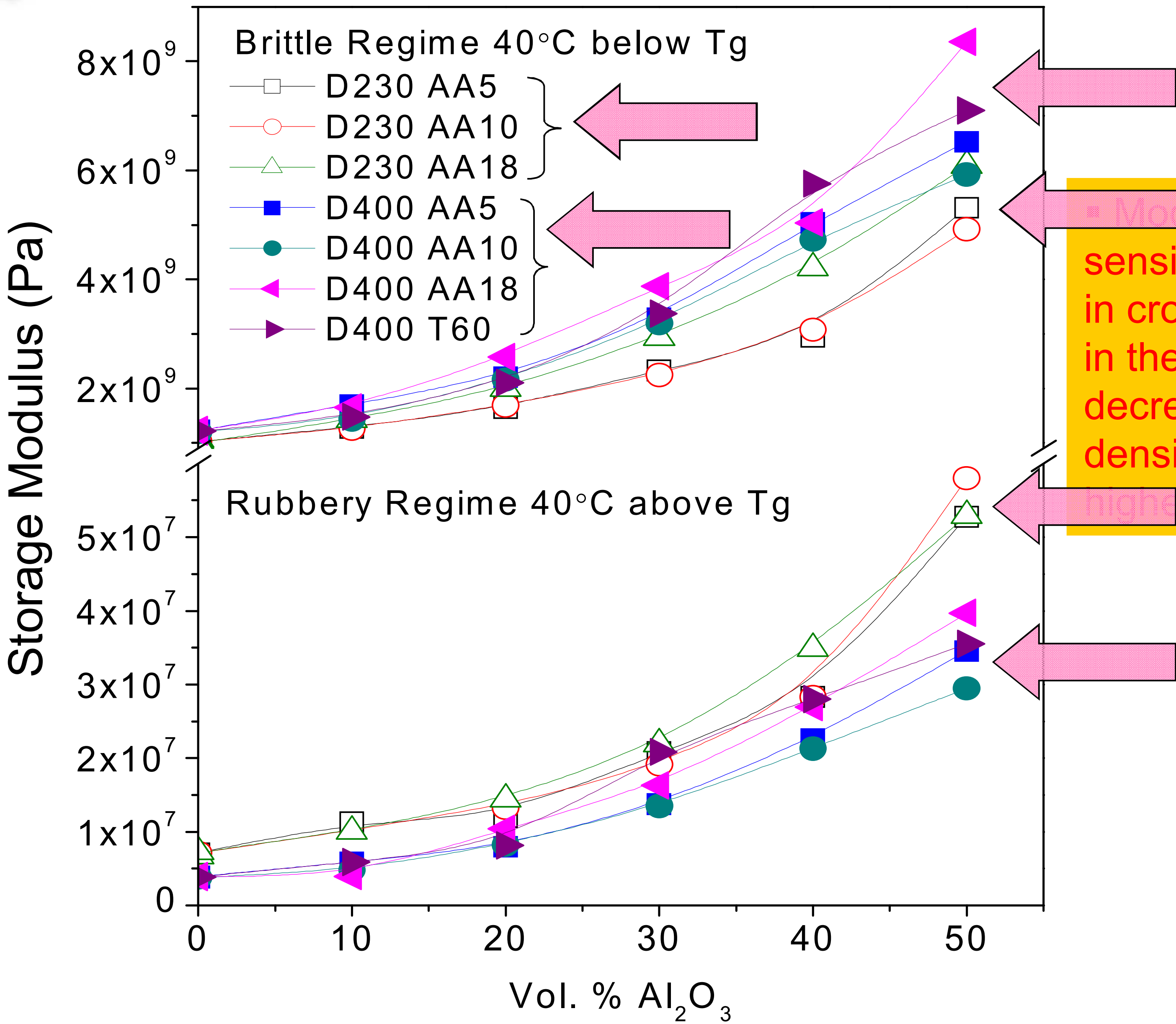




Composite preparation

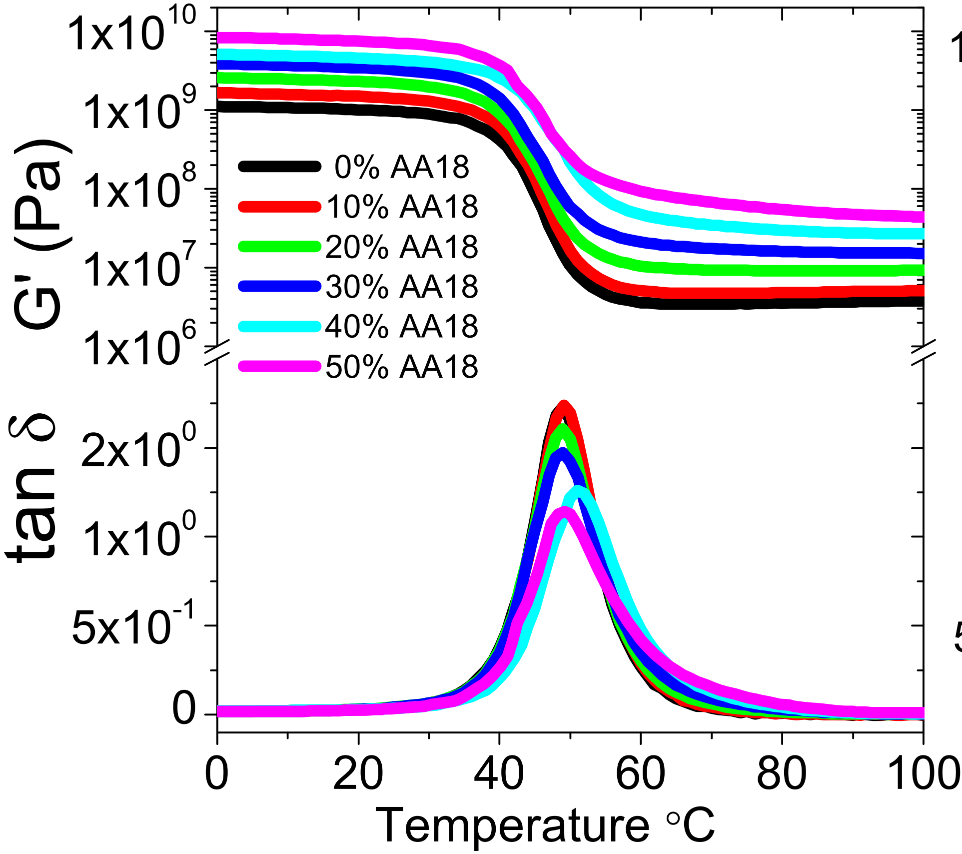
- Epoxide and diamine monomers are mixed neat
- Al_2O_3 is added to epoxy precursers (at a subjective viscosity to prevent settling)
- Added to release-coated Al molds and subjected to cure cycle

G´ in D230 and D400 with various Al_2O_3

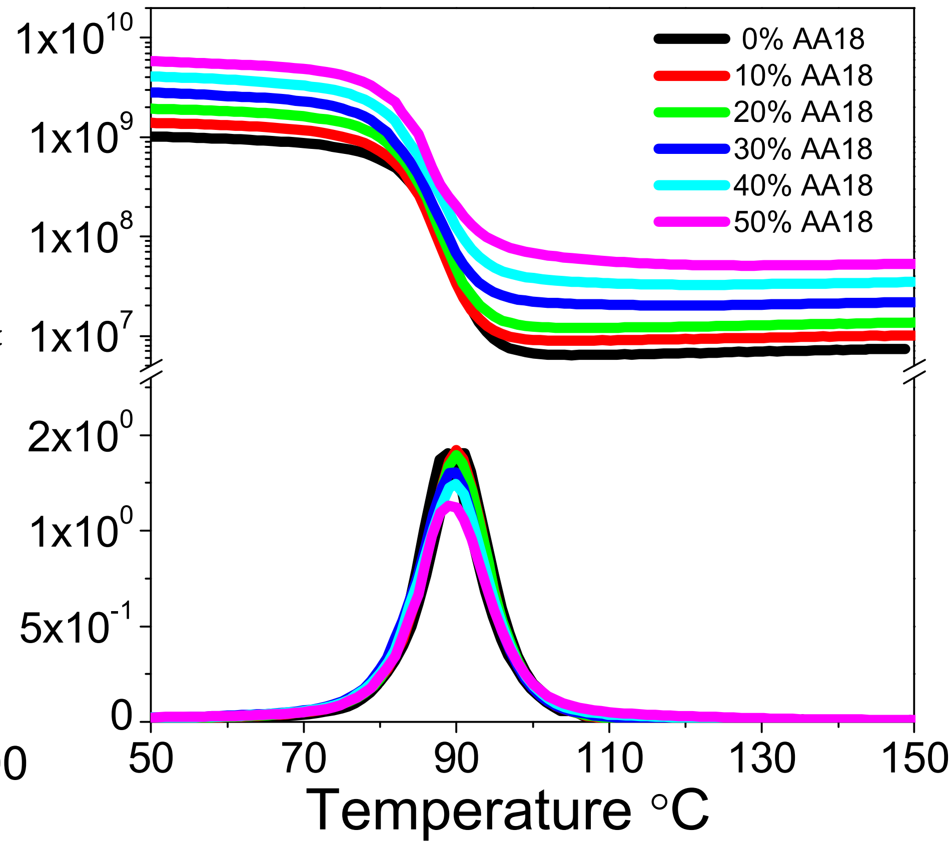


- Modulus is slightly sensitive to changes in cross-link density in the glassy region, decrease cross-link density results in a higher modulus.

G´ and tan δ in D230 and D400 with various Al_2O_3

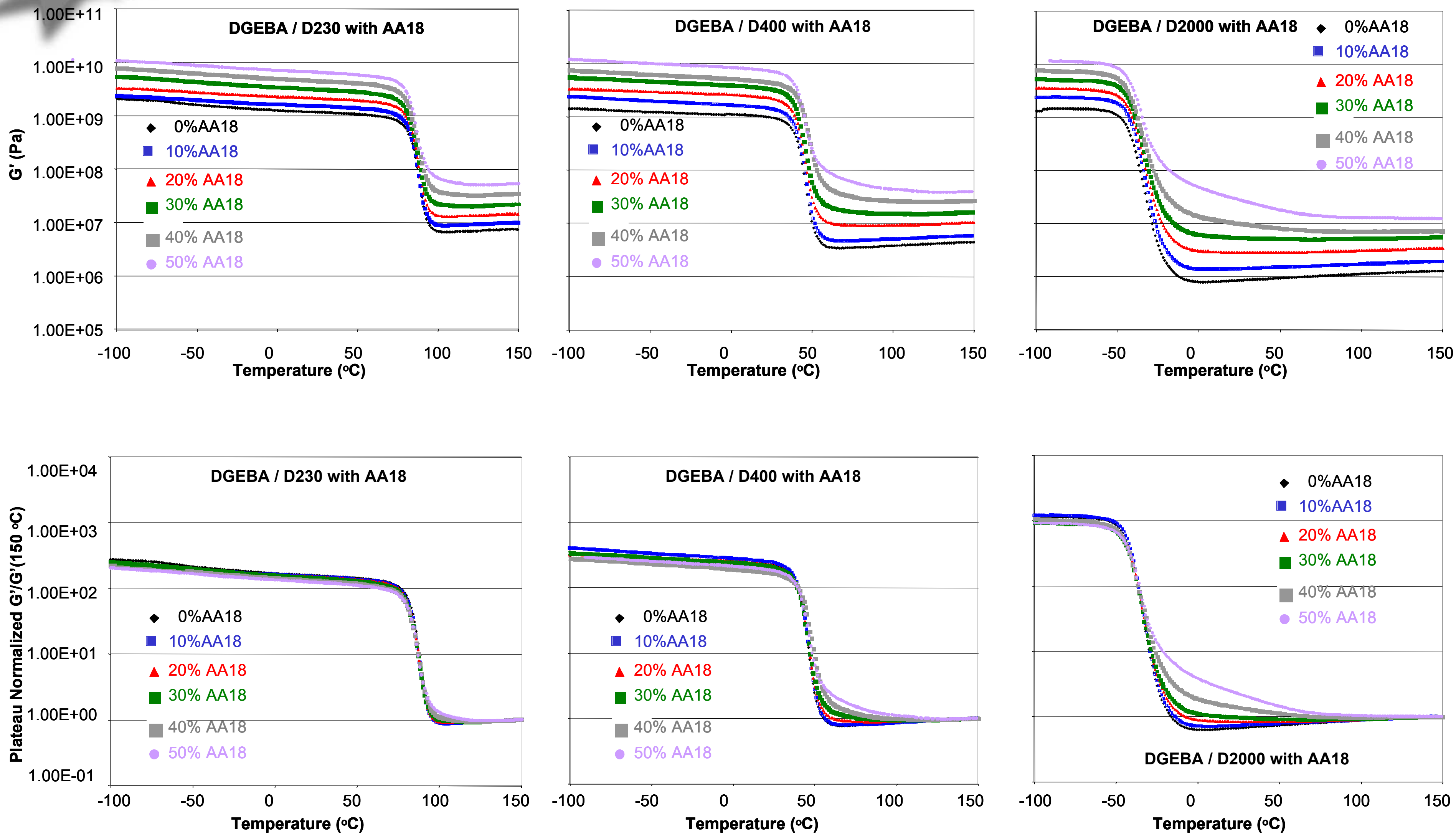


DGEBA/D400



DGEBA/D230

Broadening of Modulus Profile



• Take care with using resins in rubbery region at high filler loadings near the Tg

Broadening of Modulus Profile

Quantify the broadening by fitting with the Cumulative Normal Distribution or inverse Lorentzian function

$$y = \frac{P1}{\pi} a\tan\left(\frac{x - x_o}{\gamma}\right) + \frac{P2}{2\pi}$$

where:

p1=scaling parameter
p2=scaling parameter for temperature

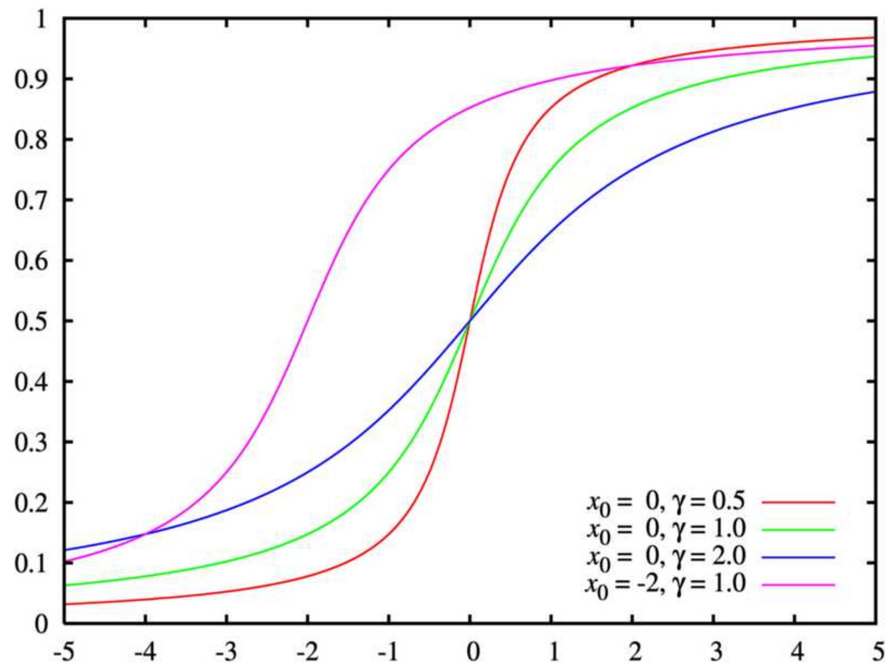
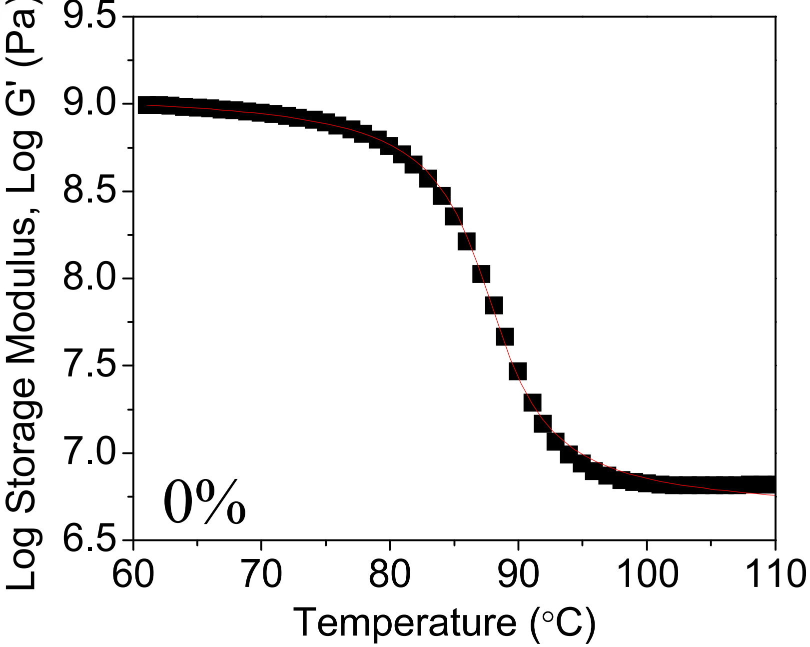
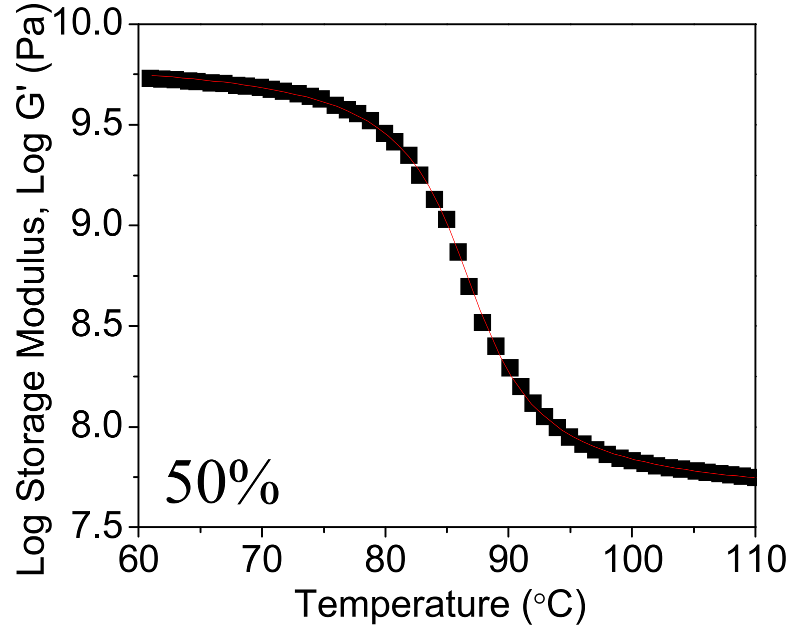


Image: http://en.wikipedia.org/wiki/Lorentzian_function

Broadening of Modulus Profile DGEBA/D230 with AA18 Al_2O_3

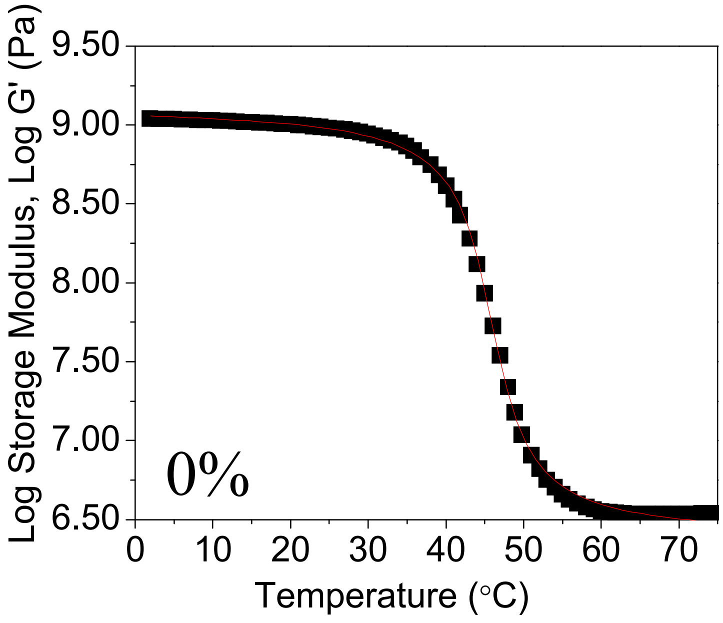


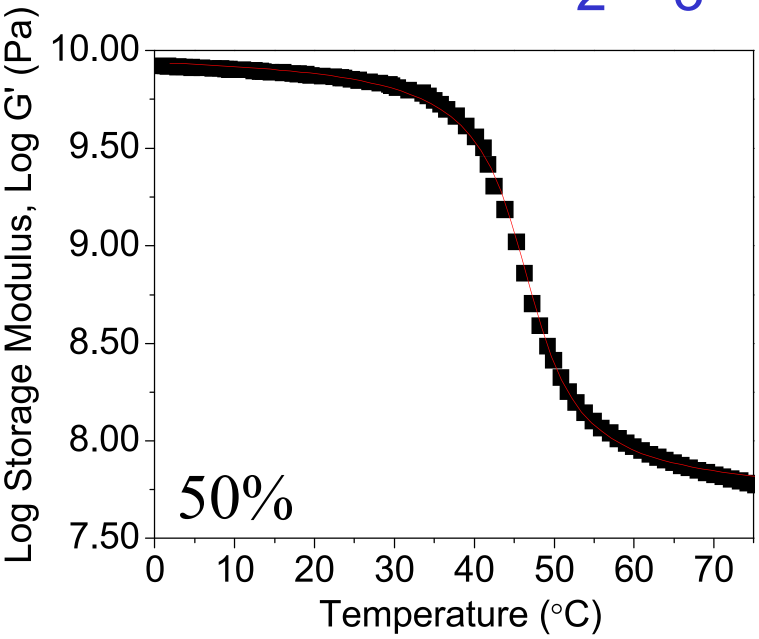


% fill	xo	γ	p1	p2
0	87.83	3.51	-2.46	49.42
10	87.31	3.53	-2.45	50.23
20	87.34	3.70	-2.48	51.08
30	86.70	4.11	-2.40	52.36
40	86.94	4.40	-2.35	53.59
50	86.71	4.29	-2.25	54.92

- Gamma increases with increasing vol. % of Al_2O_3

Broadening of Modulus Profile DGEBA/D400 with AA18 Al_2O_3

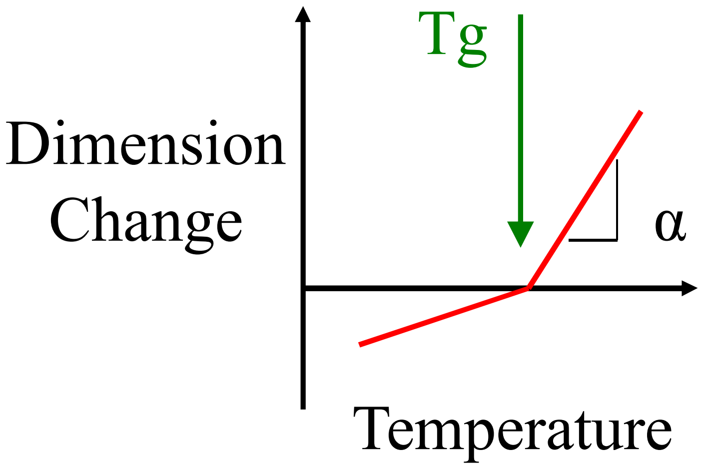




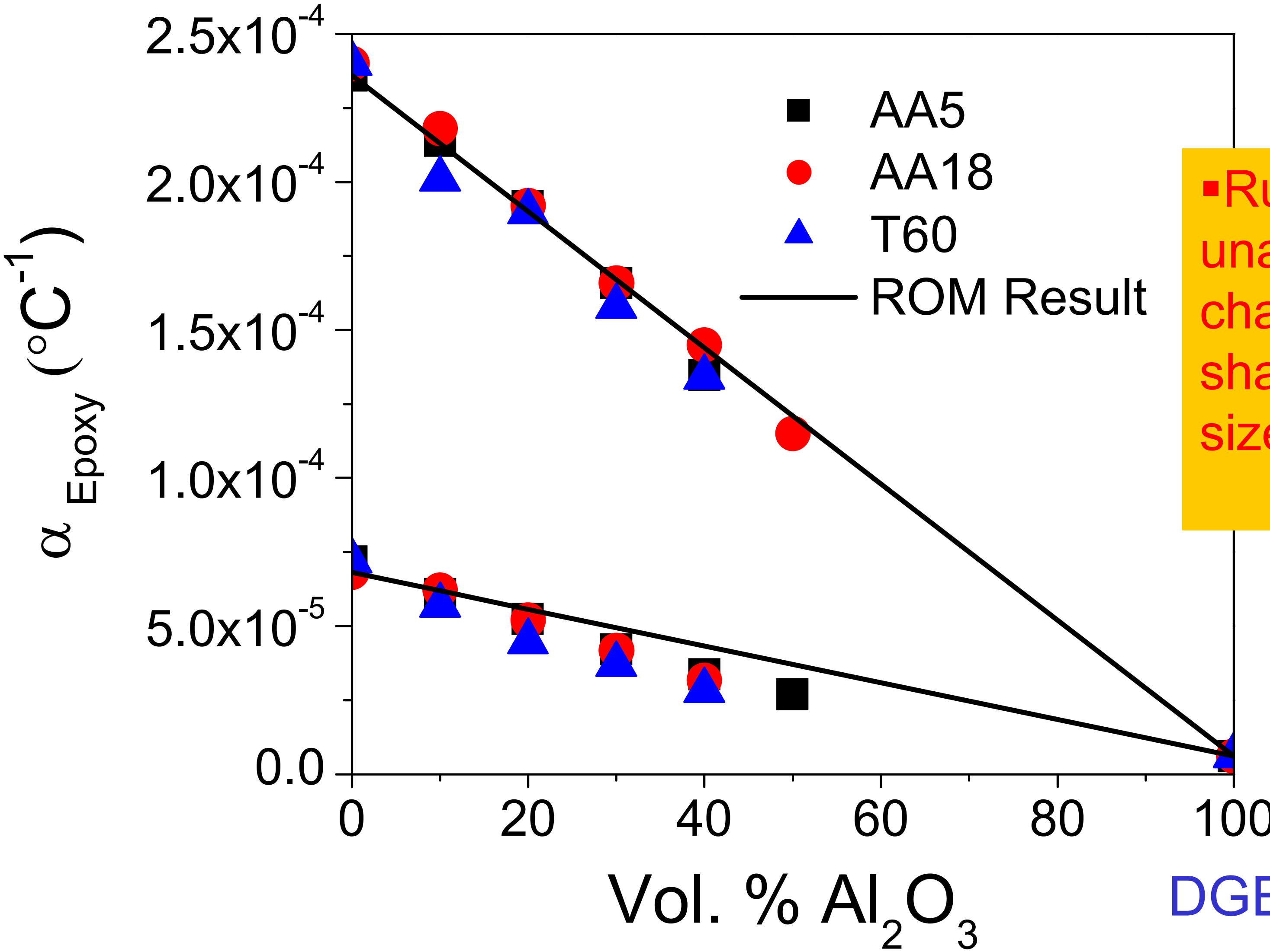
% fill	x_0	γ	p1	p2
0	45.88	3.69	-2.76	48.70
10	46.26	4.06	-2.87	49.52
20	45.85	4.12	-2.69	51.23
30	45.83	4.45	-2.60	52.68
40	48.27	4.84	-2.42	53.95
50	46.50	4.89	-2.32	55.64

- Gamma increases with increasing vol. % of Al_2O_3

Dependence of CTE (α) on the vol. % of Al_2O_3



Dependence of CTE (α) on the vol. % of Al_2O_3



- Rubbery CTE is unaffected by changes in filler shape, size, and size distribution

DGEBA/D400

Fracture Mechanisms

Fracture is one of the most important criteria for determining the usefulness of a composite specimen and marketplace viability

- Low fracture toughness leads to crack propagation and part failure
- Fracture begins from localized stresses at flaws or defects
  - Need to know the local state of stress
- Energy dissipation from brittle/ductile transitions
  - Brittle: Crazing
  - Ductile: Shear Yielding
- Griffith used energy required to generate a new surface as criterion for fracture
  - New surface can only occur when bonds are broken
- Two parameters developed to quantify fracture
  - G_c, critical energy strain release rate
  - K_c, critical stress-field around a sharp crack
    - Referred to as fracture toughness
    - Measures the ability of the material to resist crack propagation

Fracture Behavior of Polymers; Kinloch, A.J.; Young, R. J.; Chapman and Hall: London, England, 1983

Fracture Toughening

- The goal of fracture toughening is to ensure that *energy dissipating mechanisms are prevalent* in the bulk in order to:
  - Limit deleterious voids
  - Increase energy dissipating mechanism like crazing that may extend specimen life
- We add Al_2O_3 to epoxy to:
  - Increase fracture energy, G_c
    - ('energy required to form a unit area of crack')
  - Increase the plastic deformation at crack tip
    - By crazing and other energy dissipative mechanisms
  - Energy adsorption sites

Fracture Toughness

- K_{Ic} is used to quantify toughness
  - Plane-strain fracture toughness
  - Resistance of the material to fracture
  - Samples tested at T_g-40°C
  - Three-point-bend geometry

$$K_{Ic} = Y \frac{3PS\sqrt{a}}{2BW^2}$$

Where:

Y = Shape Factor, dependent on c
length and specimen depth

P = Load at Failure

S = Length of Span

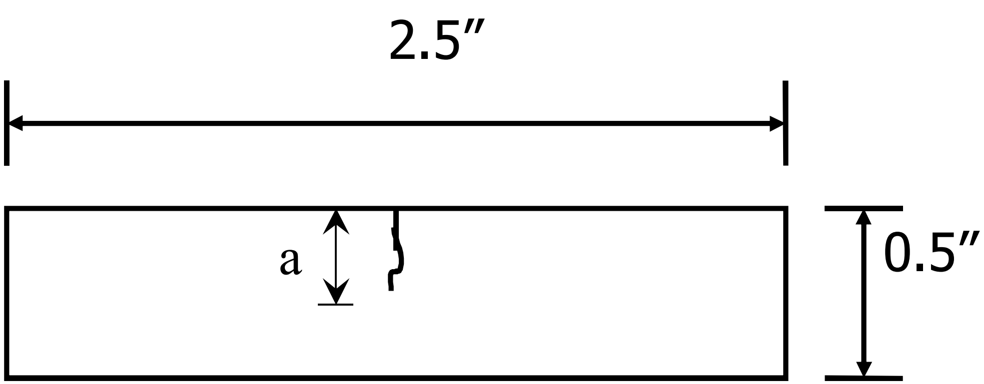
a = Crack Length

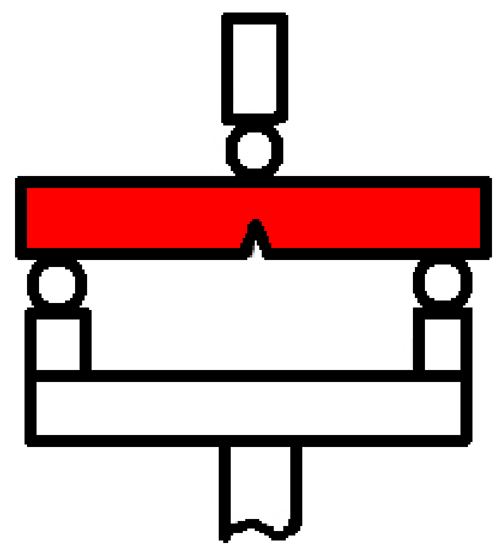
B = Thickness

W = Width

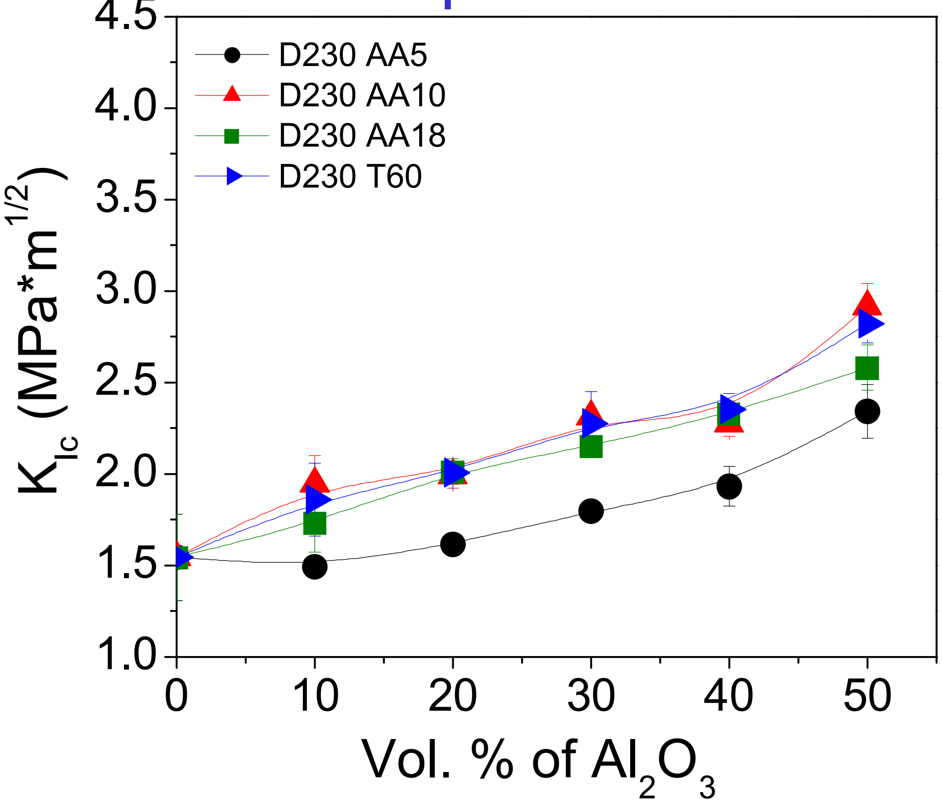
Fracture Toughness Sample Preparation

- Sample cut with diamond blade saw
  - 0.5” X 2.5” X 0.25”
- Crack is propagated by razor blade
  - Crack length should be between 20-80% of sample width
- 5-10 samples were prepared from 1-3 different sample sets
- Crack length must be longer than the length of the razor blade insertion

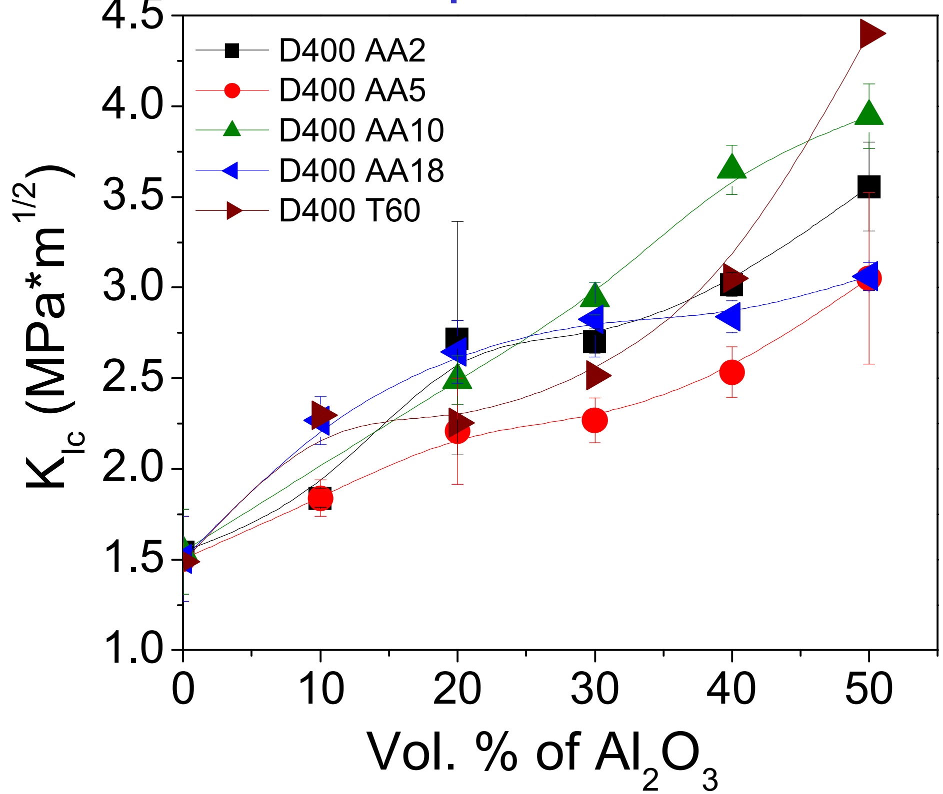




DGEBA/D230 with various particle sizes

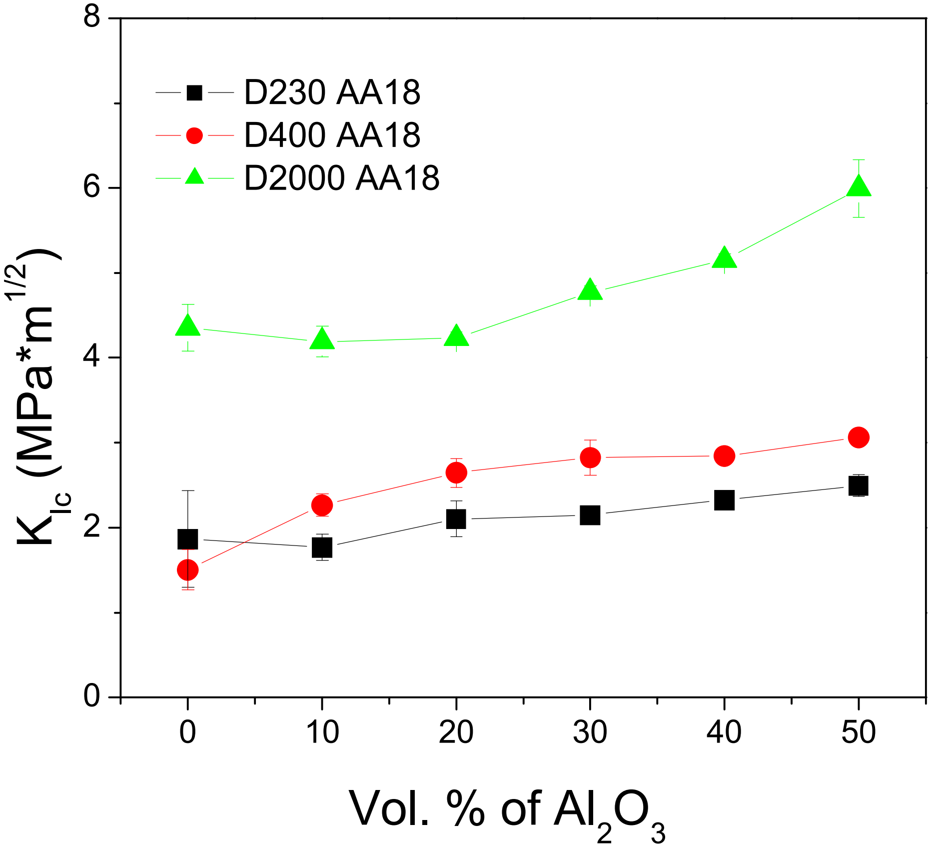


DGEBA/D400 with various particle sizes



- Fracture toughness increases with vol.% Al_2O_3
- Particle size has no effect on this length scale
- Small changes in crosslink density are acceptable

Effect of Molecular Weight of PPO Group/Cross-link density on Fracture Toughness



- Small changes in crosslink density are acceptable
- Filler size does not impact fracture toughness where large changes in crosslink density will

Summary of conclusions thus far:

•Particle shape, size, size distribution, does not effect rubbery or glassy G', rubbery or glassy CTE, or fracture toughness

•T_g of polymer is unaffected by addition of Al_2O_3

•Large changes in crosslink density are required for a dramatic change in fracture toughness

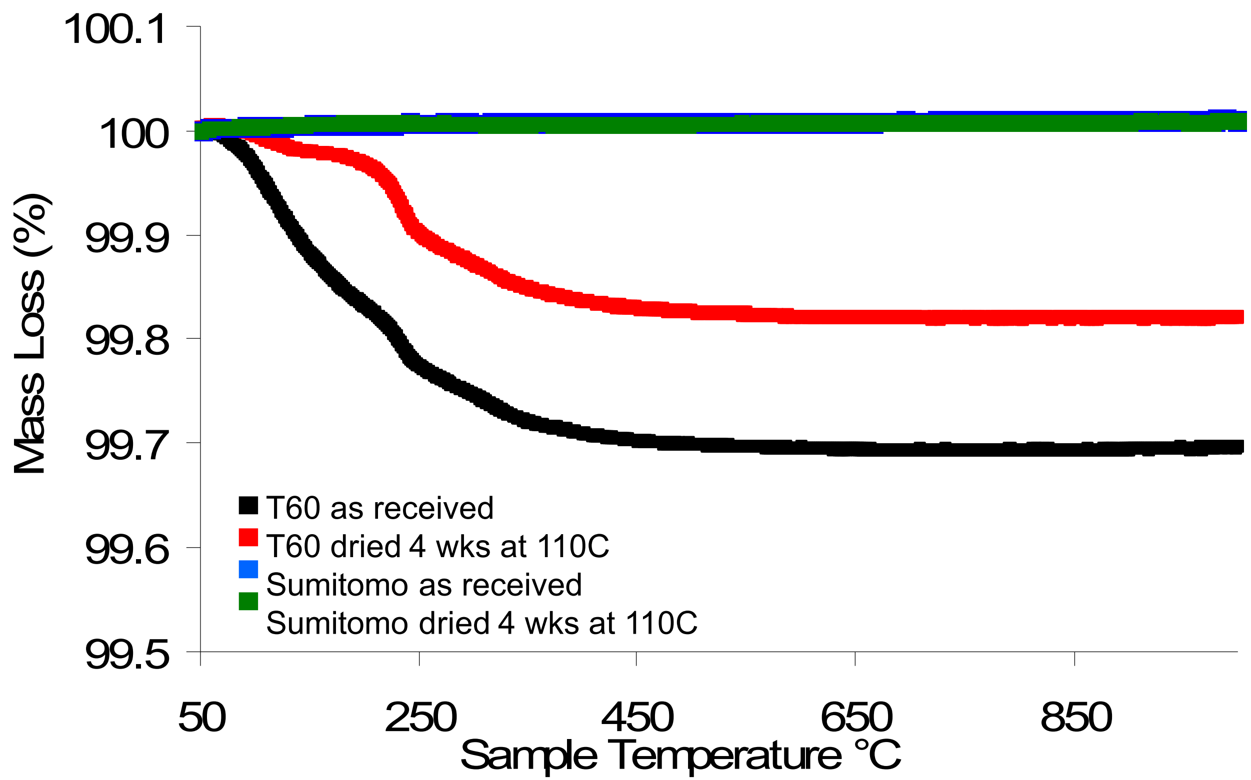
•Broadening observed in rubbery region near T_g:

- •Consideration must be given to a elastomeric system is it will be used near the T_g

Major composite properties do not change with epoxy or Al_2O_3 variables

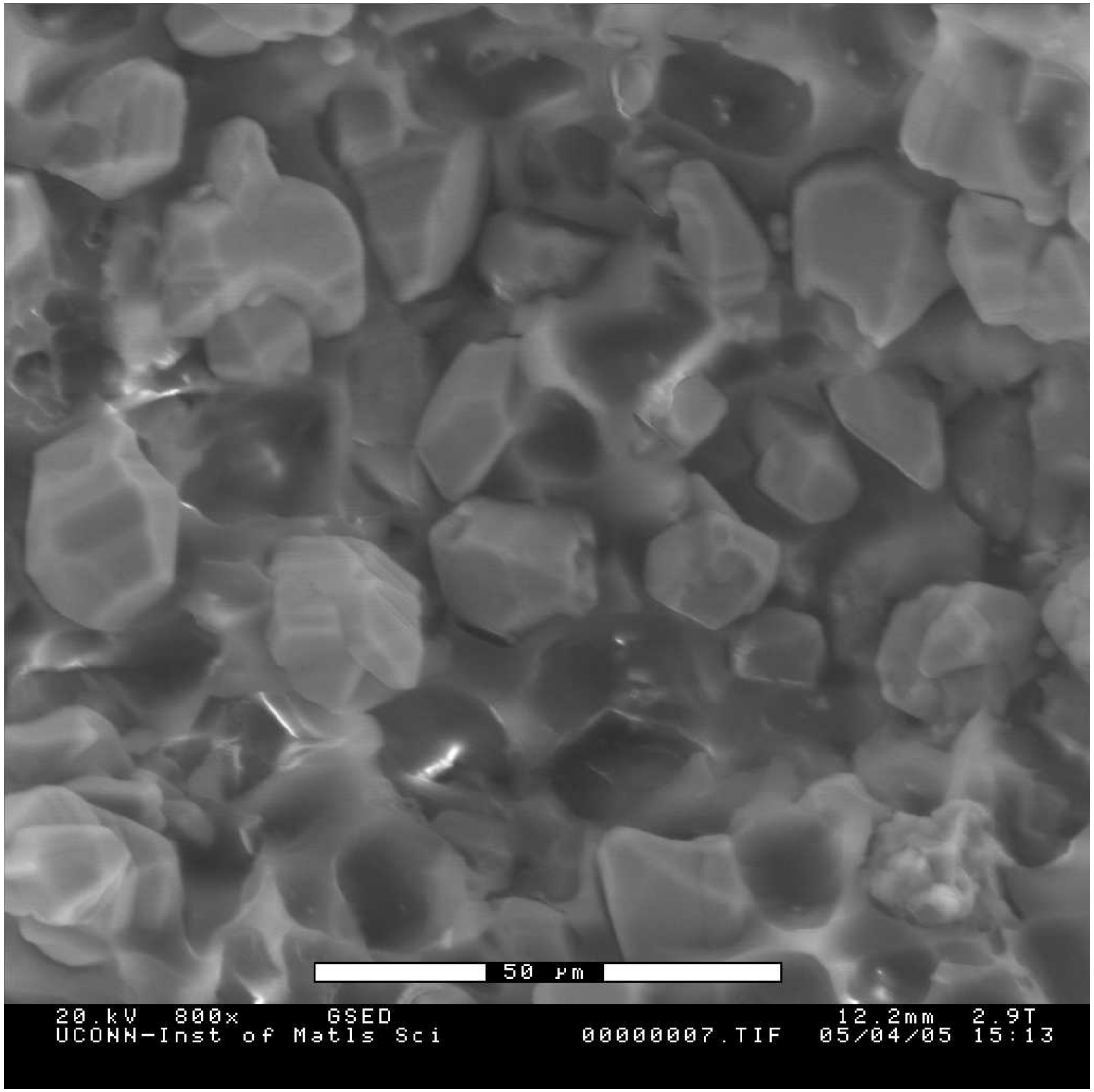
Thermogravametic Analyses of Al_2O_3 Particles

- Filler pull-out
  - Insufficient adhesion with epoxy matrix
- Al_2O_3 is dry
- Lack of effective surface hydroxyl groups

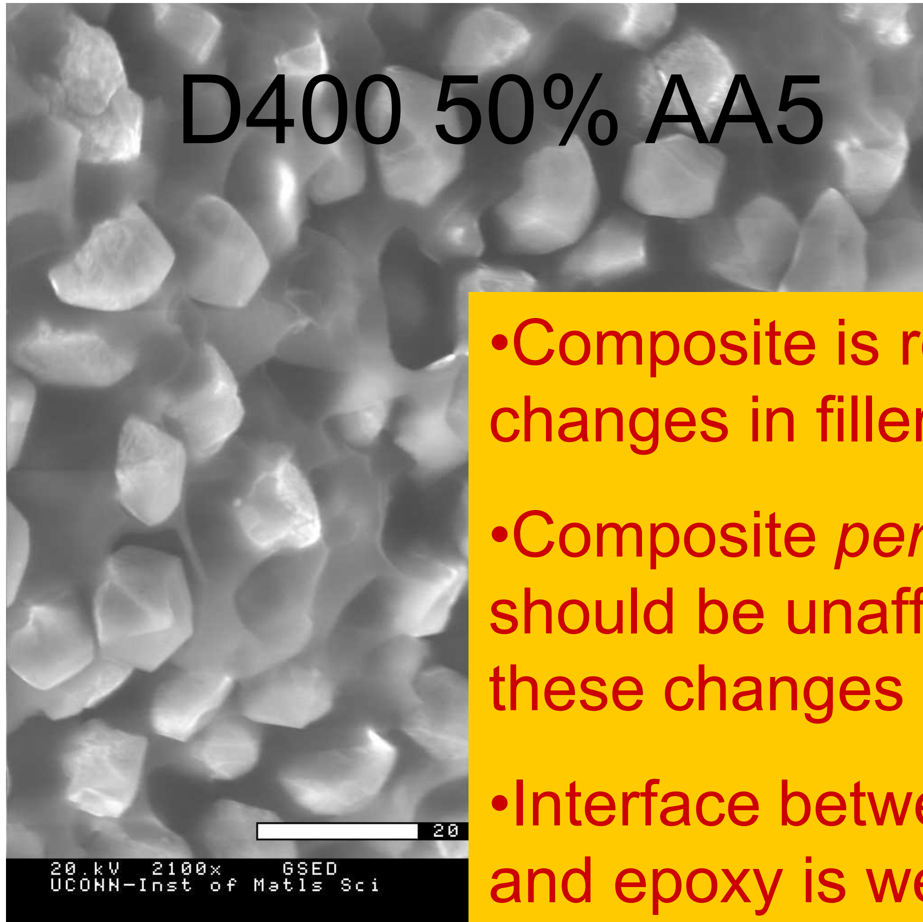


SEM Conclusions

D230 50% AA18



SEM Conclusions



•Composite is robust to small changes in filler and resin

•Composite *performance* should be unaffected by these changes

•Interface between Al2O3 and epoxy is weak

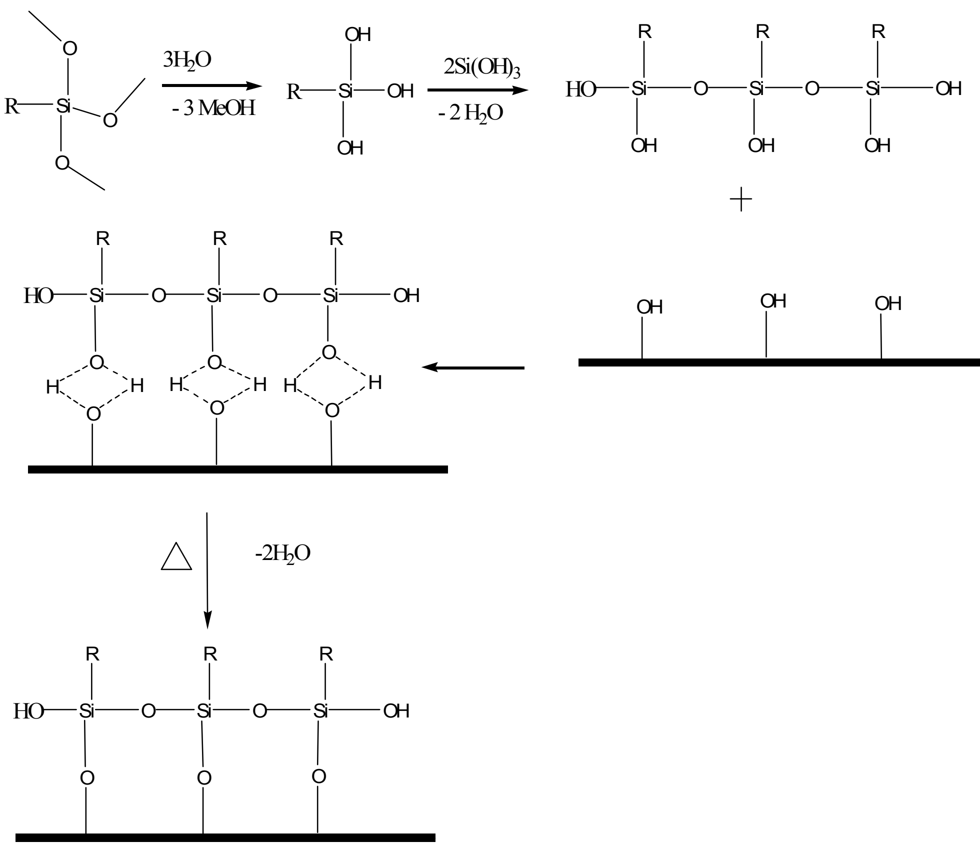
- No Agglomeration
- Crack propagation is occurring at the surface of the Al_2O_3
- Clear pull out of Al_2O_3
  - *Weak interfacial region*

The art of silane coupling agents

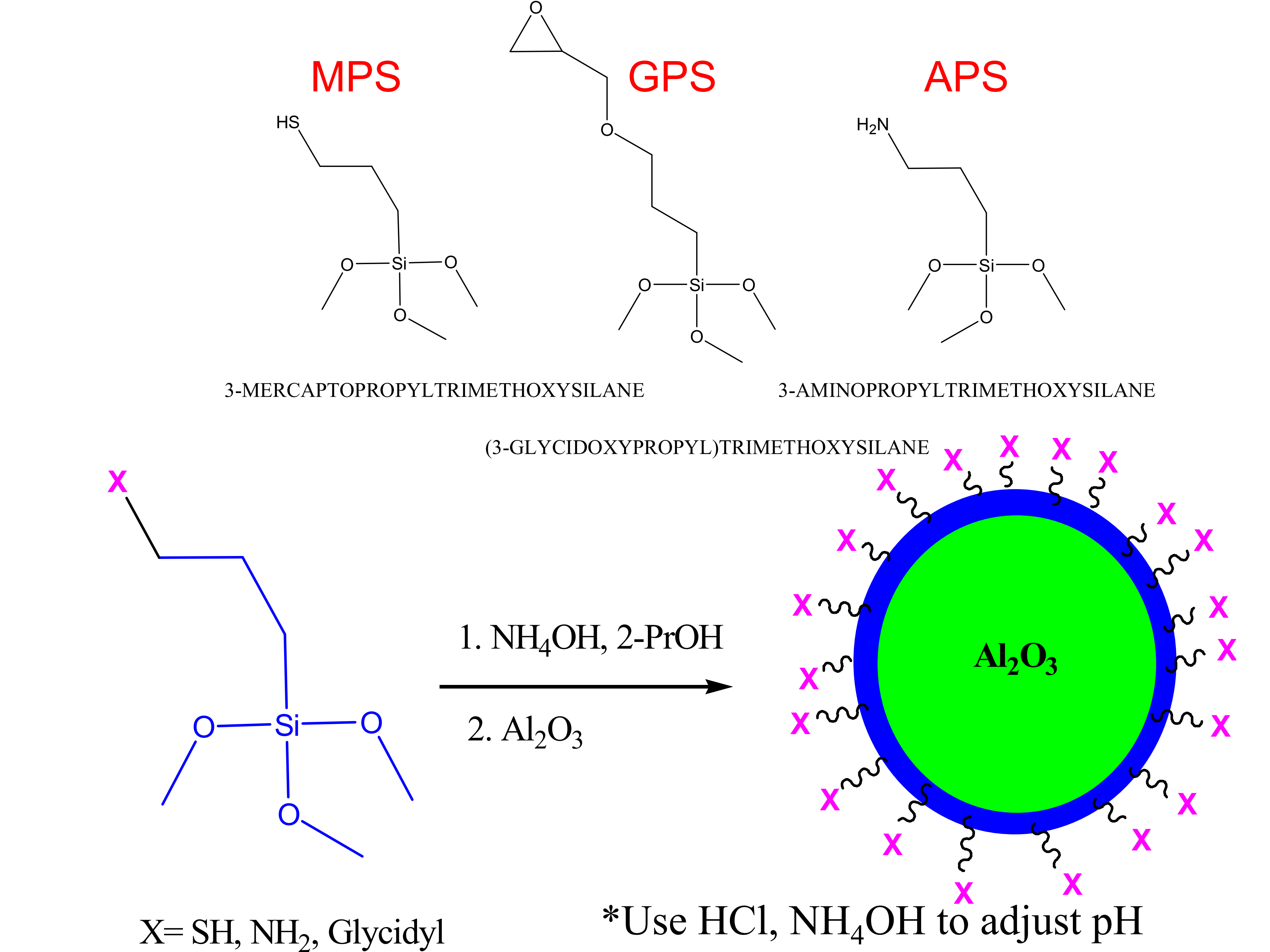
- SCAs long used as adhesion promoters in glass fiber reinforced composites to increase stability and improve water resistance
- SCAs have been shown to improve mineral filled composites and on alumina plates for joint durability
- Try to achieve good adhesion from intimate molecular contact
- SCAs may:
  - Introduce a route for chemical bonding between filler and matrix *via* ionic, covalent and metallic interfacial bonds.
    - Possible dispersive or polar forces and other secondary bonds
  - Provide a restricted layer where the restricted mobility of the polymer in the area of the filler
  - Create a chemical composition gradient at the interface do to preferential adsorption on the surface
  - Provide wetting and surface energy effects where the coupling agents improve the wetting of the filler leading to more intimate contact
  - Mechanical interlocking may assist if there are irregularities on the surface substrate to govern adhesion
  - Cause an electronic transfer on contact if the two have different electronic band structures

Investigate the use of silane coupling agents to improve Al_2O_3-epoxy interface

- Hydrolysis-polymerization of trialkoxysilanes is a complex problem of acid-base catalysis that is dependent on the chemical composition of the silane, availability of water and type of solvent
- Use reactive and non-reactive silanes
- Silanes applied by condensation reaction *via* Al_2O_3 surface hydroxyl groups
- Solution chemistry attention with respect to pH and catalysts
- 3-Aminopropyltrimethoxysilane, (3-Glycidoxypropyl) trimethoxysilane, 3-Mercaptopropyltrimethoxysilane



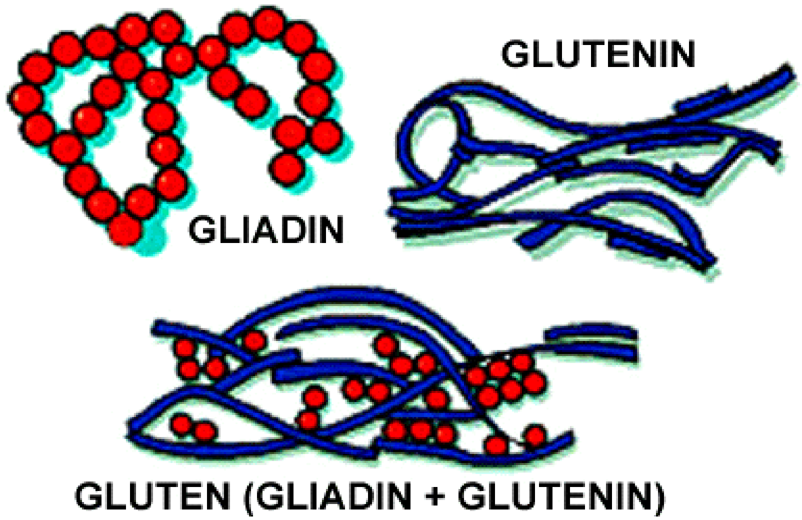
Scheme: adapted from Gelest Co.


MPS
GPS
APS
HS
O
O
H2N
Si
O
3-MERCAPTOPROPYLTRIMETHOXYSILANE
3-AMINOPROPYLTRIMETHOXYSILANE
(3-GLYCIDOXYPROPYL)TRIMETHOXYSILANE
X
1. NH4OH, 2-PrOH
2. Al2O3
Al2O3
X= SH, NH2, Glycidyl
*Use HCl, NH4OH to adjust pH

Al_2O_3 with thiol silane for inclusion in biodegradable wheat gluten composites

What is the Plant Protein: Wheat Gluten?

- Made of 2 types of proteins
  - Gliadin
    - Contributes viscous effects
    - MW less than 50,000
    - Responsible for extensibility and cohesion
    - Only intra molecular disulphide linkages
      - Makes them “globular and compact”
  - Glutenin
    - Contributes elastic effects
    - MW of 80,000 to several million
    - Both inter and intra molecular disulphide linkages



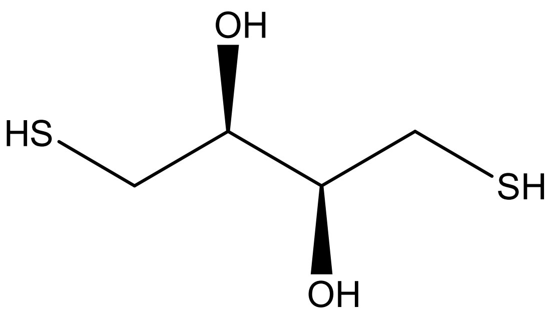
- Gluten is insoluble in aqueous and salt solutions due to highly non-polar amino acid residues

Image: http://www.agsci.ubc.ca/courses/fnh/301/protein/protq4.htm

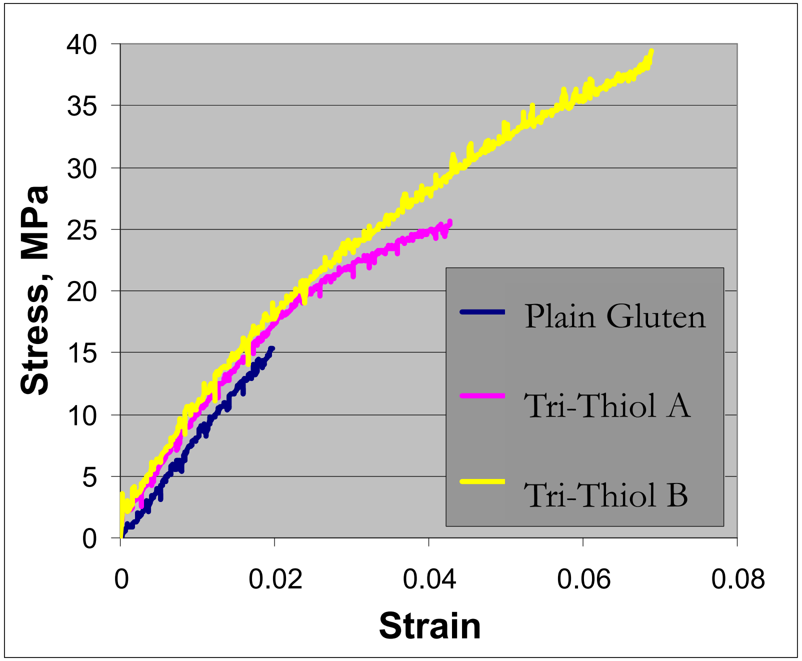
Wheat Gluten as a commodity plastic

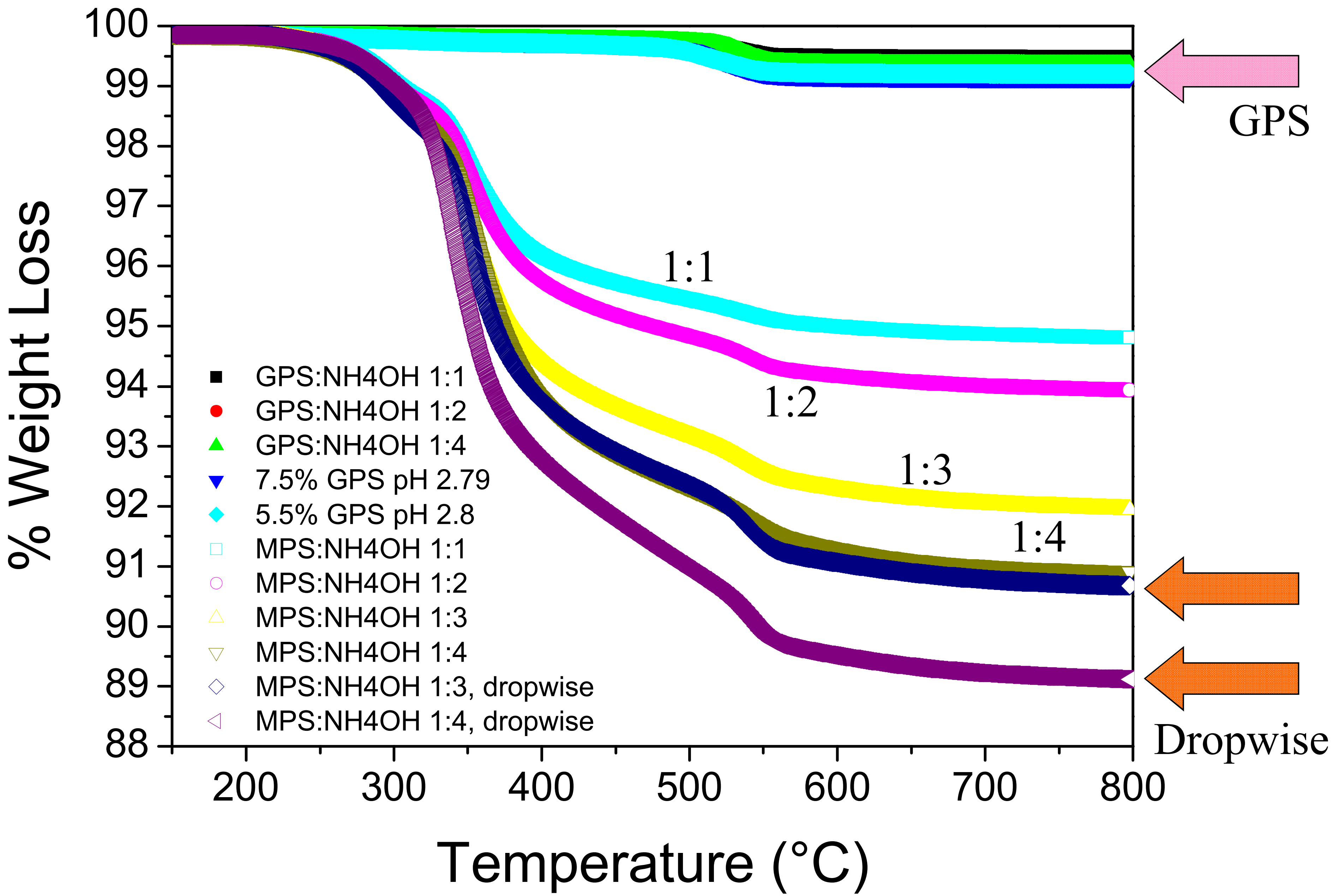
- Excellent prospect to replace current plastic commodity market because of low cost and ample supply
- Aqueous based environmental friendly processability
- Molding of wheat gluten creates additional inter molecular bonding
- Mold gluten with
  - Higher Density powder
    - Mold to consolidated parts
  - Low density powder (high water content created by short lypholization):
    - Low packing density will make a rigid foam
    - Mold to consolidated parts with high packing density following pressure and temperature pre mold treatment

Tri-thiol Modification of Gluten

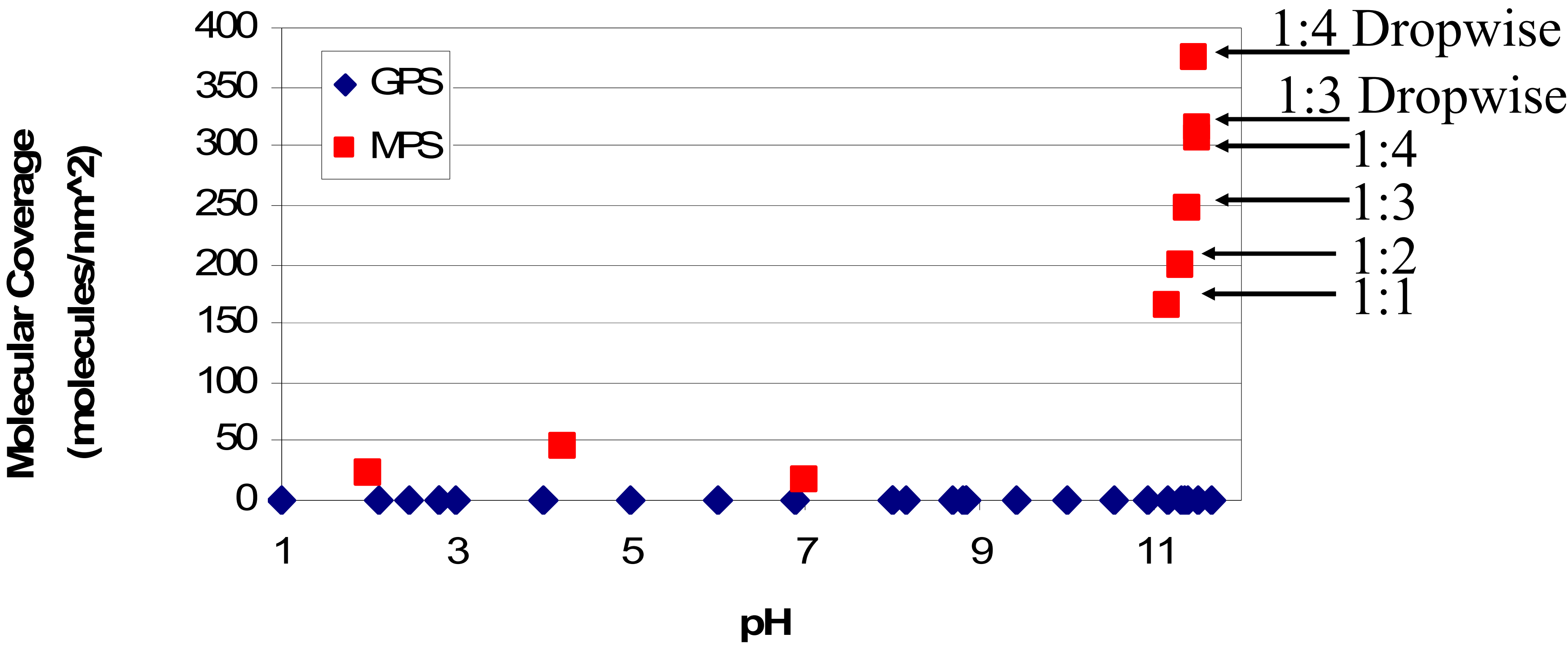


- DTT (1,4-Dithiothreitol) has been shown to reduce the gluten structure in acidic medium
  - Improves solubility
  - Improves ductility
  - Improves toughness
- Tri-thiol acts not just as a plasticizer because the stress-strain tests show that the same initial stiffness but tri-thiol modified shows in 4 fold increase in toughness
- Tri-thiol first reduces the disulphide linkages and then crosslinks




% Weight Loss
Temperature (°C)
100
99
98
97
96
95
94
93
92
91
90
89
88
200
300
400
500
600
700
800
GPS:NH4OH 1:1
GPS:NH4OH 1:2
GPS:NH4OH 1:4
7.5% GPS pH 2.79
5.5% GPS pH 2.8
MPS:NH4OH 1:1
MPS:NH4OH 1:2
MPS:NH4OH 1:3
MPS:NH4OH 1:4
MPS:NH4OH 1:3, dropwise
MPS:NH4OH 1:4, dropwise
1:1
1:2
1:3
1:4
GPS
Dropwise

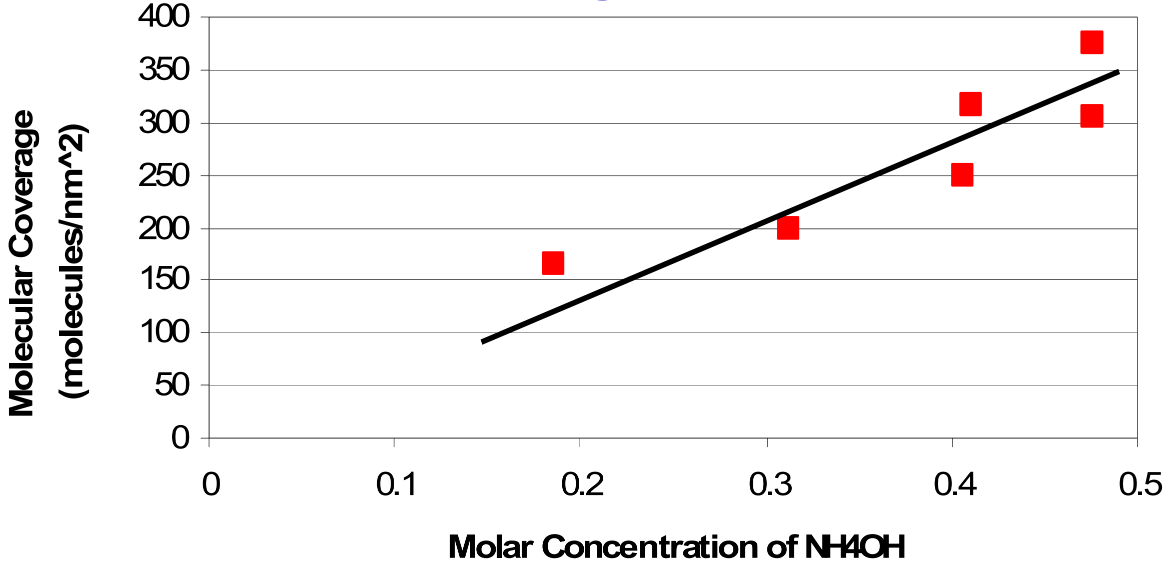
Dependence of Molecular Coverage on pH of MPS and GPS on Alumina



- No dependence observed
- MPS shows increase based on mole ratio of NH4OH

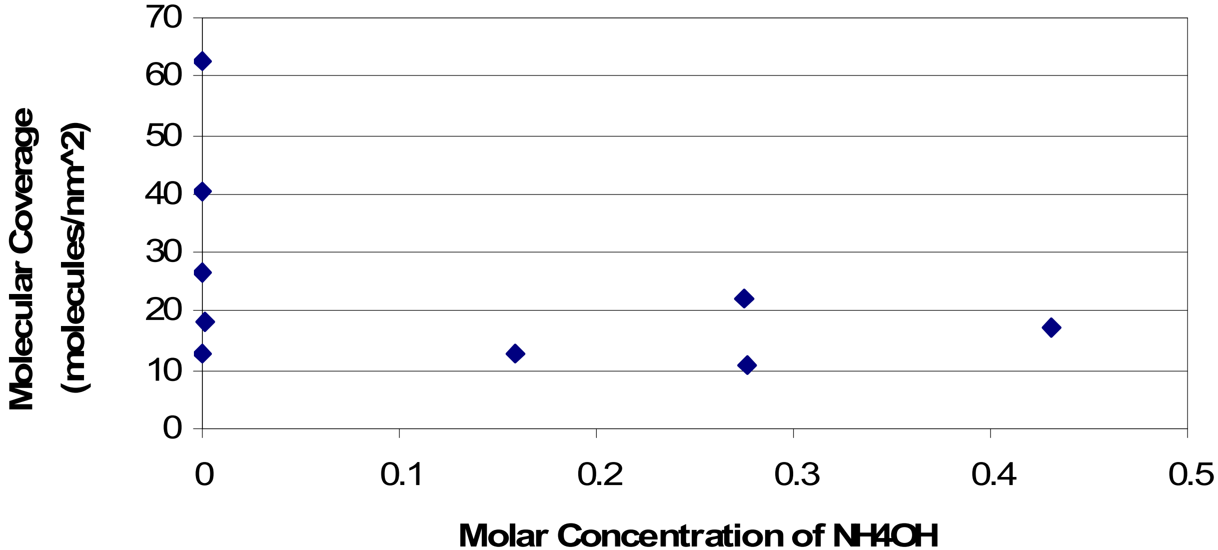
Dependence of Molecular Coverage on the molar concentration of NH4OH in solution

MPS



- Linear increase in MPS coverage with NH_4OH as catalyst

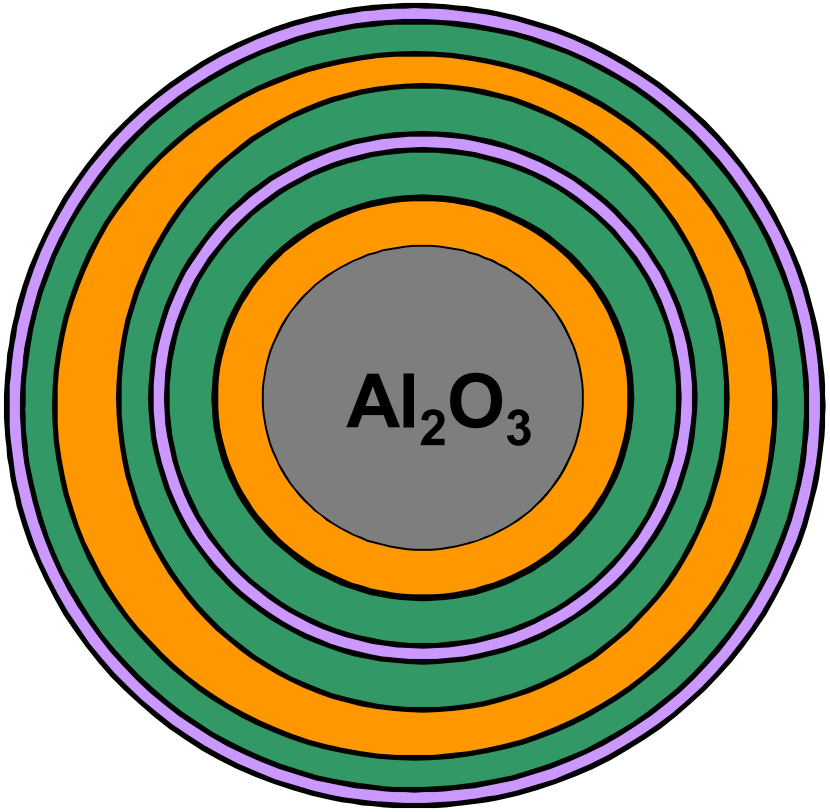
GPS



- No trend in coverage due to NH_4OH

So why the success of MPS?

It is possible that we are above the pH at which the thiol group oxidizes (pH~9.8). Therefore the S-H becomes a S-S and forms layers, or it just provides another route for silane homopolymerization.



Layers are:

1) Alumina

2) Siloxane

3) Organic of silane

4) S-S crosslink

5) Organic of silane

6) Siloxane

7) Organic of silane

8) S-S crosslink

Detect by FTIR: Different resonance of S-S versus S-H

- Porosity?

Diffuse Reflectance Infrared Fourier Transform (DRIFT)

- Collects scattered IR energy
- Used for measurement of particles and powders
- IR beam reflected off the surface of the particle or transmitted through it
- Transmission-reflectance pattern repeats, increasing path length
- Scattered IR is collected in spherical mirror to the detector

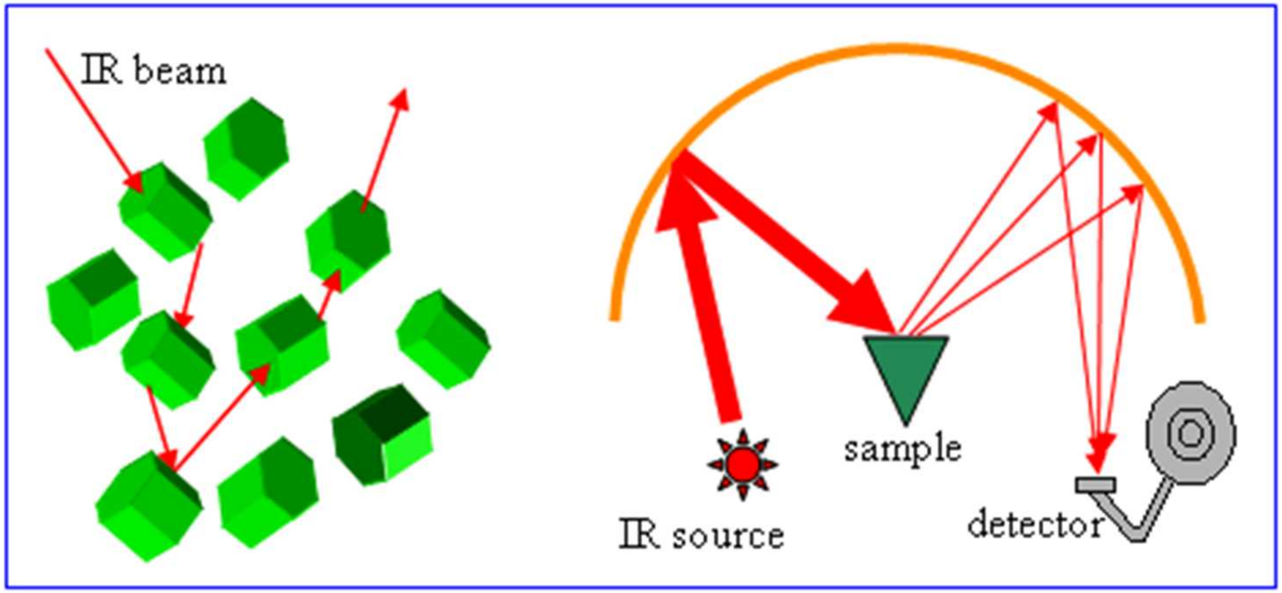
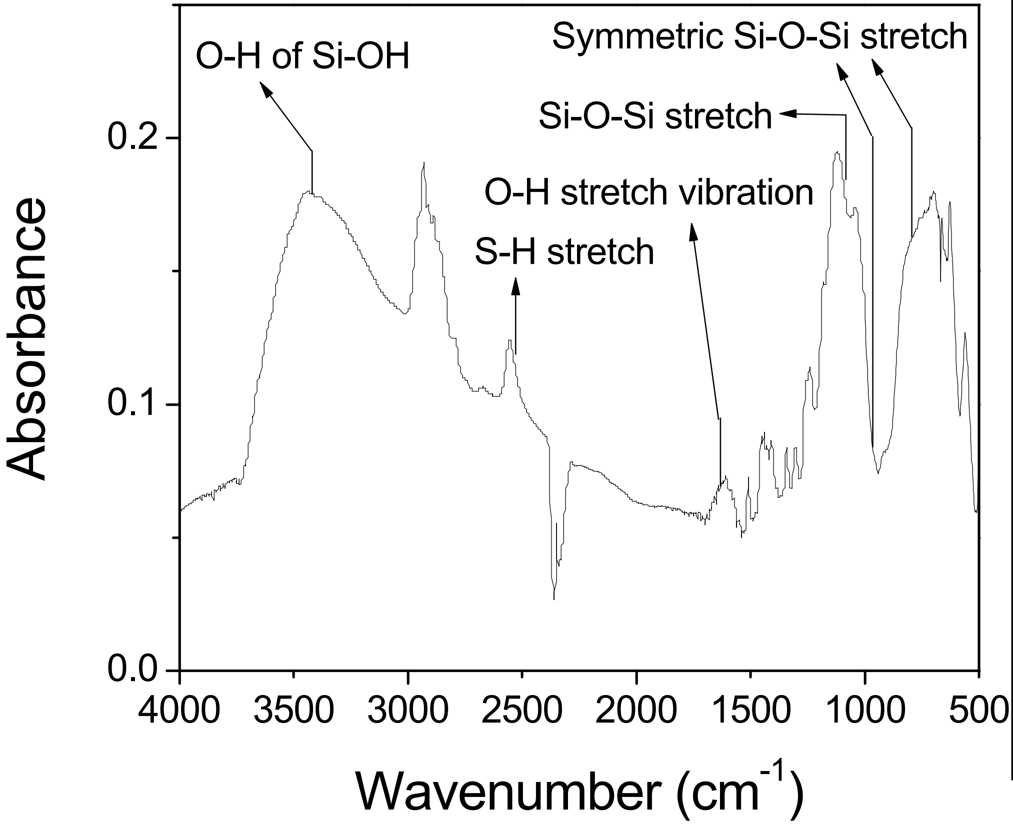


Image: http://www.nuance.northwestern.edu/KeckII/ftir7.asp

FTIR of MPS coated T60 Al_2O_3

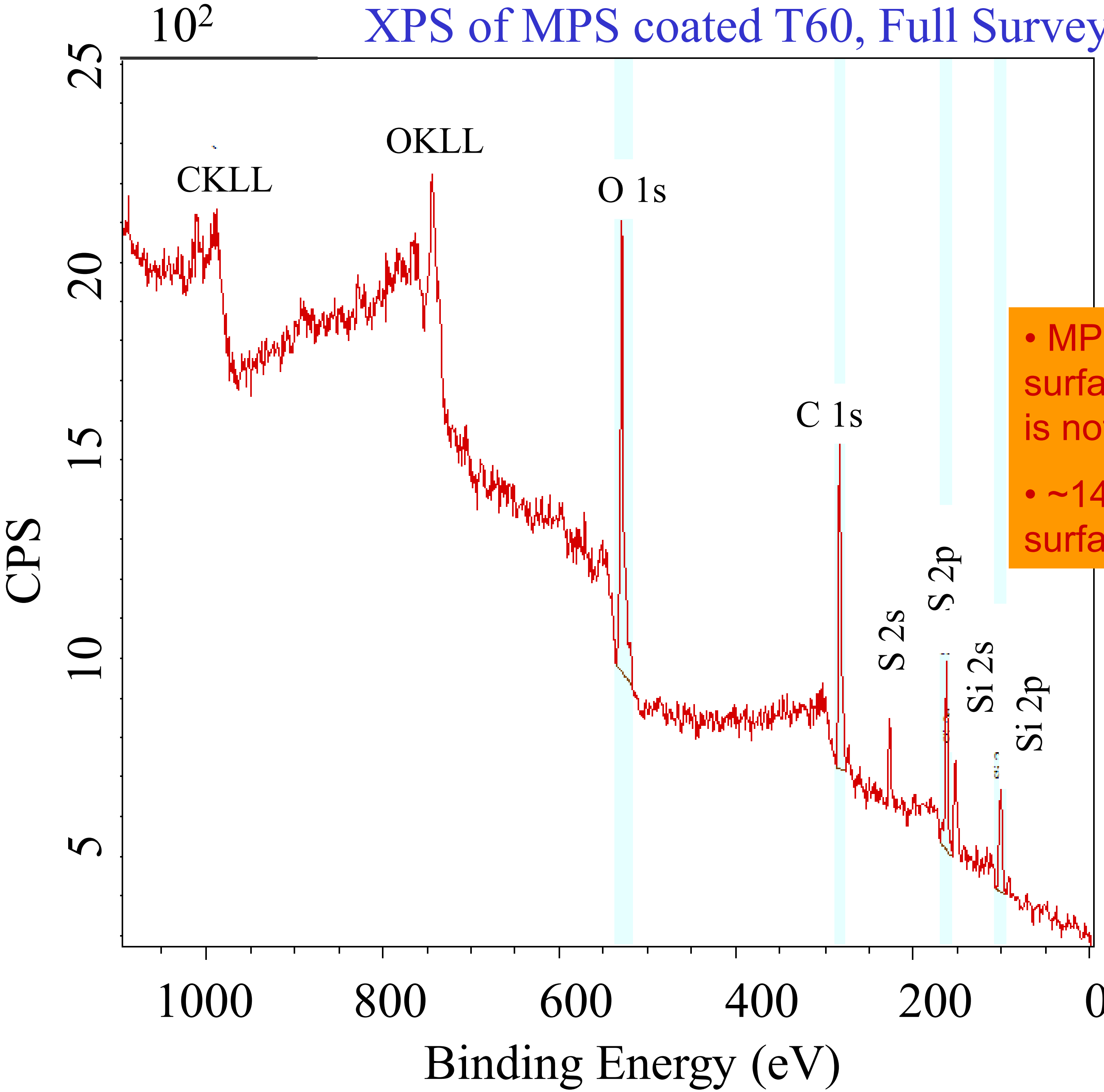


Assignments of Peak Frequencies of MPS on Al_2O_3

Wavenumber (cm^{-1})	Assignment
3404-3448	O-H stretching of Si-OH group and water of crystallization
2000-1800	Overtones and combination modes of bulk SiO_2 vibration
1735	C=O stretching, saturated aliphatic esters
1640-1620	O-H stretching vibration
1467	$-CH_2$-scissoring; CH_3 asymmetric (bending) deformation
1102-1105	Si-O-Si stretching
963-968	Symmetric Si-O-Si stretching
801	Symmetric Si-O-Si stretching
468-473	Symmetric Si-O-Si stretching

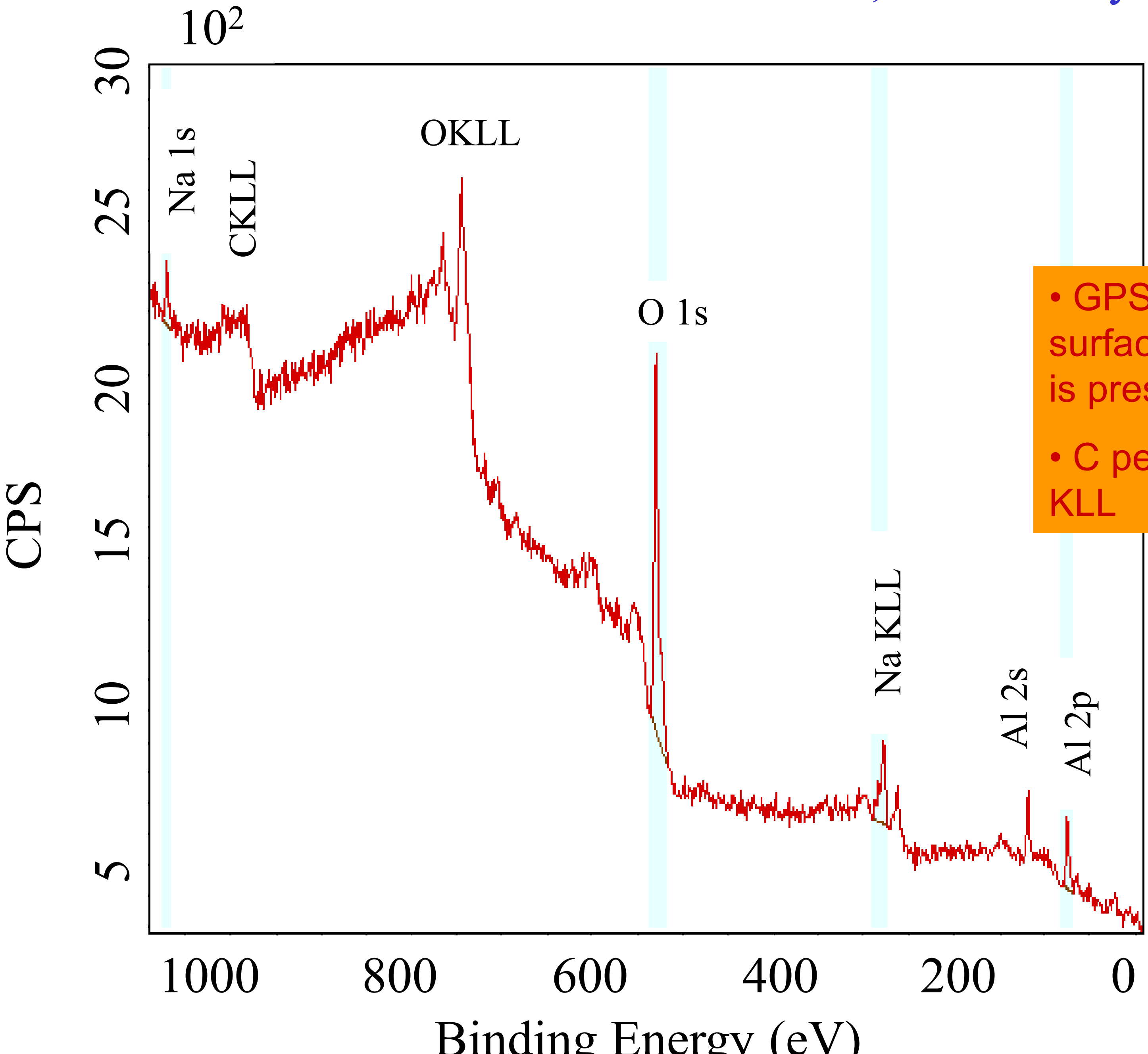
Ray, S., Bhowmick, A. K *J. Appl. Poly. Sci* **2002,** *83*, 2255–2268.

XPS of MPS coated T60, Full Survey



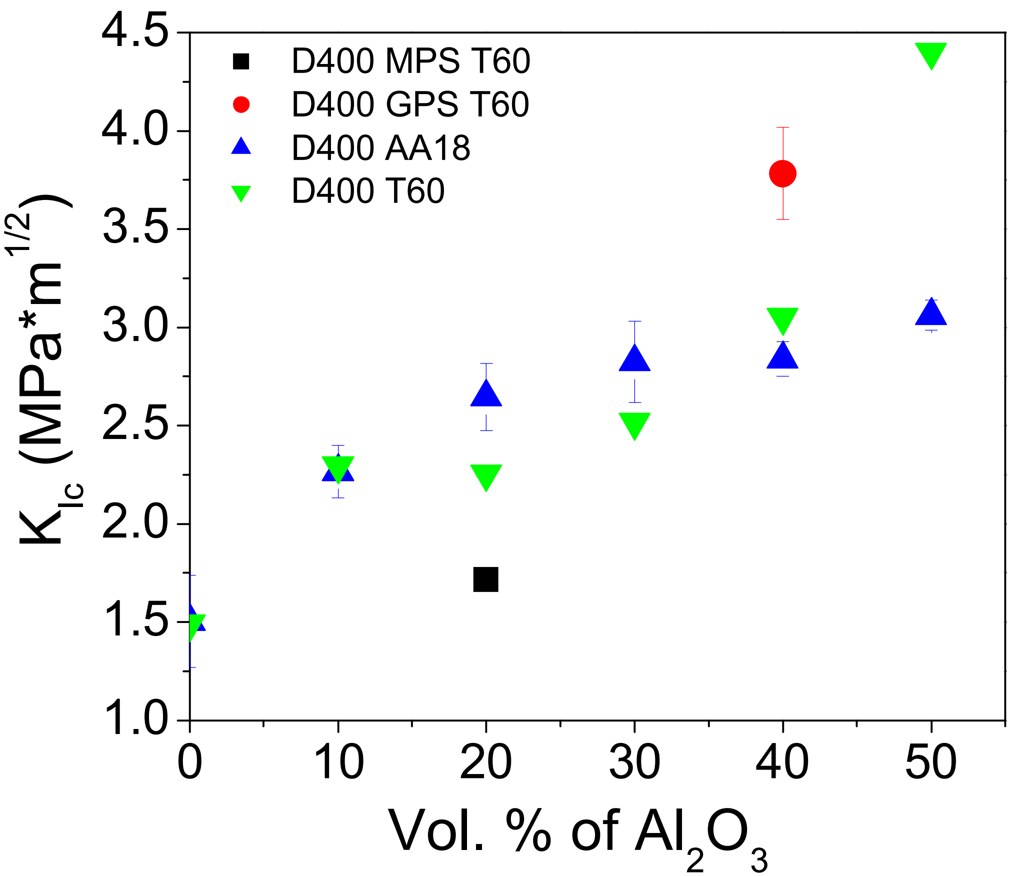
- MPS has sufficient surface coverage, Al peak is not present
- ~14% Sulphur on the surface

XPS of GPS coated T60, Full Survey



- GPS has insufficient surface coverage, Al peak is present
- C peaks obscured by Na KLL

Fracture Toughness of DGEBA/D400 with MPS and GPS coated T60 Al_2O_3



- GPS shows an increase due to the chemical bonding with the amine functional groups and the epoxide resin
- MPS coated (1:2 MPS to NH_4OH) does not increase fracture toughness
- Investigation of other property changes will be forthcoming

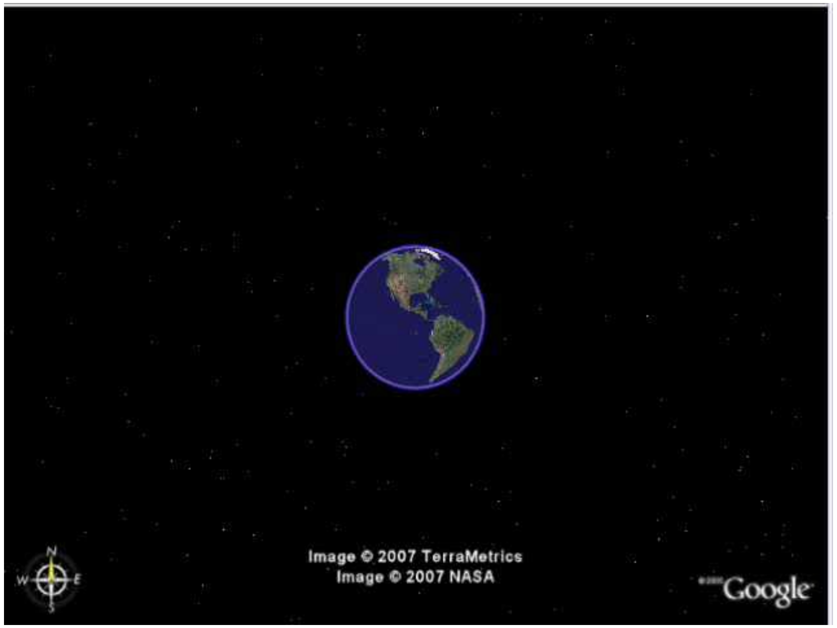
Where does this leave us?

- Excellent control of MPS via NH4OH catalyst
- Less coverage of GPS
  - Coverage is sufficient to improve fracture toughness
  - Ring opening of the epoxide in solution
  - Change solvent/water conditions

- Use the copolymerized MPS and GPS coated Al_2O_3 in epoxy

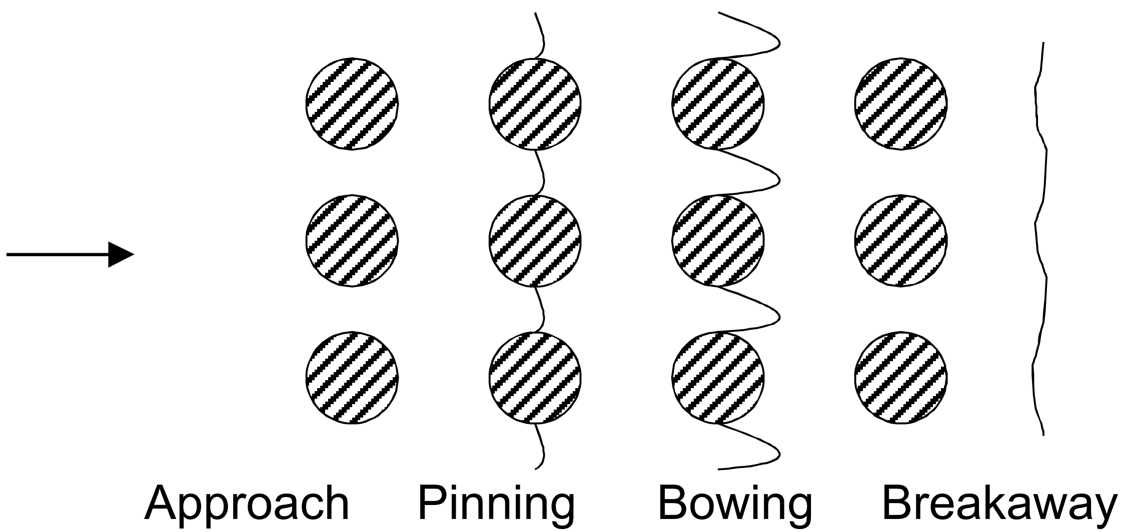
Acknowledgements

- Sandia National Laboratories, Albuquerque, NM
  - Dr. Joe Lenhart
  - Dr. Saskia King
- University of Connecticut
  - Prof. Richard Parnas



SEM Conclusions

- No Agglomeration
  - Homogenous composite
- Crack front bowing
  - Unclear if additional shear or craze events



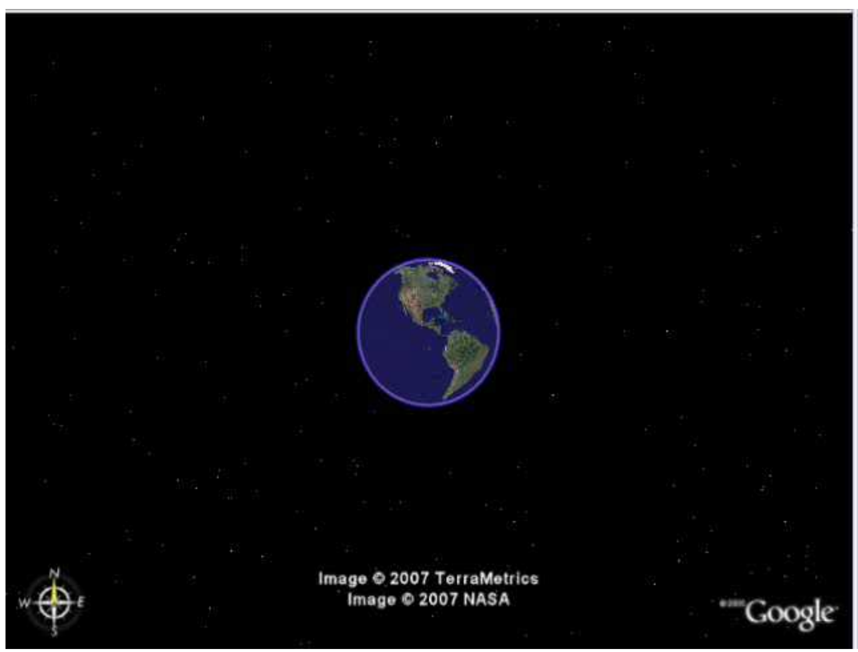
Representation cracking pinning mechanism after Phillips and Harris

Sandia Nat. Labs Collaboration

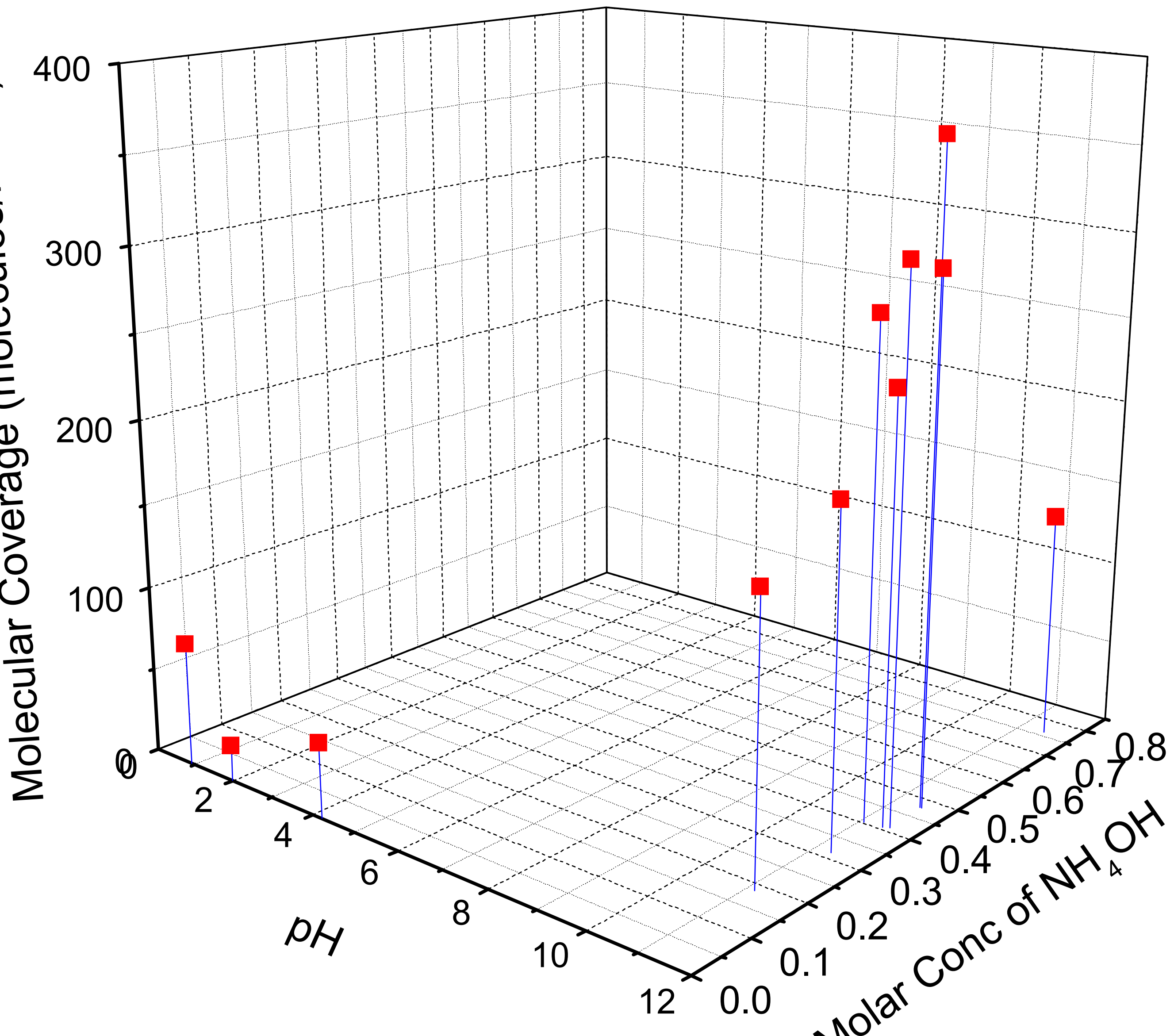
•Completed first year course work and qualifiers at UConn

•Resided in Albuquerque, NM, working at Sandia for 4-6 months returning to UConn to complete my coursework

•Research at Sandia, while based in fundamental science, had set deliverables from internal customers



Dependence of Molecular Coverage on both NH_4OH Molar Concentration and pH of deposition solution of MPS



MPS

Dependence of Molecular Coverage on both NH_4OH Molar Concentration and pH of deposition solution of MPS