FUNDAMENTAL DESIGN OF SUSTAINABLE MATERIALS: SOLUTIONS TO GLOBAL WARMING

Richard Wool
Department of Chemical Engineering
University of Delaware

NCMC-14

Gaithersburg MD Nov 5, 2008

Objectives and Questions for NCMC-14

1. Can we use bio-based materials to solve global warming?

2. What is the largest unsolved problem in solid state physics-have we solved it with bio-based materials?

3. Role of bio-based materials in Renewable Energy-Wind, Solar, Hydrogen

4. The Dream Team?

Advanced Bio-based Green Materials


ACRES GROUP, UNIVERSITY OF DELAWARE

ACRES Group on Robert Redford's Sundance Channel—
Big Green Ideas for a Small Planet, June 16 2008

Can we make high performance carbon fibers from Chicken feathers-H_2?

Can chicken feathers give 6 wt% H_2?

Modulus E ~ 50-100 GPa?

Hydrogen as Energy Carrier

Hydrogen Powered UD Bus[3]

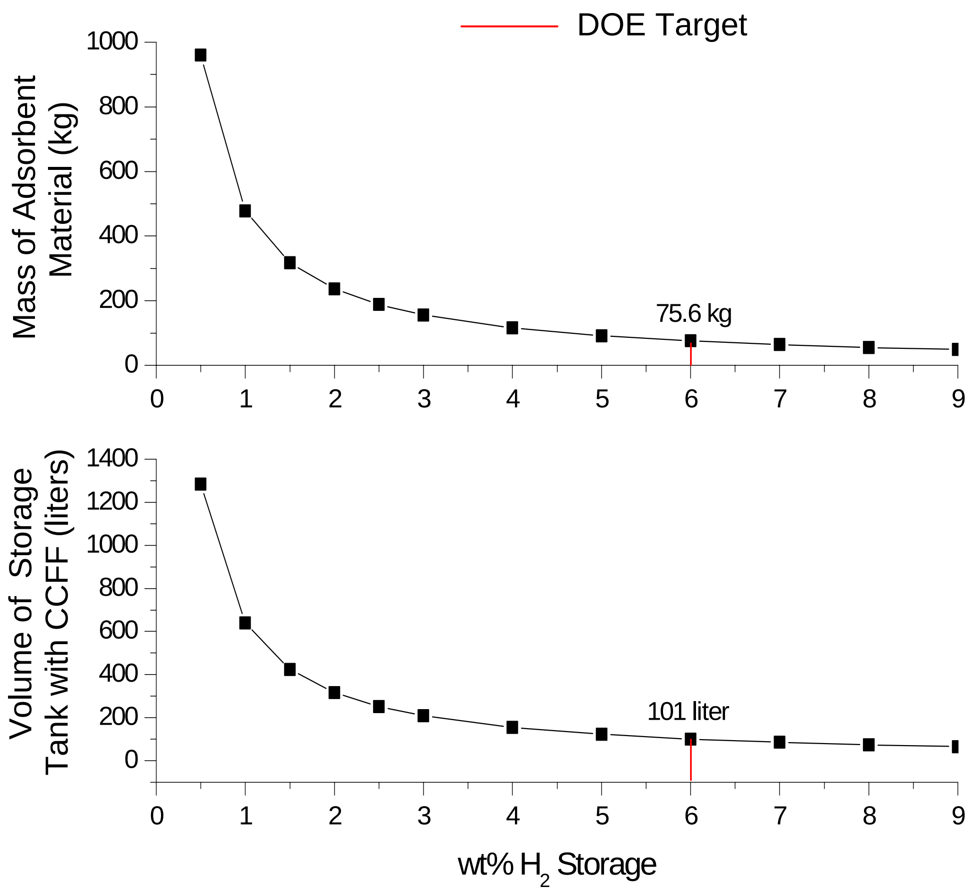
- Why hydrogen?
  - Clean source, no CO_2 emission, only product is H_2O for fuel cell application

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O + Energy$$

  - Energy density is ~3 times larger than gasoline[1]
  - Fuel cells are at least 2 times more efficient than combustion engines[2]
- Production and storage of H_2 are main bottlenecks for using it as a fuel

1 Louis Schlapbach, MRS Bull., 2002
2 Jesse L. C. Rowsell and Omar M. Yaghi, Angew. Chem. Int. 2005,44, 4670-4679
3 UDaily Archive April 9, 2007

How to reach 300 miles range?

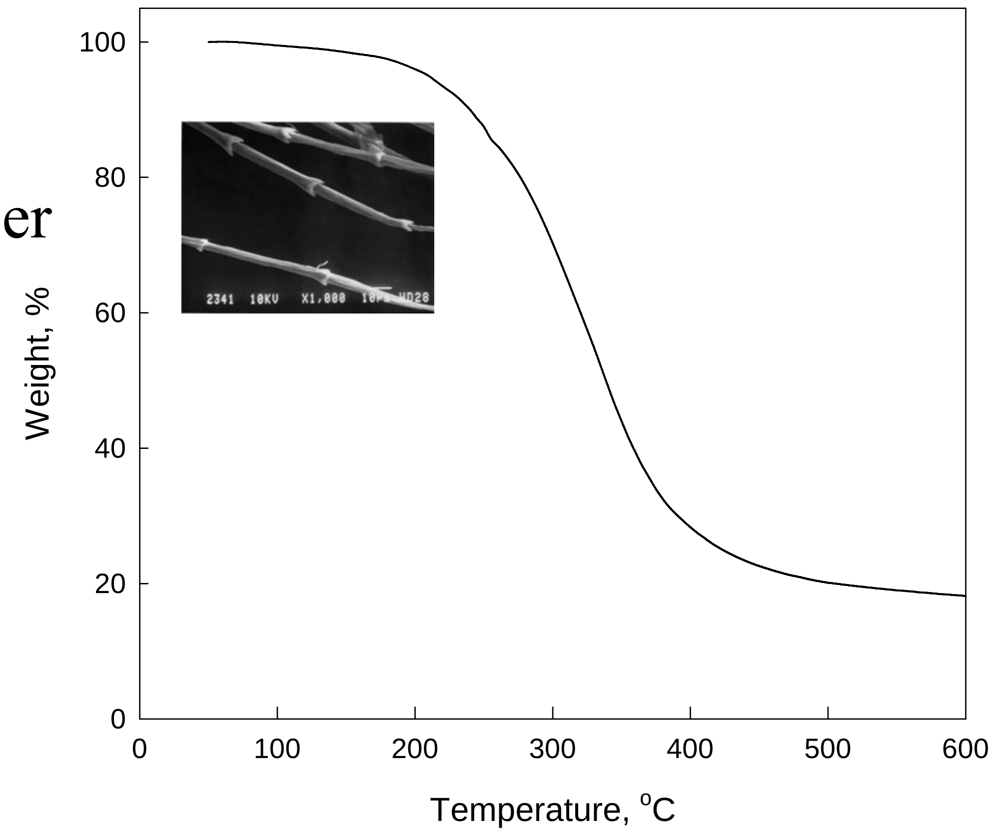


Required adsorbent mass and CCFF tank volume to build a car with 300 miles range

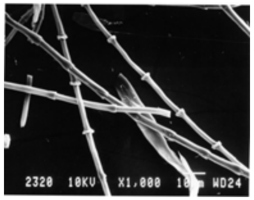
- Hydrogen's extreme low density requires huge tanks!
- Relatively high wt% H_2 storage values has to be achieved!
- Material has to be as cheap as possible!

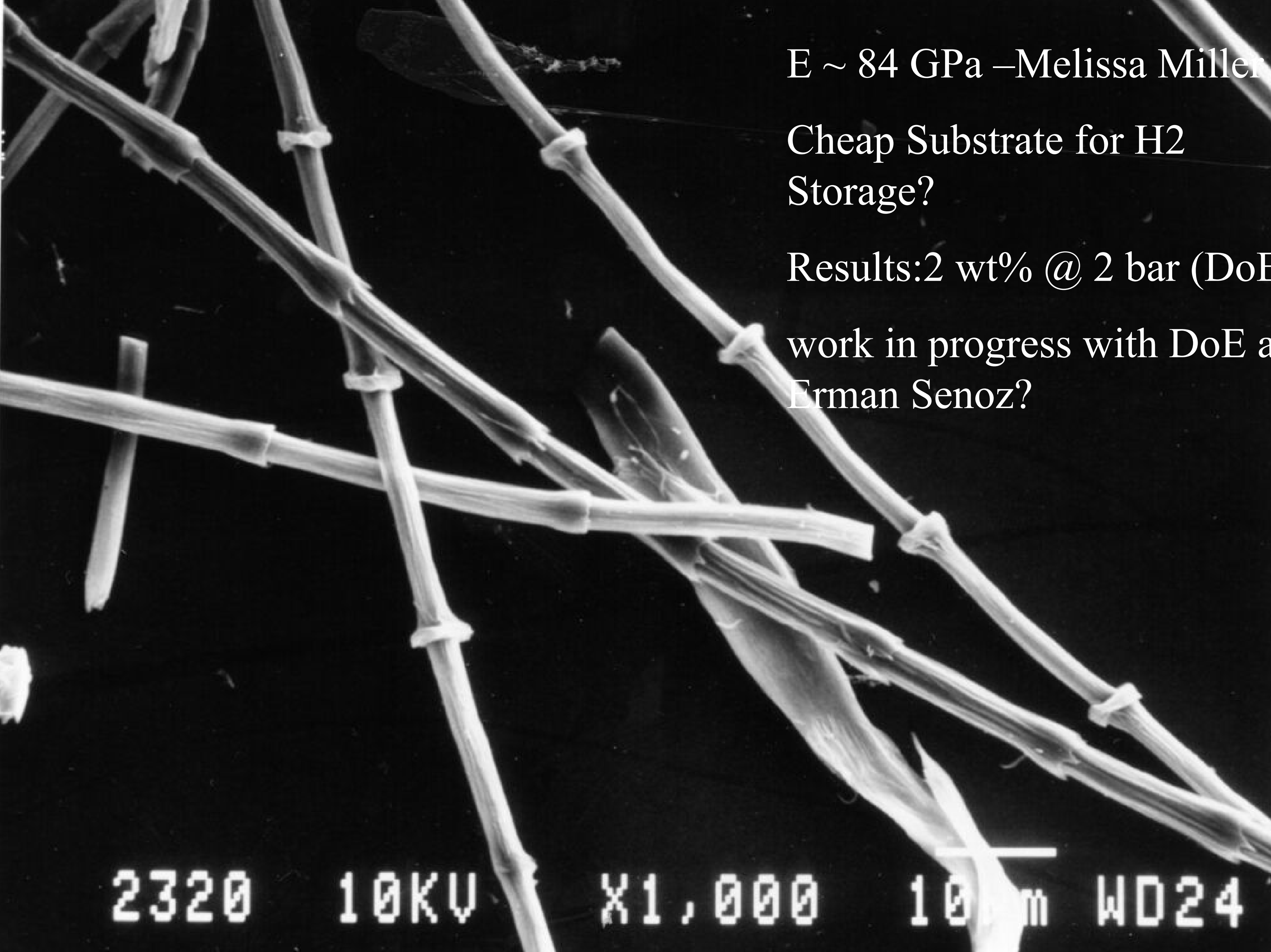
Carbonization of Keratin Fiber

Chicken feather fiber



Carbon Microtubes with fractal walls, pores ~ 6A





E ~ 84 GPa –Melissa Mille

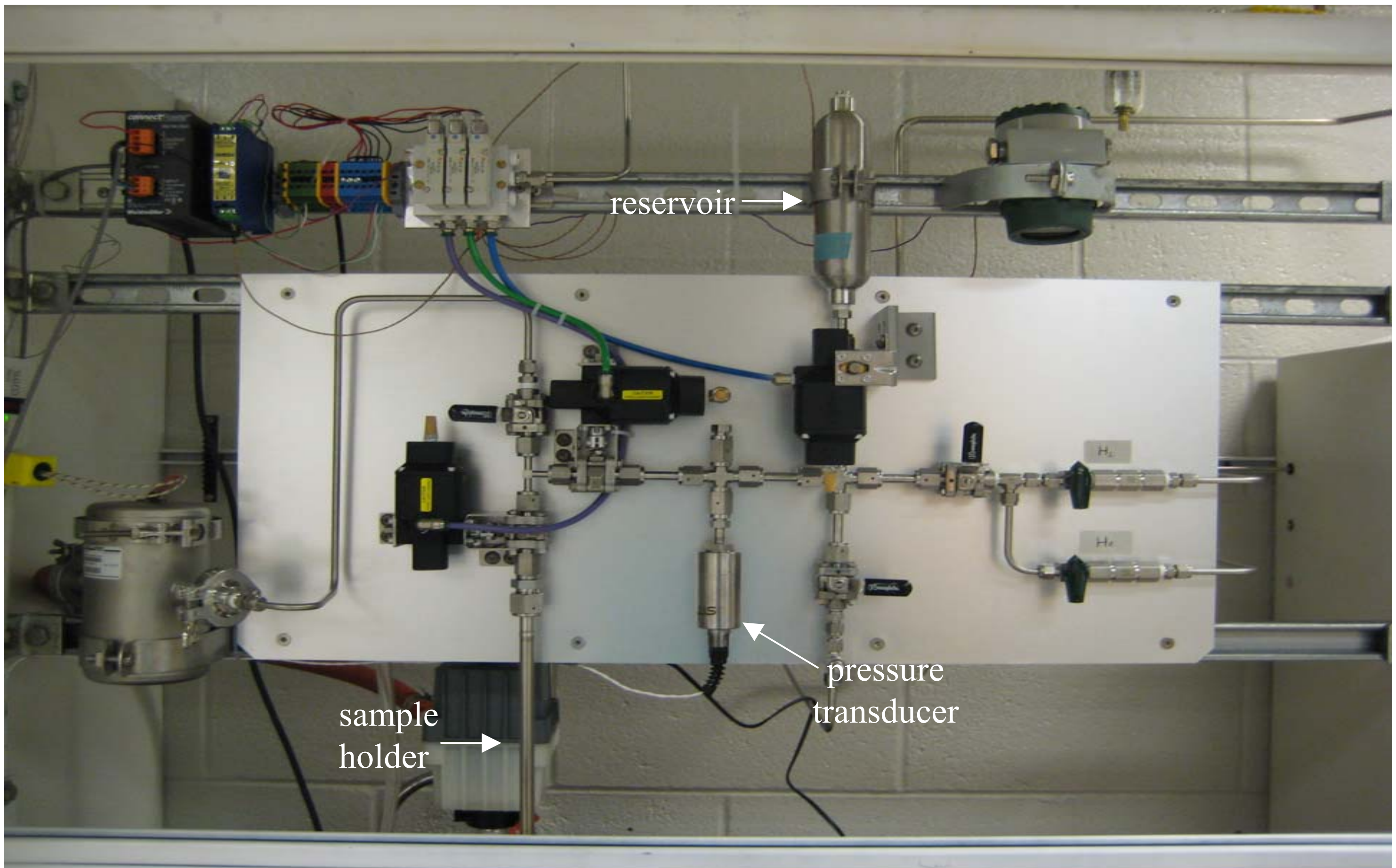
Cheap Substrate for H2 Storage?

Results:2 wt% @ 2 bar (DoE

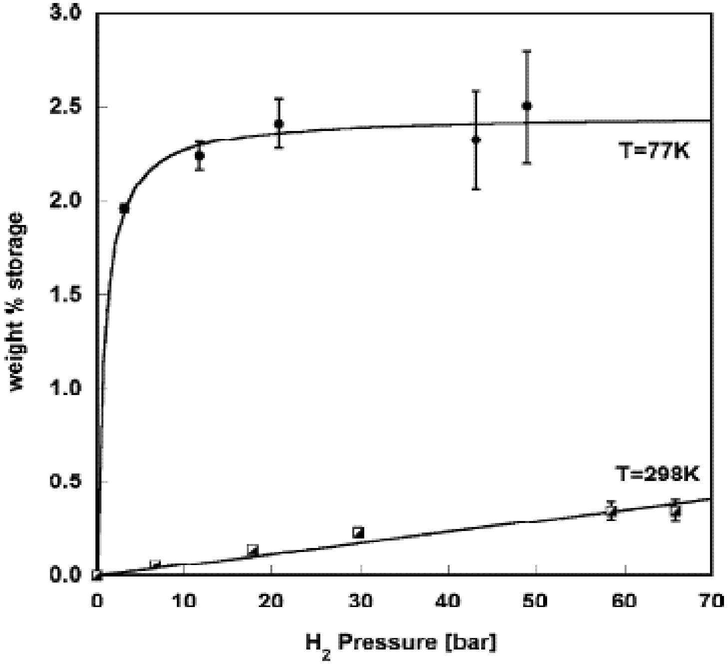
work in progress with DoE a

Erman Senoz?

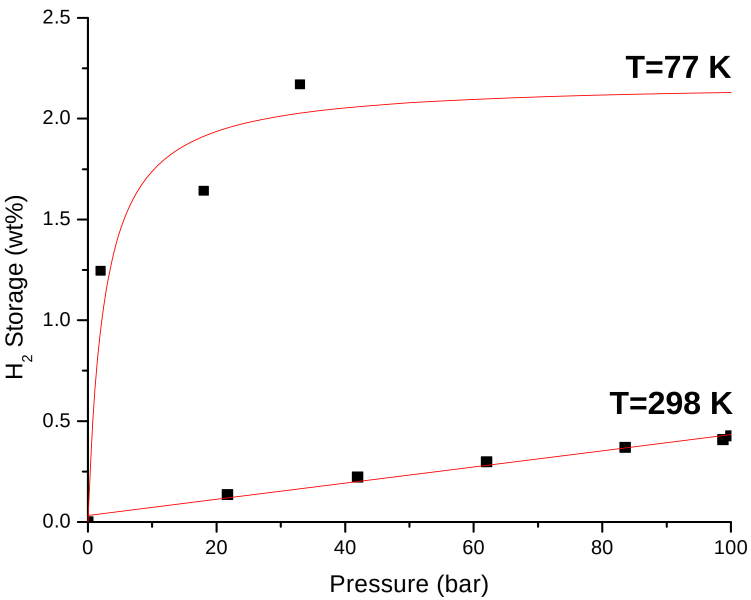
H_2 STORAGE (SIEVERT'S) APPARATUS



H_2 STORAGE RESULTS



Hydrogen adsorption isotherms at room temperature and 77 K with Henry type and Langmuir type equation for purified SWCNTs[1]



Hydrogen adsorption isotherms at room temperature and 77 K for CCFF

1 B. Panella et al., Carbon 43 (2005) 2209-2214

Progress on H_2 Storage

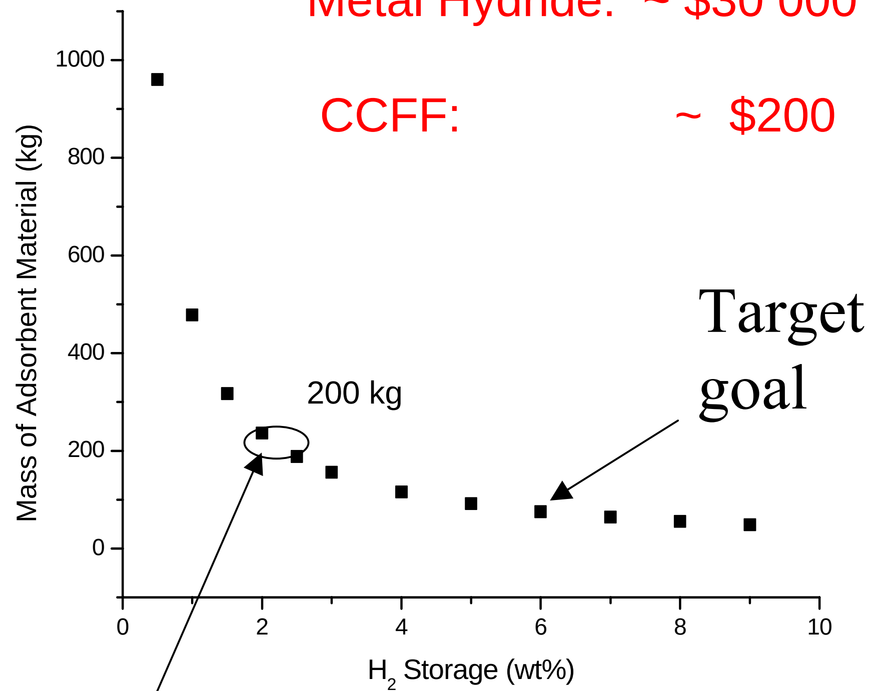
CNT: ~ $1.2 million

Metal Hydride: ~ $30 000

CCFF: ~ $200

- Surface of the fibers is not completely keratin, carbonization doesn't increase the carbon content.

- Initial results from the equipment are consistent with the literature and NREL (up to 2wt% at 77K)
- H_2 storage capacity of CCFF is as high as that of purified SWCNTs[1]



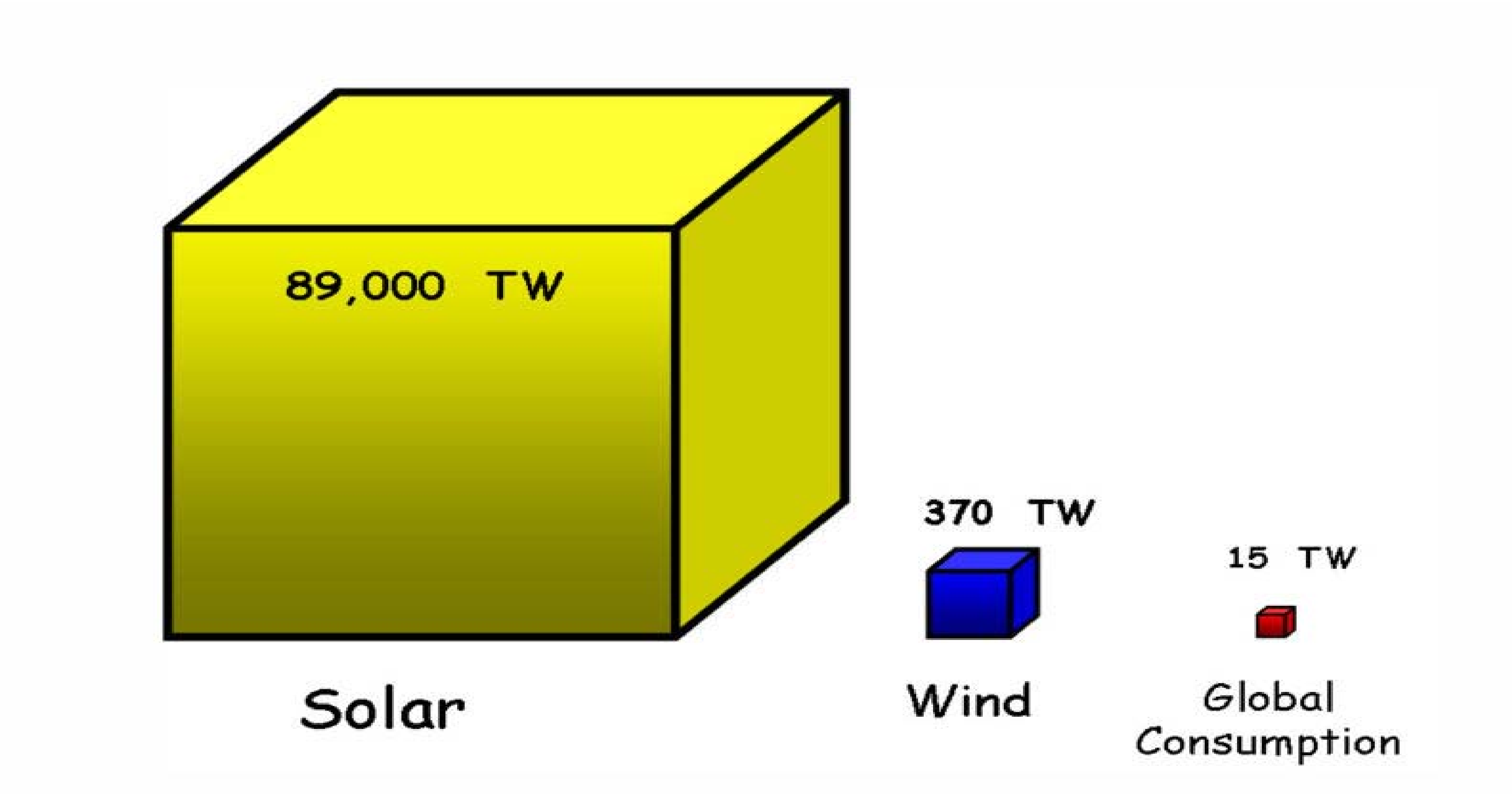
Today, we can drive 300 miles on H_2 with a 200 kg (~100 gal) tank of feathers

1 B. Panella et al., Carbon 43 (2005) 2209-2214


BIO-FUEL SUCCESS STORY
COST FACTORS
BIO-FUELS VS BIO-BASED
MATERIALS

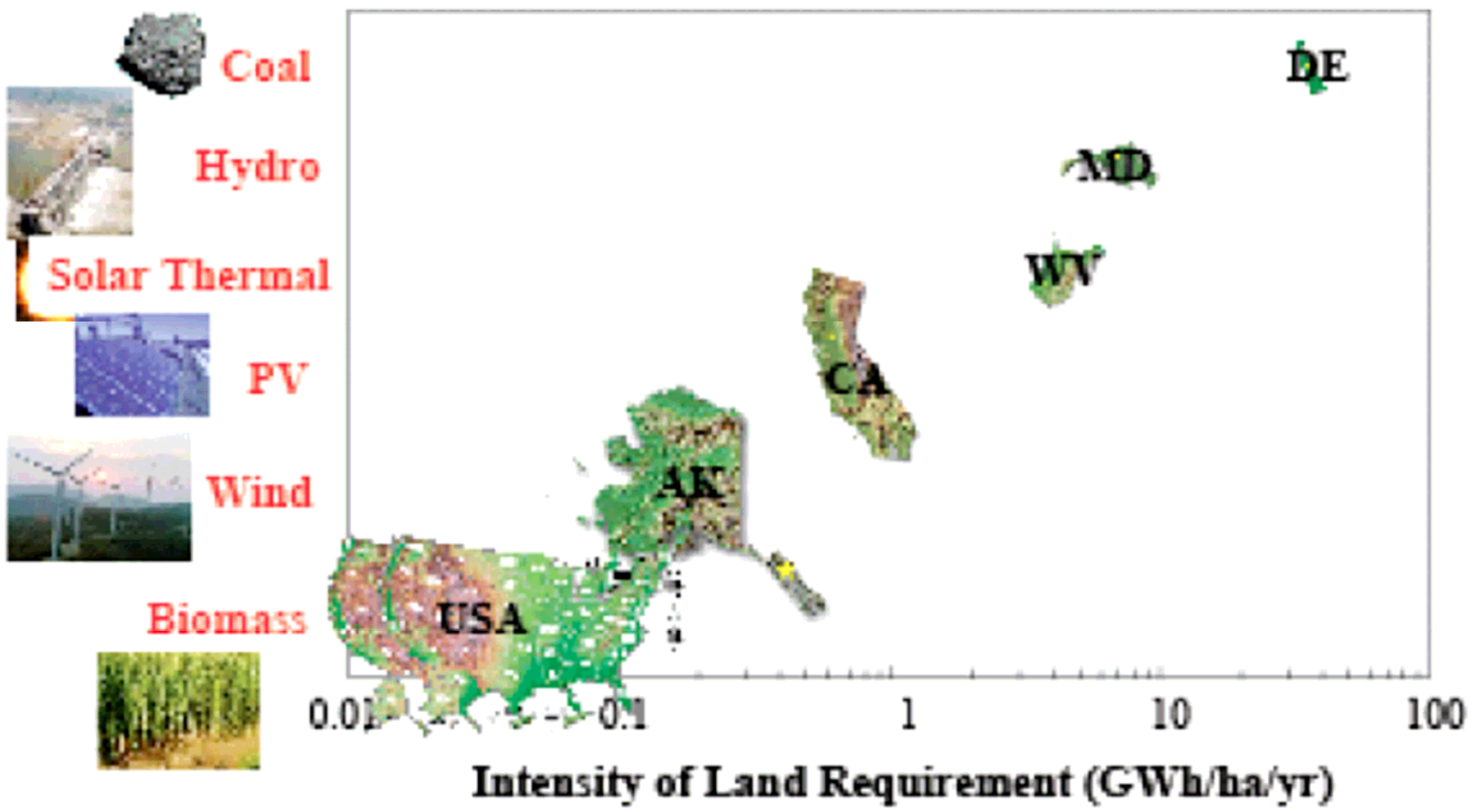

biodiesel
costs $7-8
Sells for $4
Gal of bio-
based resin
costs $10-12
Sells for $18
The Bio-Fuel Program is considered to be
an International Disaster

Available Renewable Energy



A. Rahim. Green Engineering, 2007, UD

Land Requirements to Produce 100 Quads



Source: International Energy Agency; Benign Energy? The Environmental Implications of Renewables, 1998

Graphic: Prof. L.T. Thompson (UD '82), U. Michigan

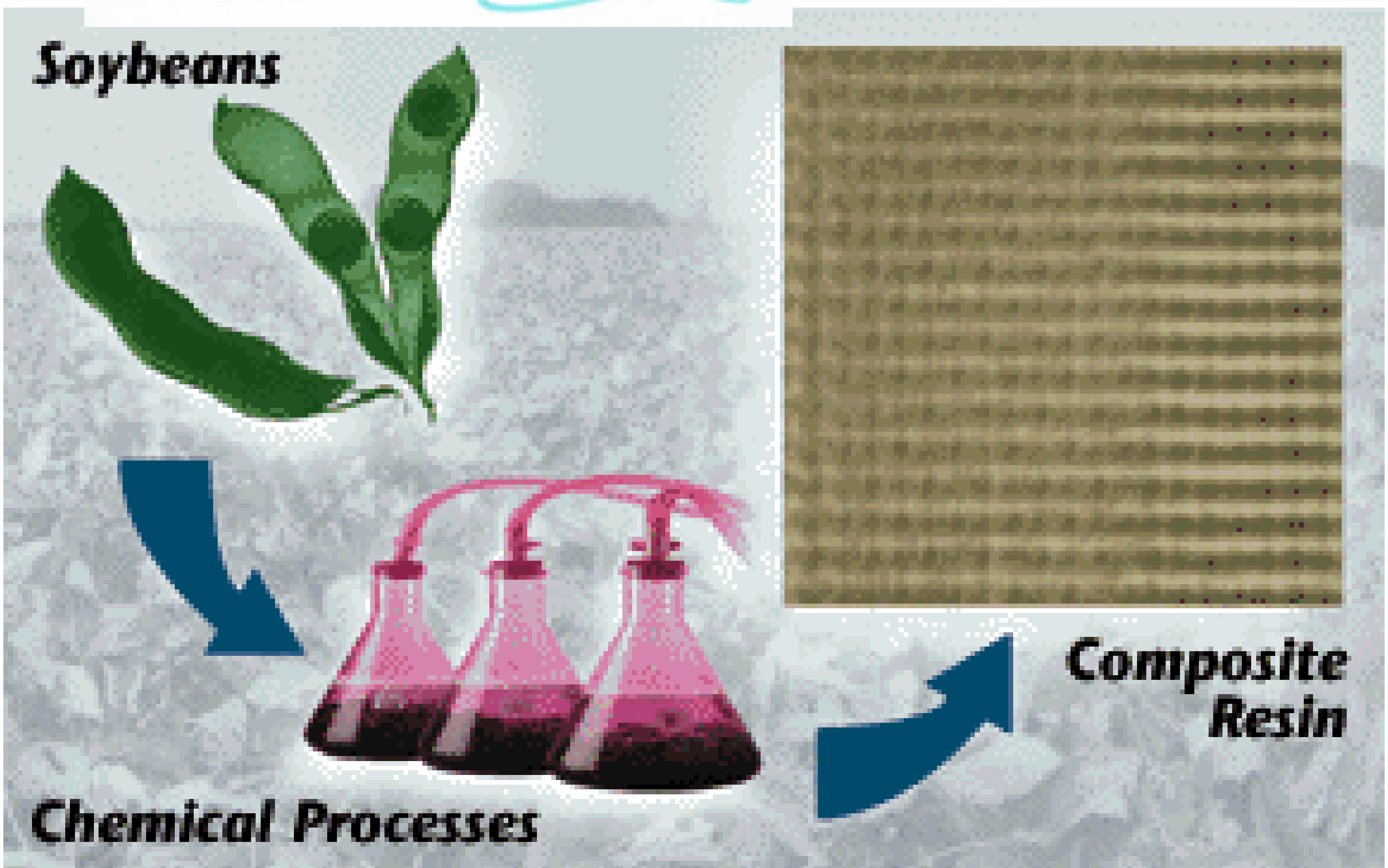

Delaware approved Offshore Windfarm on June 26 2008
MD, NJ, TX, MA, others to follow
18 tons of composites in 66 meter blade.
9 tons soyoil/blade
Delaware—here we come!

2000 turbines will require 120,000,000 lbs of petroleum based resin + steel + towers

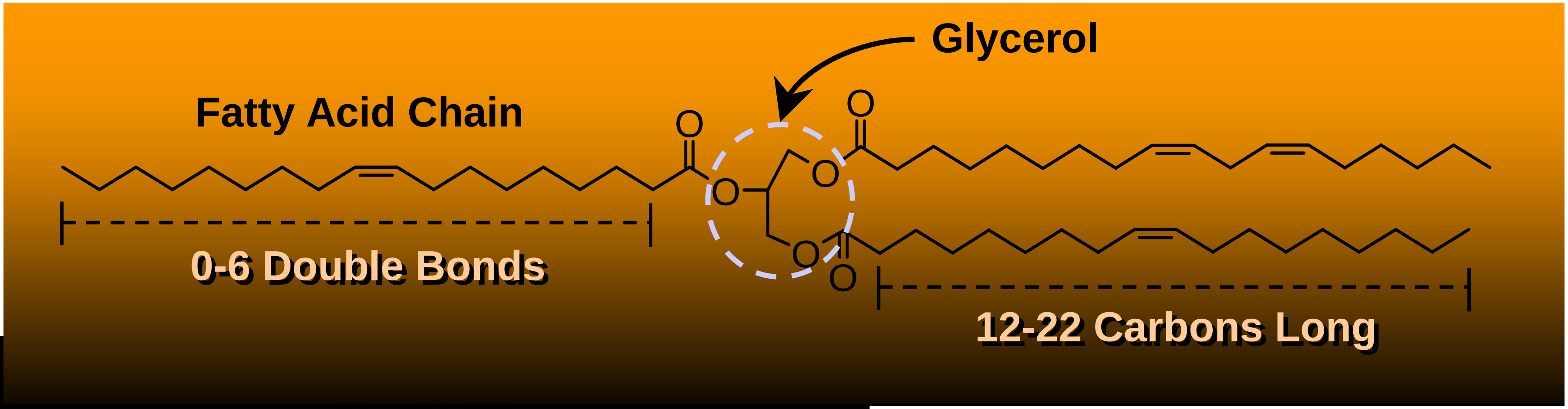
Lets do it with bio-based materials!

University of Delaware

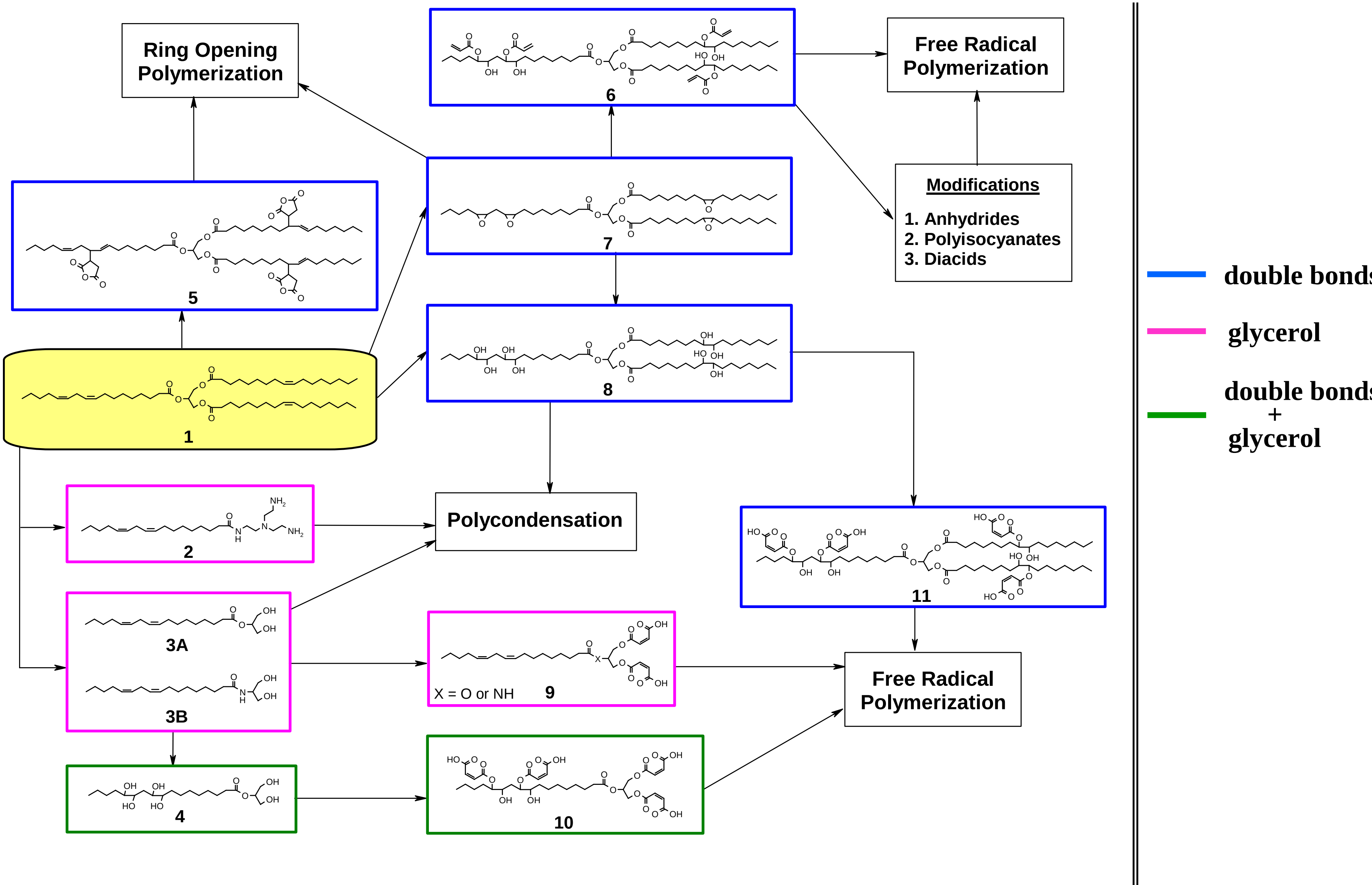
CARA



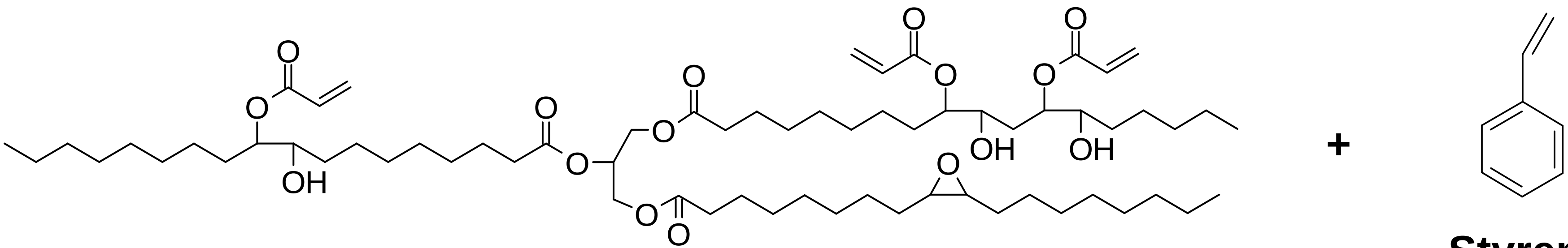
Oils to Plastics



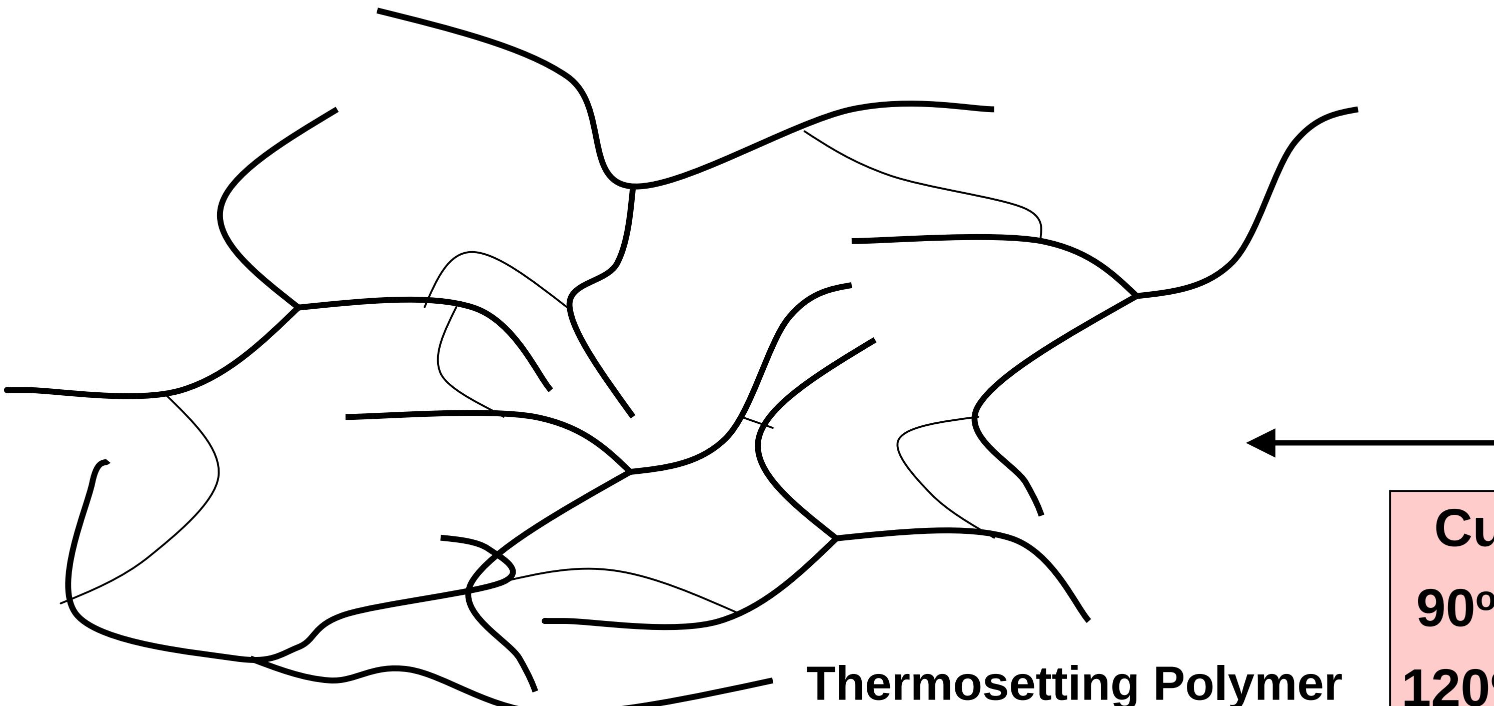
Plant Oils to Composite Resins   R. P. Wool et al (Patent 2000)



High Performance Composite Resins
Polymerization of Triglycerides



Styrene

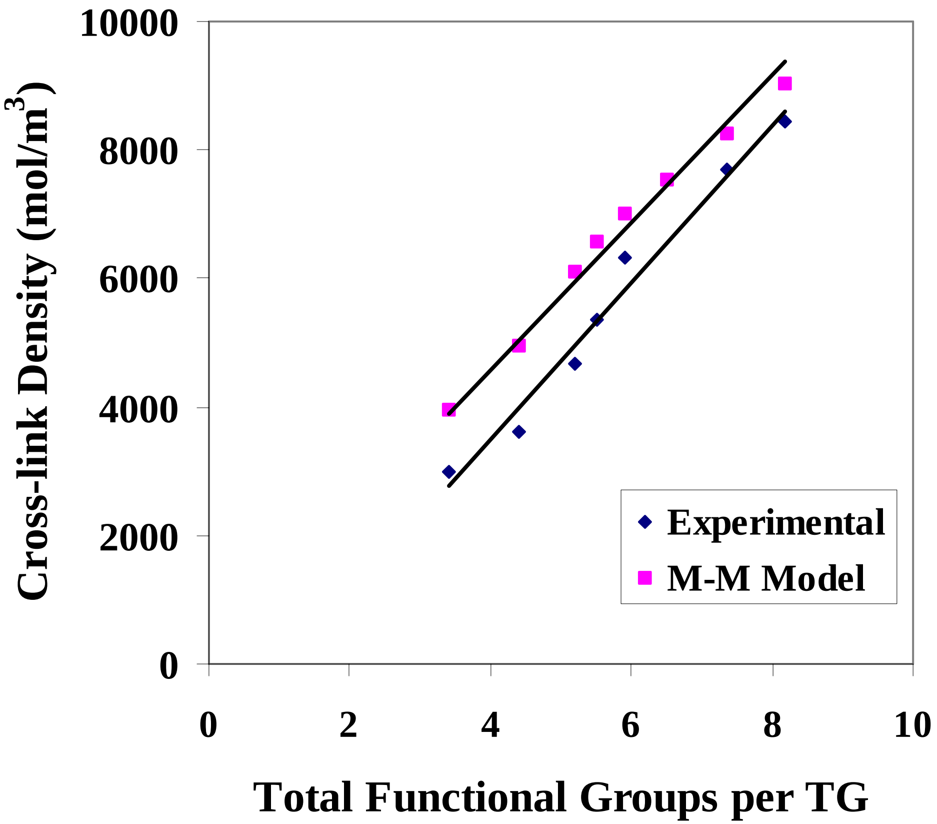


Free radical initiator: Hi Point 90

Thermosetting Polymer

Cure Cycle:
90^{o}C for 2hrs
120^{o}C for 2hrs

Cross-link Density v Predictions



$v = v_o(x\, f - f_c)$

(LaScala, Wool 2004)

$f_c = 1$

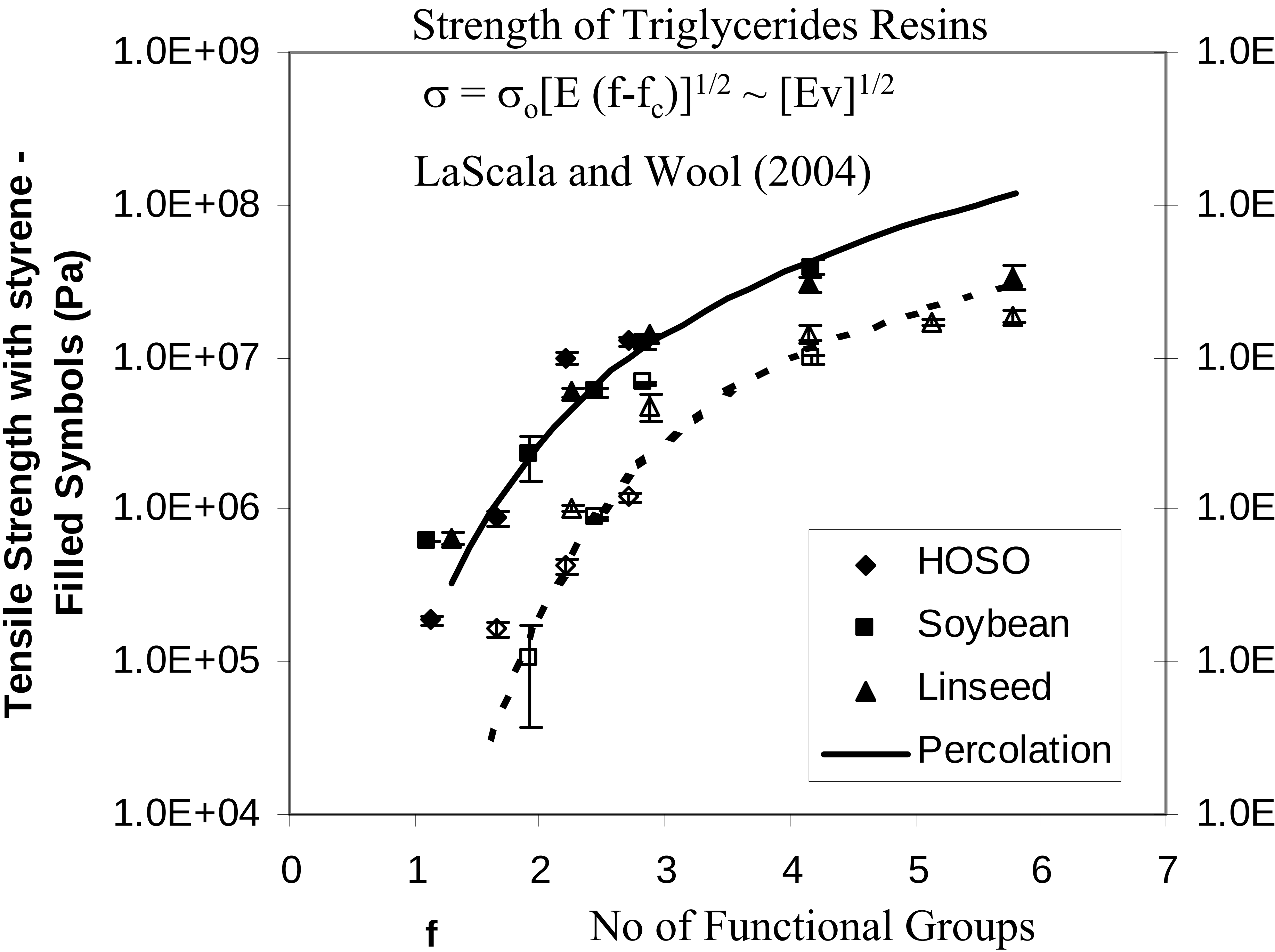
x = degree of reaction

$v_o(f)$ ~ Miller-Macosko

Inspection—LaScala

Computer Simulation (SNL)

Crosslinks ~ No. Chemical Groups f



Strength of Triglycerides Resins
σ = σo[E (f-fc)]1/2 ~ [Ev]1/2
LaScala and Wool (2004)
1.0E+09
1.0E+08
1.0E+07
1.0E+06
1.0E+05
1.0E+04
Tensile Strength with styrene - Filled Symbols (Pa)
0
1
2
3
4
5
6
7
f
No of Functional Groups
HOSO
Soybean
Linseed
Percolation

Fundamental Problem with Soy-based Thermosets!

Scaling Law correct: (LaScala and Wool)

Fracture Stress $\sigma \sim [2Ev\, D_o(p-p_c)]^{1/2}$

Exact for PLA, PE, PP, PS (Craze dominated)

E = Modulus

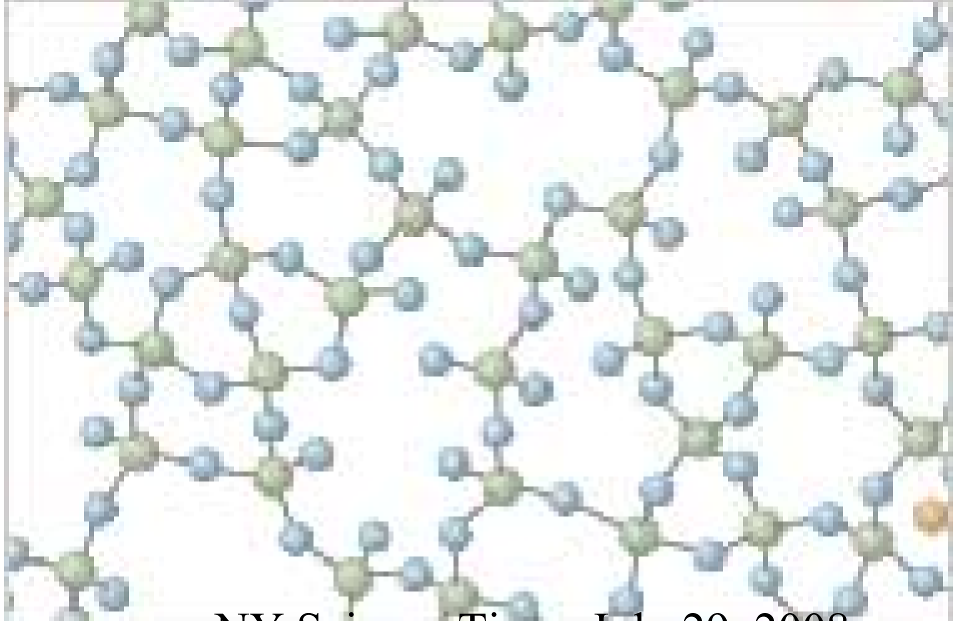
v = crosslink density

D_o = 80 Kcal/mol

BUT--Magnitude off (too high) by ~ 2 orders of magnitude

New Theory needed for thermosets—Yield Dominated

NEW THEORY OF YIELD, CTE AND Tg



NY Science Times July 29, 2008

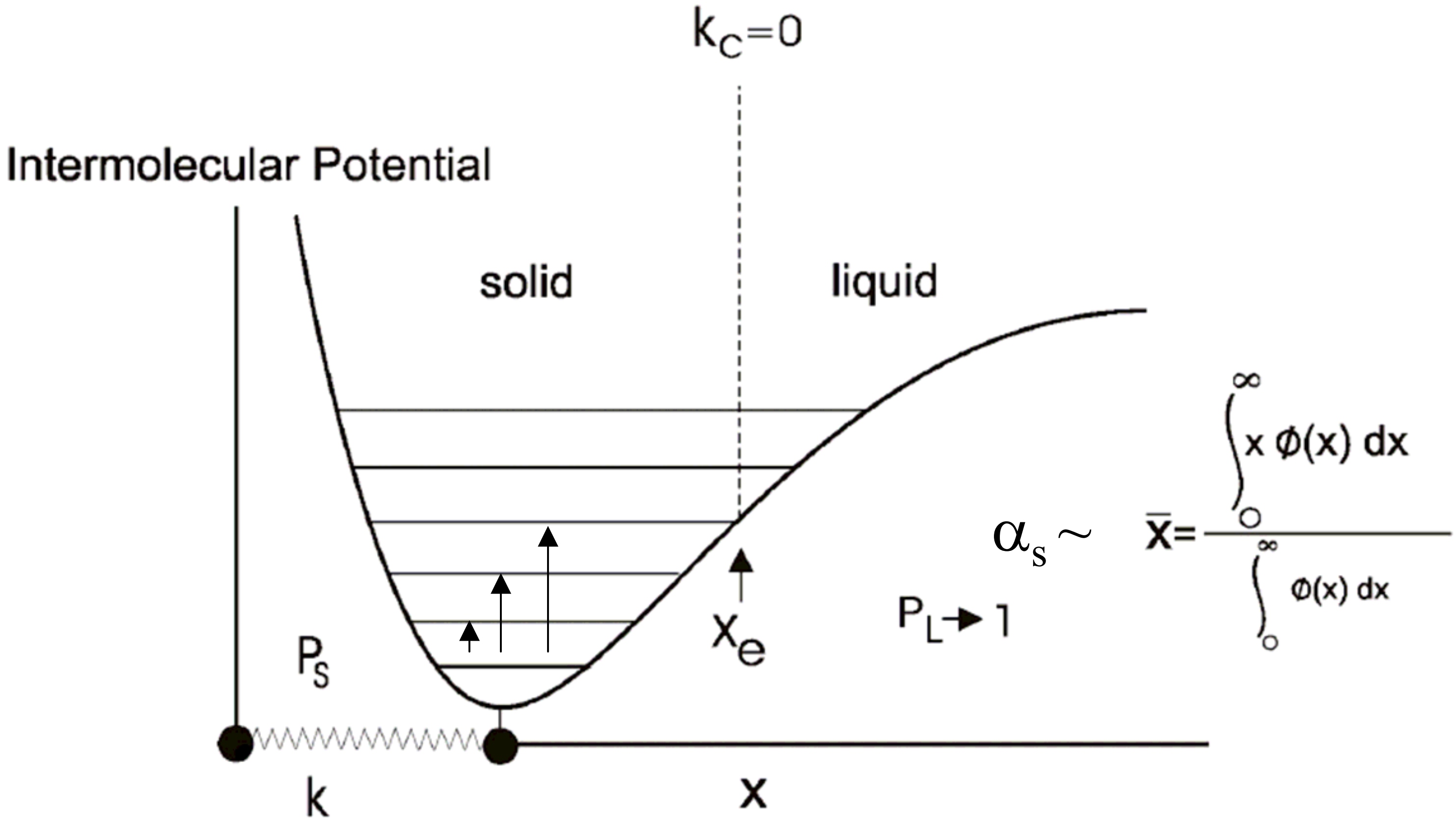
Phillip Anderson, Princeton, Nobel Prize winner (1995):

“The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition”

NY Times—”the solution is certainly Nobellable”

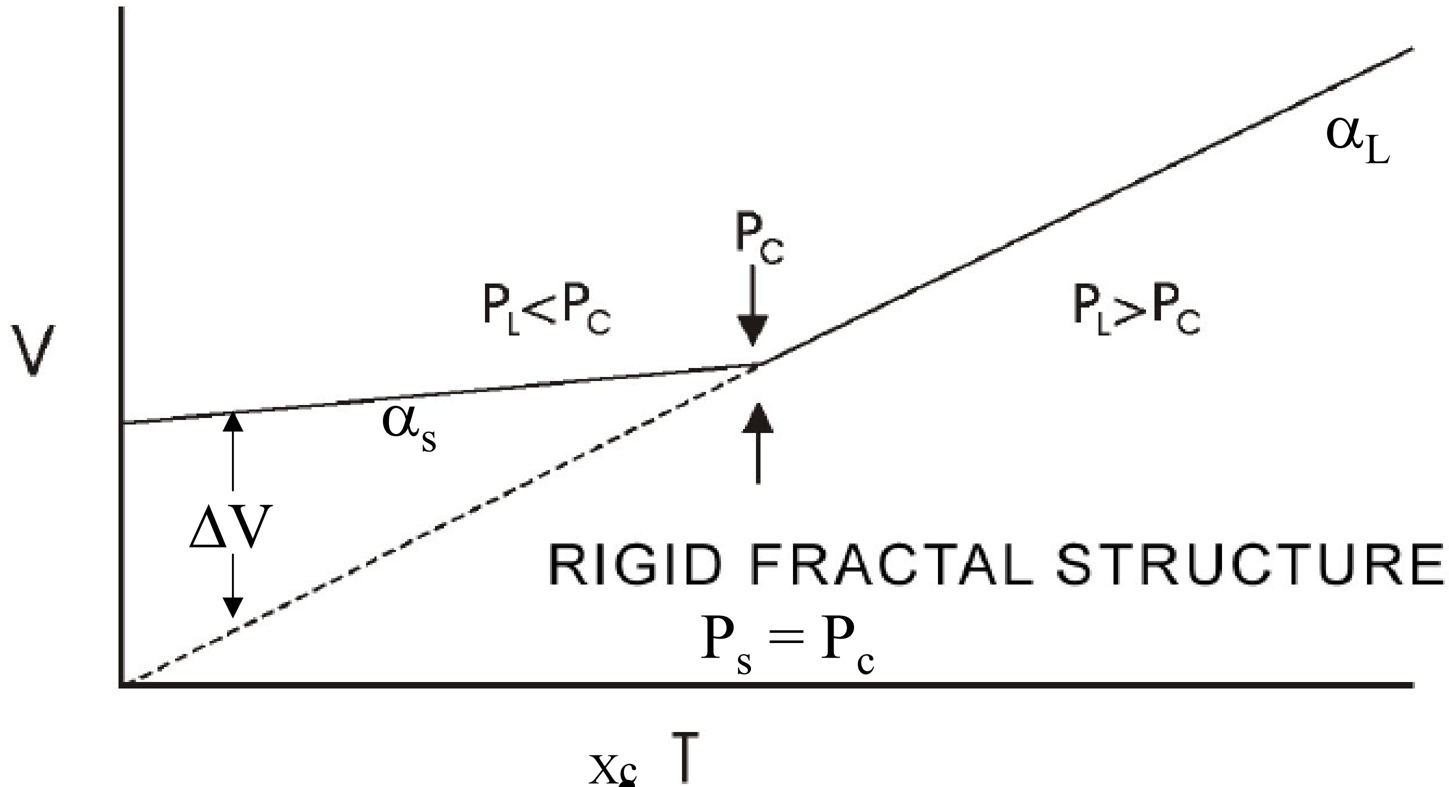
Twinkling Fractal Theory of the Glass Transition

R.P. Wool, J. Poly. Sci., Physics 2008



Diatomic anharmonic Morse oscillator

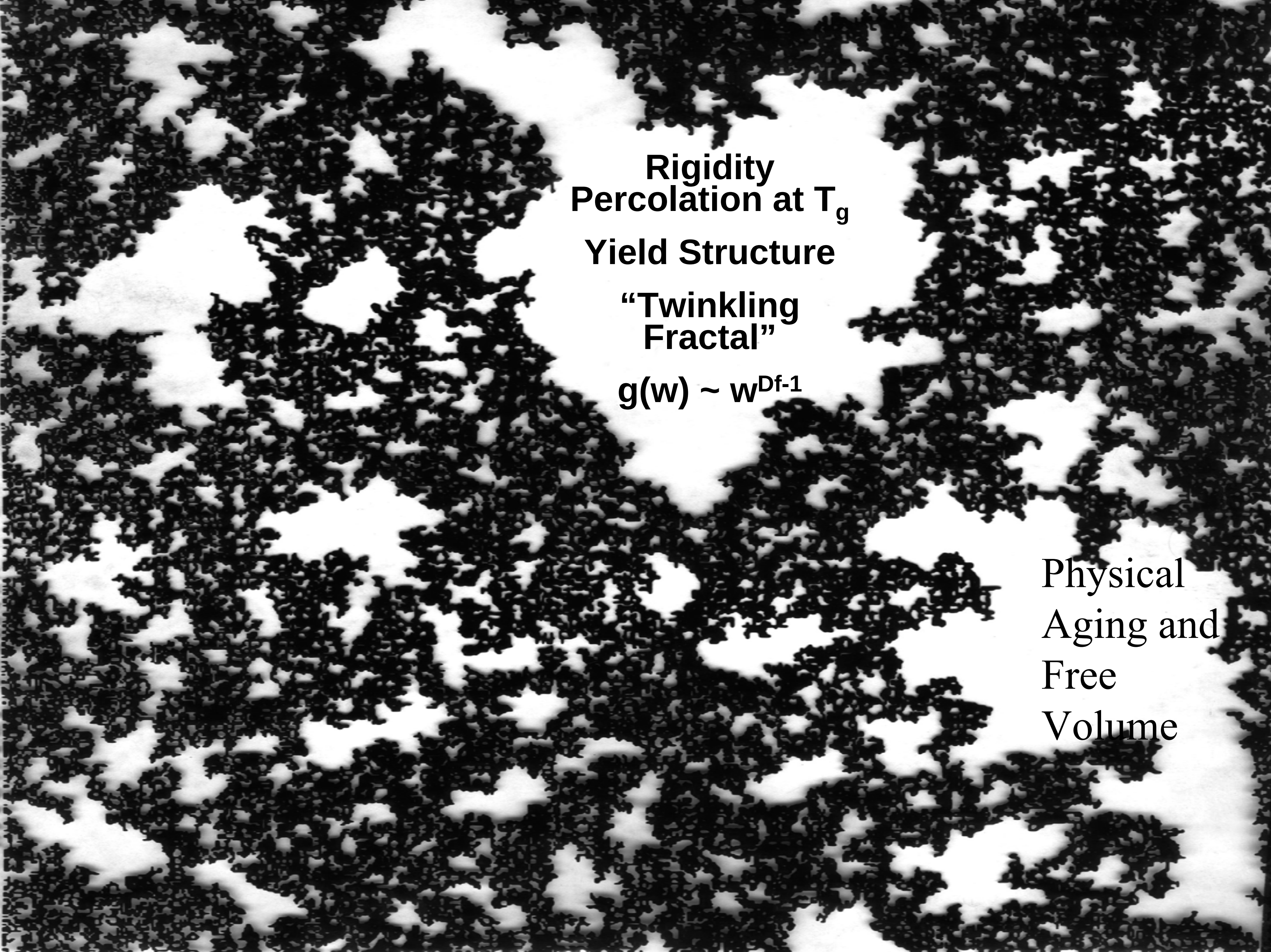
$U(x) = D_o[1-e^{-ax}]^2$ with Boltzmann energy levels and populations $\phi(x) \sim \exp[-U(x)/kT]$ shows the Liquid ($X > X_c$) and Solid ($X < X_c$) phase diagram.



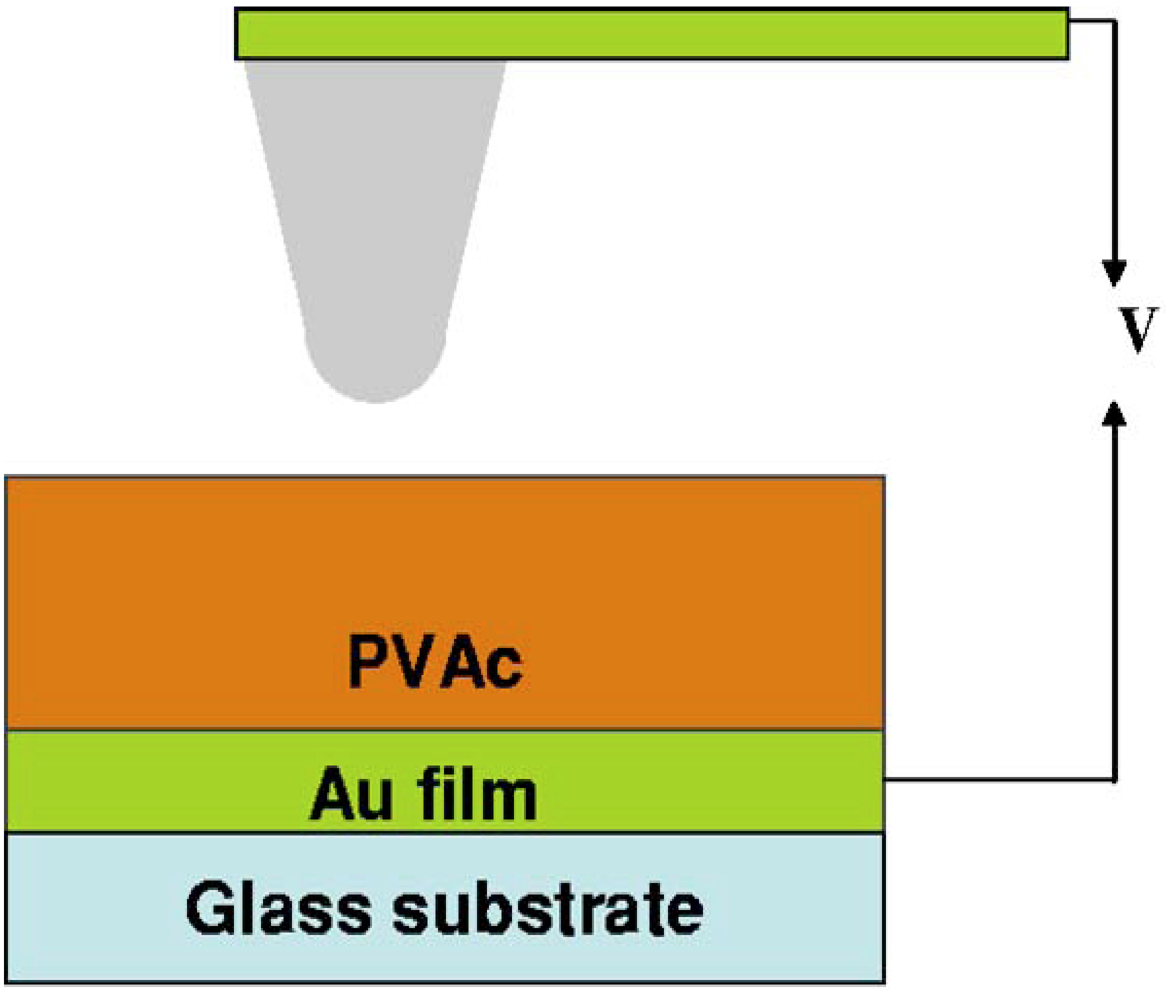
Solid Fraction: $$P_S(T) = \int_o^{Xc} \phi(x)\, dx = p_c \text{ at } T_g$$

$$T_g = 2D_o/9k; \quad \alpha_L = 3k/4D_oR_oa; \quad \alpha_s/\alpha_L = p_c; \; \alpha_L * T_g \approx 0.03$$

Example: if D_o = 3.5 kcal/mol, T_g = 391 ^oK (118 ^oC); using R_o = 3 A and *a* = 2/A, then α_L = 71 ppm/^oK.


Rigidity Percolation at T_g
Yield Structure
“Twinkling Fractal”
$g(w) \sim w^{Df-1}$
Physical Aging and Free Volume

Experimental Proof of TFT

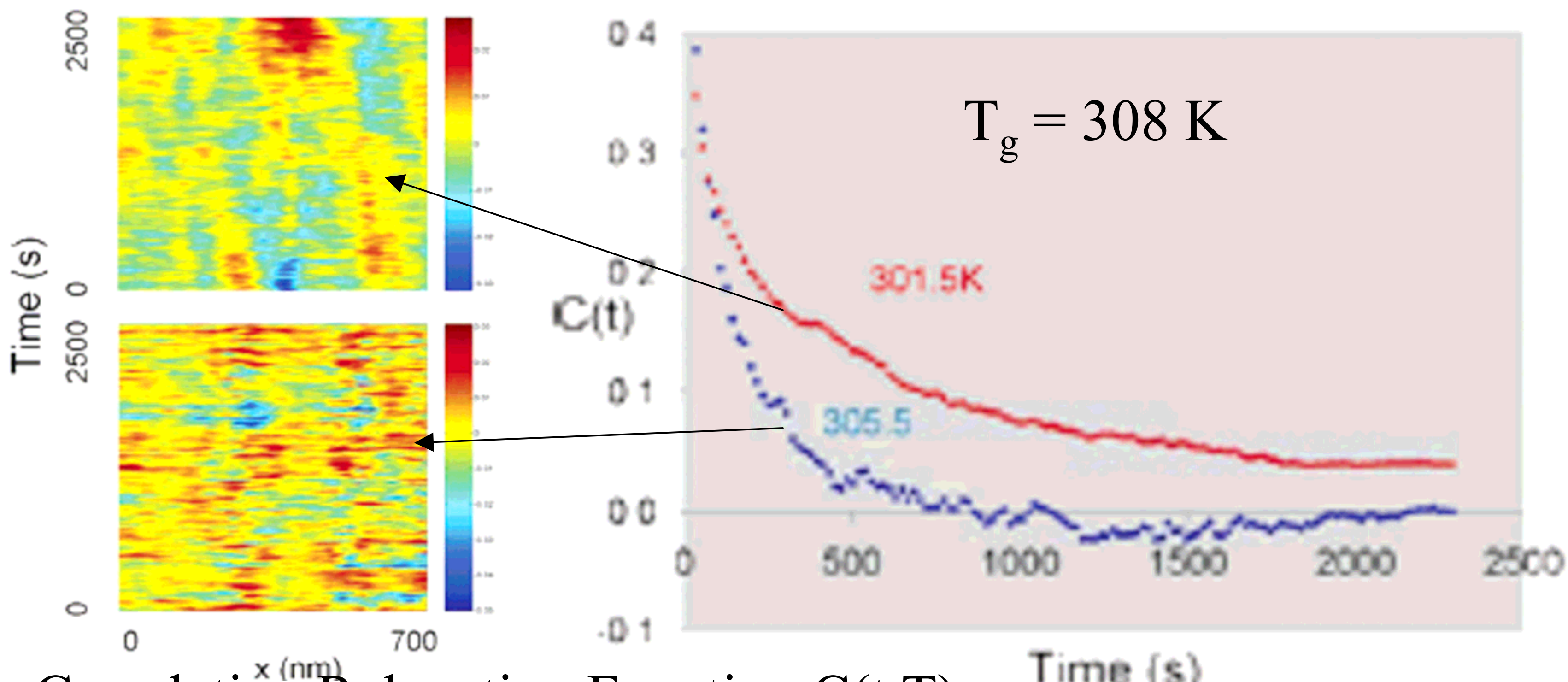


Local dielectric spectroscopy of polymer films at Tg

P. S. Crider, M. R. Majewski, Jingyun Zhang, H. Oukris, and N. E. Israeloff[a]

Spatio-Temporal Fluctuations (Twinkles) in PVAc near Tg

Dielectric AFM Spectroscopy, N. Israeloff et al, Nano Letters, 6(5) 887 (2006)



Auto Correlation Relaxation Function C(t,T)

$$C(t, T) = \int_{\omega o}^{\omega = 1/t} \omega^{df-1} \exp - [\, \omega t + \exp\text{-}|\beta(T^2 - T_g^{\,2})|/kT] \, d\omega$$

(TFT Prediction)

$C(t) \sim t^{-1/3}$—short times or low T

$C(t) \sim t^{-4/3}$—long times

$C(t) \sim t^2$ when $w<w_c$ at v long times

A VERY NICE PREDICTION!

$$\alpha_L * T_g \approx 0.03$$

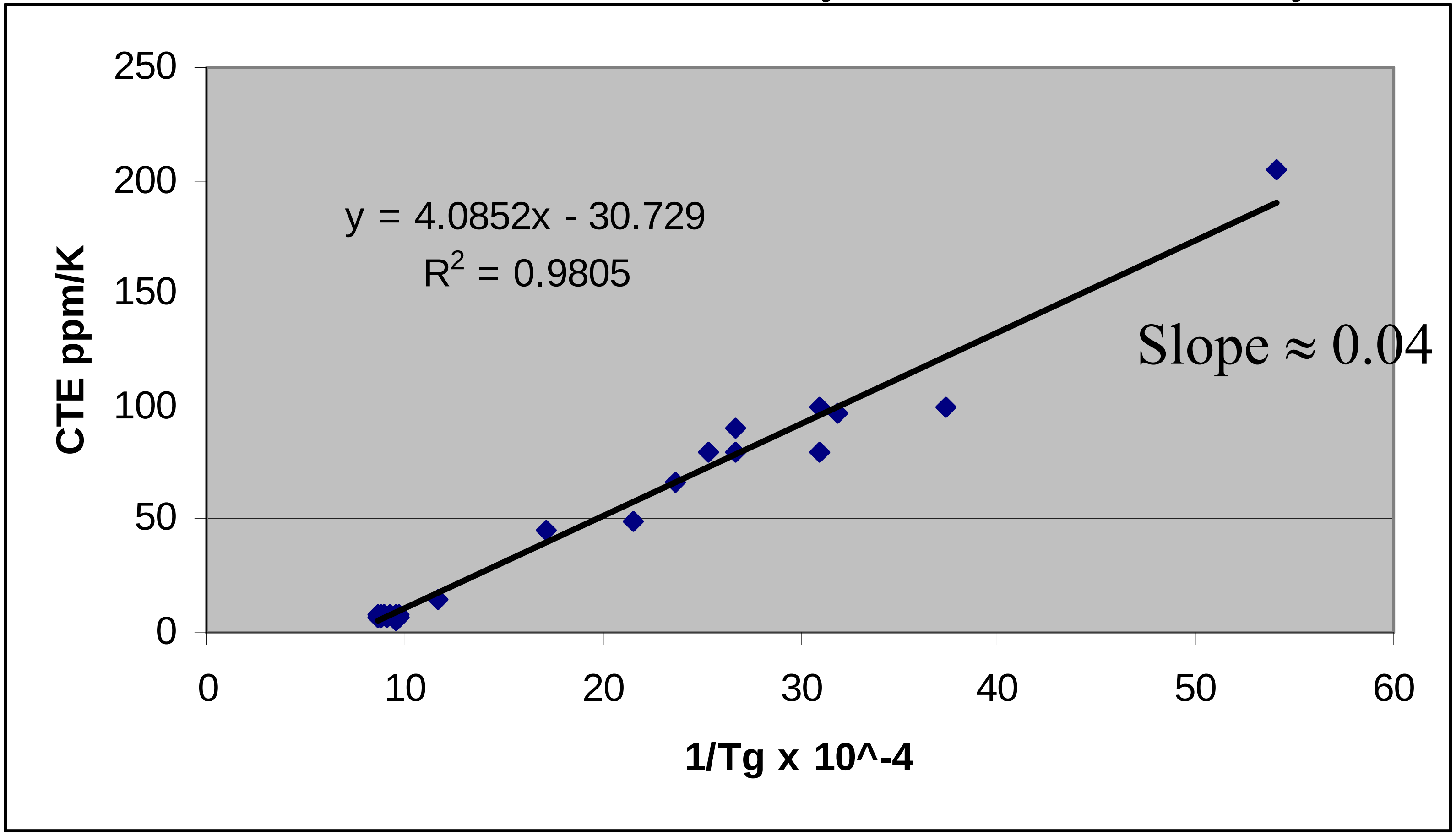
$$\alpha_L = \tfrac{3}{4}\, k/(D_o a R_o) \qquad T_g = 2D_o/9k$$

$$\alpha_L * T_g = 1/6aR_o \approx 1/6*2Å^{-1}*3Å \approx 0.03$$

Polymer	α_L ppm	T_g °K	$\alpha_L * T_g$
PE	100-200	223	0.02-0.4
PP	100	268	0.027
PS	80	373	0.03
PC	66	423	0.028
N66	80	323	0.026
PMMA	90	373	0.033
PA12	97	313	0.03
PBT	100	323	0.032
PPA	80	394	0.031
PPS	49	363	0.02

$$\alpha_L * T_g = 1/(6\ aR_o) \approx 0.03$$

Metals----Ceramics-----Polymers------------- Glycerol

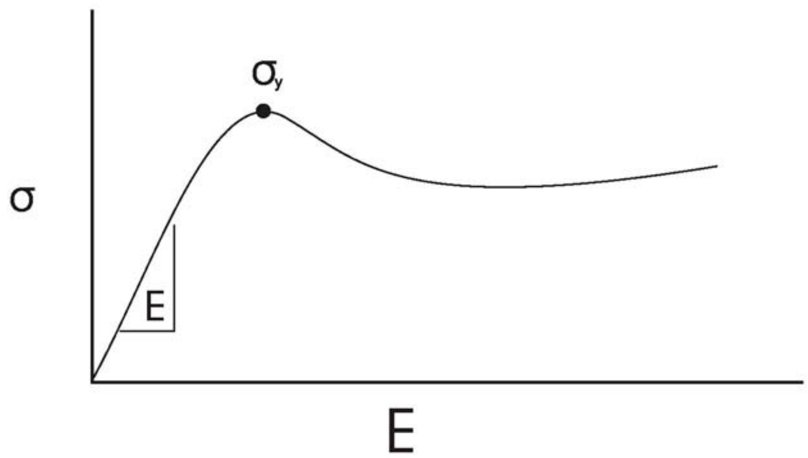


Twinkling Fractal View of Yield,

Percolation Theory of Yield

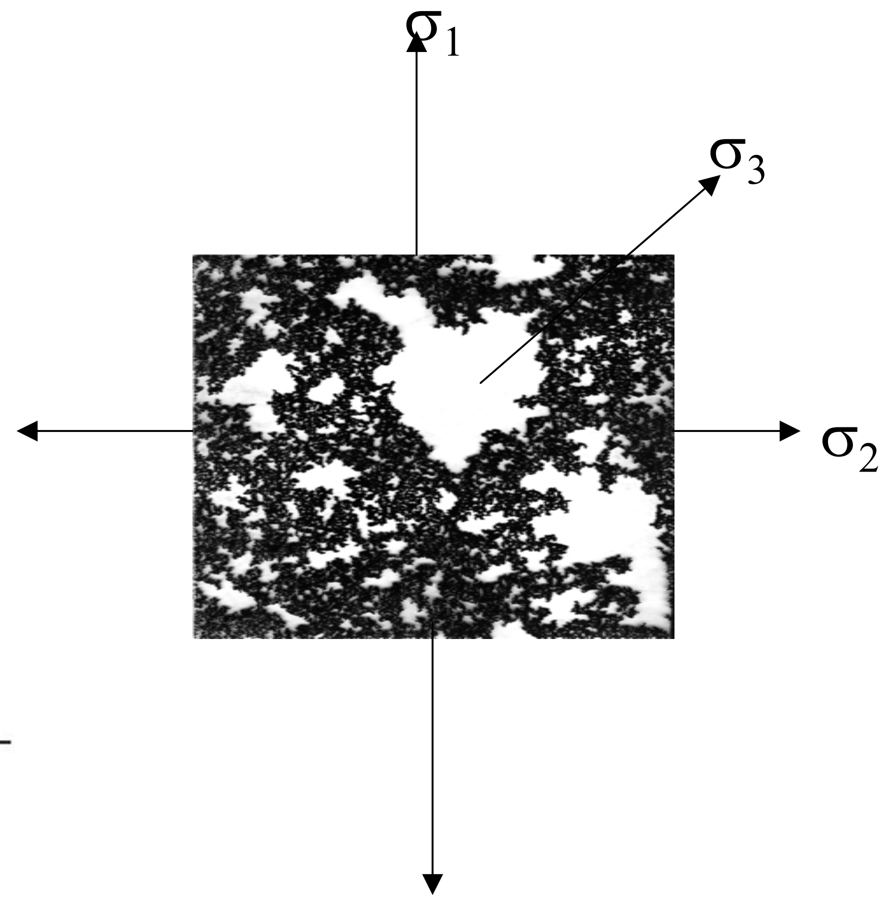
$$\frac{\sigma^2}{2E} \geq \frac{U(X_c)}{V_m} |P-P_c|$$

$V_m \simeq$ Molar Vol ; $U(X_c) = 0{\circ}08D_o$



$$\sigma_y = \left[0{\circ}16ED_o|P-P_c|/V_m \right]^{1/2}$$

D_o/V_m = Cohesive Energy Density



Rate ~ 1/(Twinkle Frequency w)

Density States $G(w) \sim w^{Df}$; ($D_f = 4/3$)

Liquid Armor Transition

How Stiff? ~ 2.8 GPa

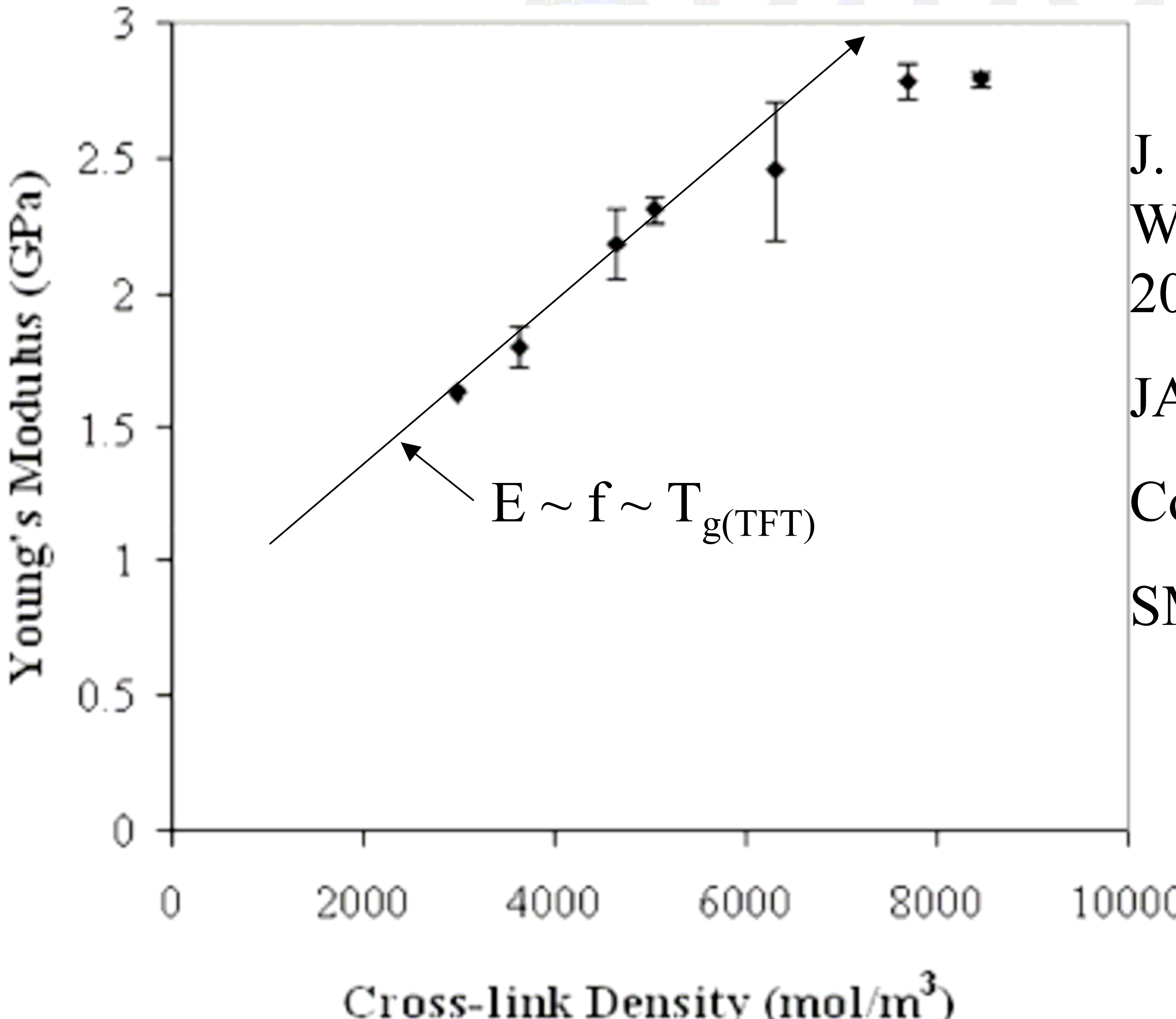


FIG. 9. Effect of crosslink density on the Young's modulus of triglyceride-based polymers.

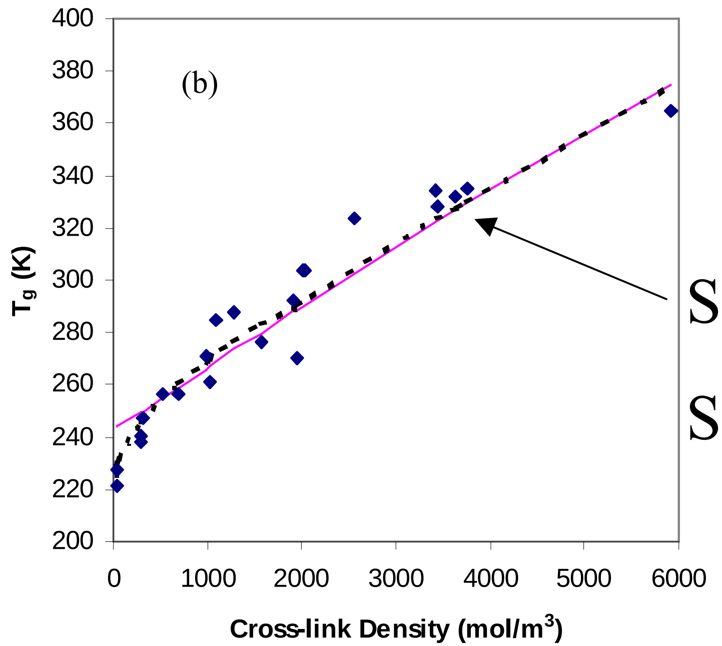
J. Lu and R.P. Wool (Patent 2005)

JAPS 2007

Composite Resins

SMC + BMC

T_g vs Crosslink Density v.



Slope = 0.024 $^oK\ m^3/mol$

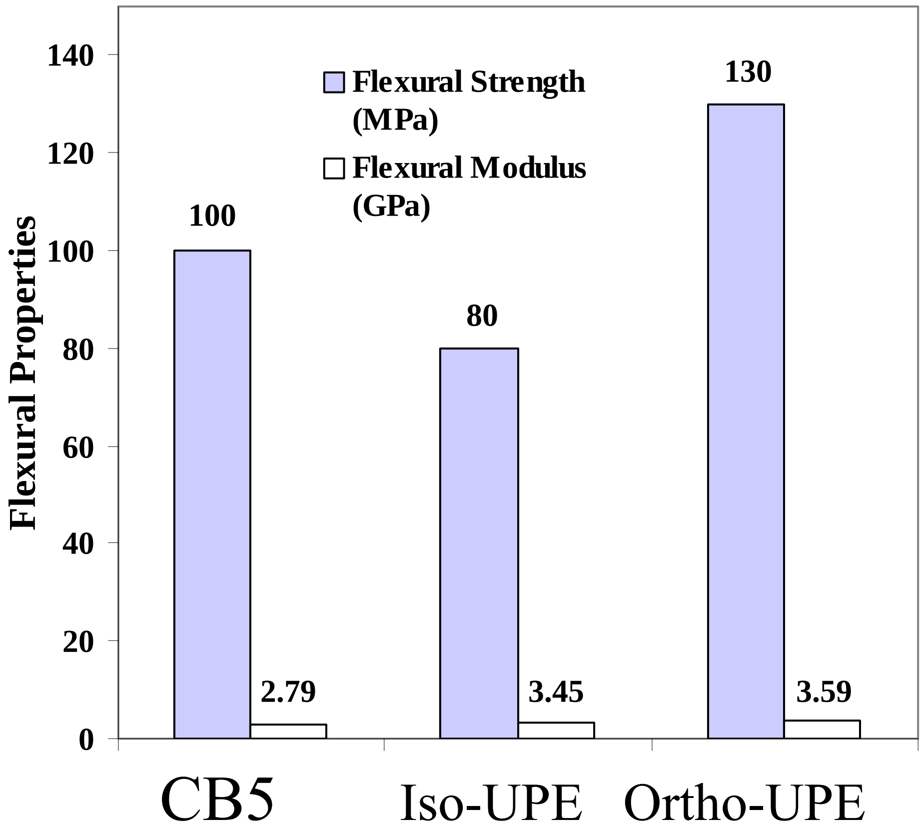
Slope = $T_g^o M_j/p_c\rho$

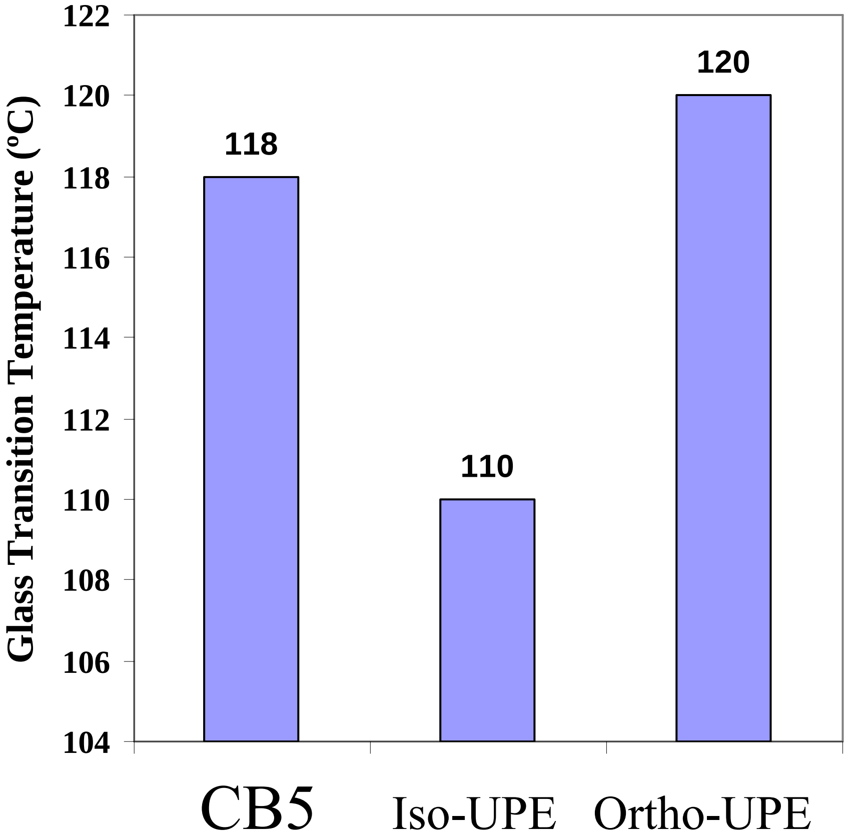
The Tg of model acrylated crosslinked triglycerides with 30 wt% styrene is shown as a function of crosslink density v (LaScala and Wool 2006)

TFT Prediction: $\mathbf{T_g(v) = T_g^o + (T_g^o M_j/p_c\rho)\ v}$

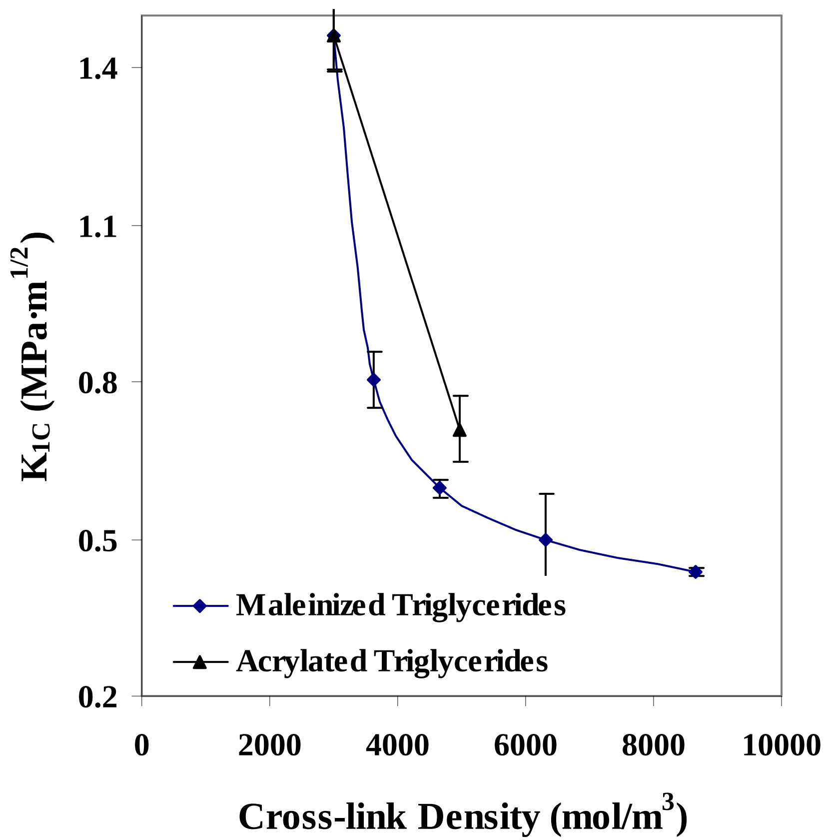
<u>Example</u>: $T_g^o = 242\ ^oK$ at v = 0 intercept, $p_c \approx 0.4$, $\rho = 1.1$ g/cc and $M_j \approx 43$ g/mol, then the predicted slope ≈ 0.024 $^oK\ m^3/mol$, which is in excellent agreement with experiment

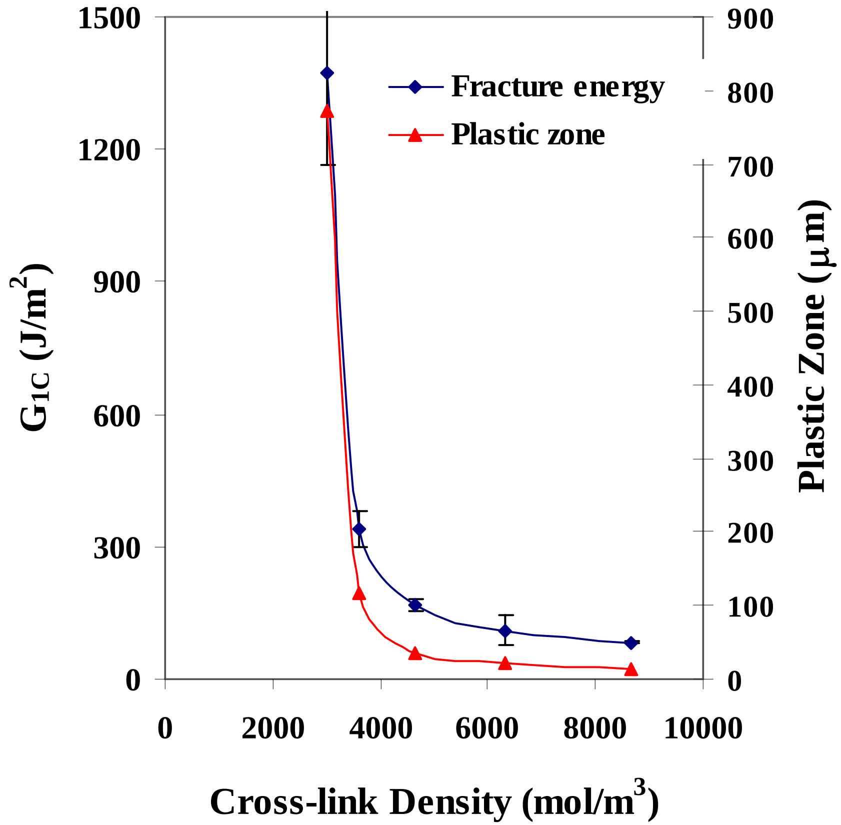
Comparison of Cara CB5 Resin to Petroleum- UPE Resins





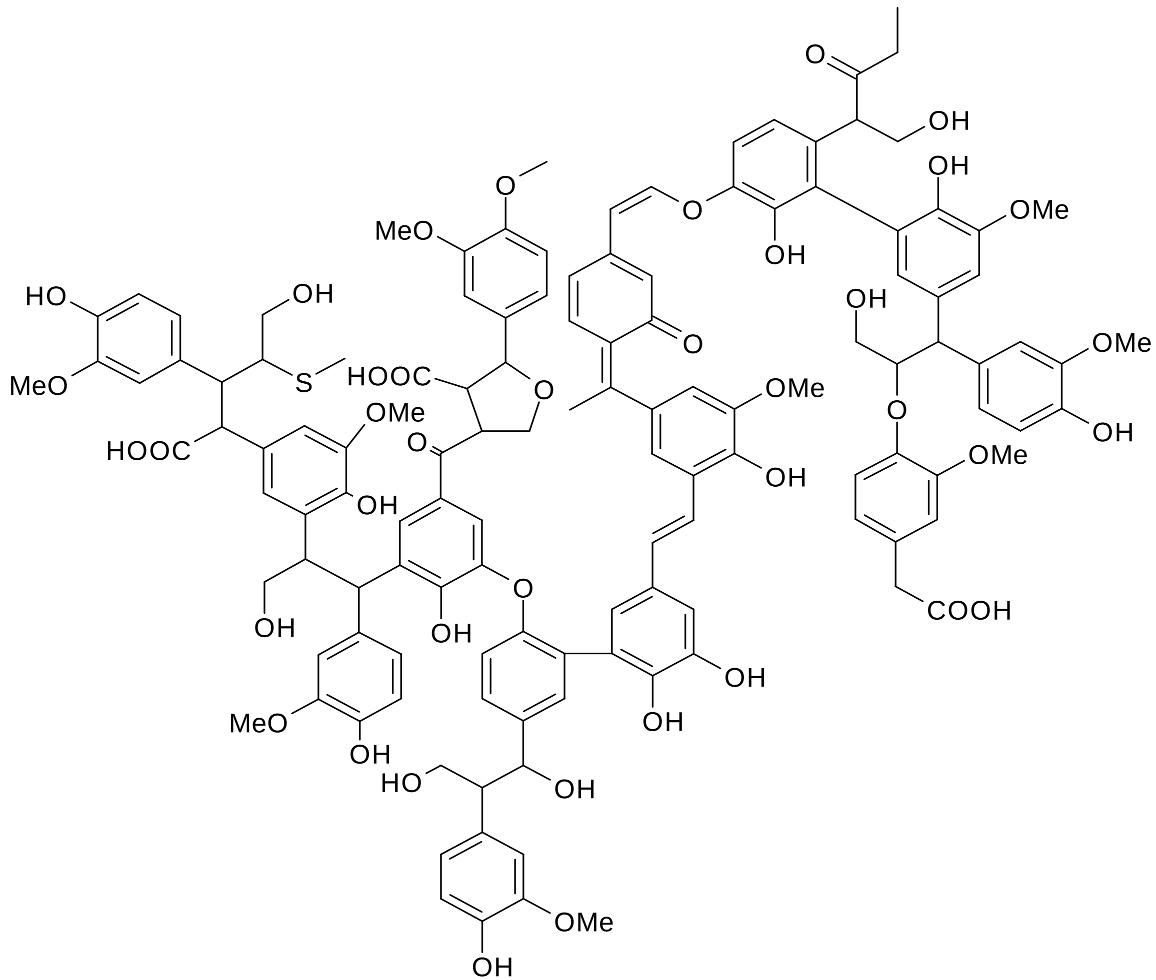
Fracture Toughness $G_{1c} \sim v^{-1/2}$ J. Lu 2006





$$r_p = \frac{1}{2\pi}\left(\frac{K_{1C}}{\sigma_y}\right)^2 = \frac{EG_{1C}}{2\pi\sigma_y^2}$$

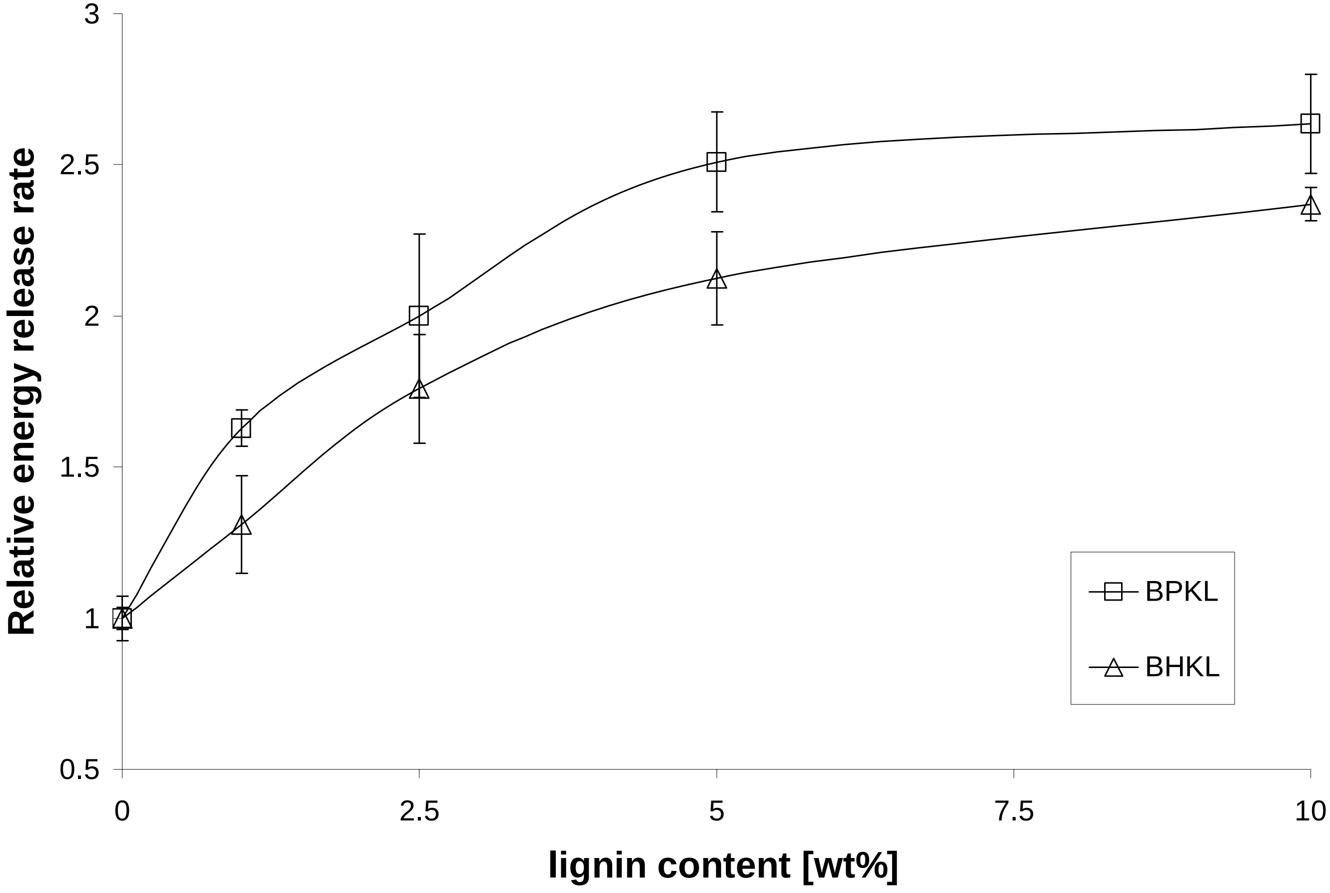
Can Lignin Toughen a Thermoset? Enhanced connectivity, free radical trapping, co-monomer, fiber sizing in Composites?



Structure of Lignin

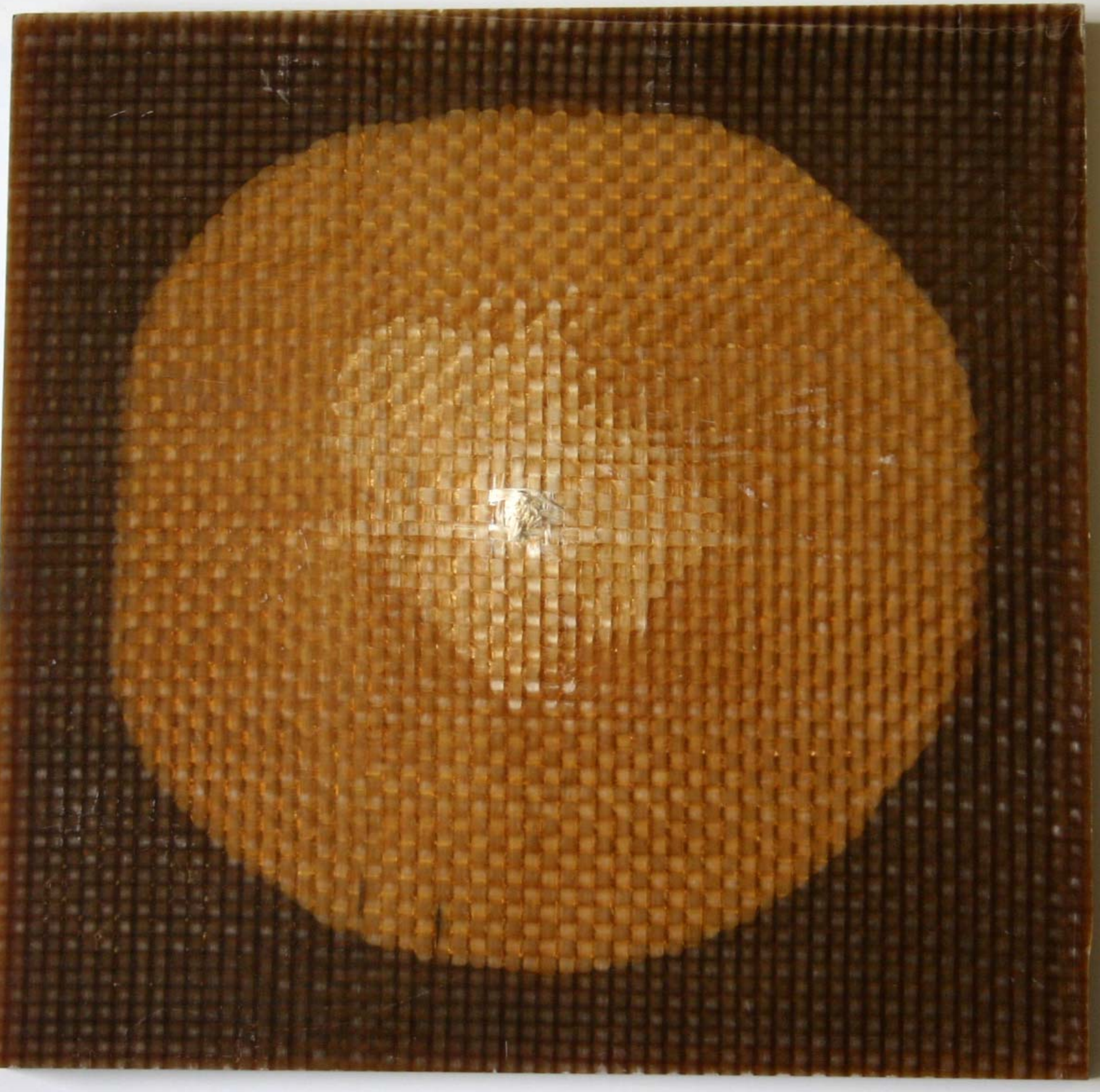
Solubilized Butyrated Lignin Toughening of Soy Resin

Wim Thielemans and R. P. Wool



Ballistic Impact Resistant plate with 50 mm fragmentation round

Will provide Tornado resistance as well as hurricane resistance



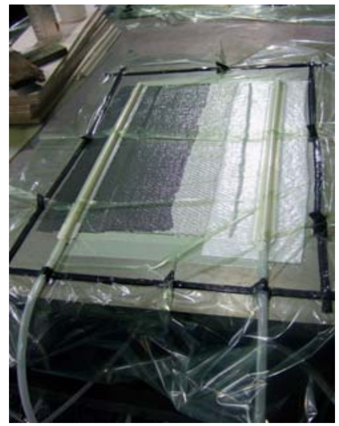
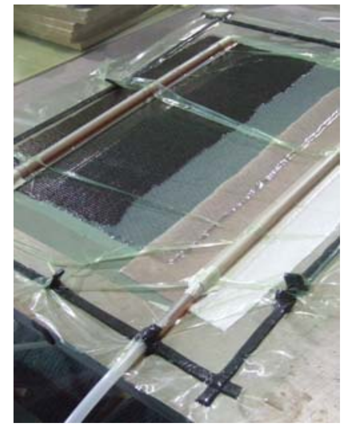
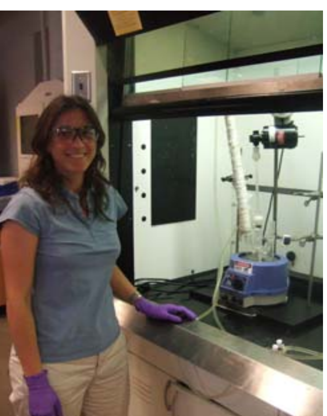
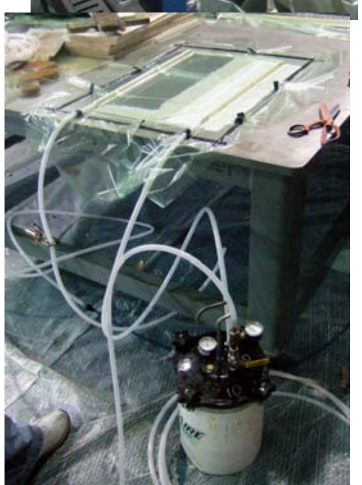
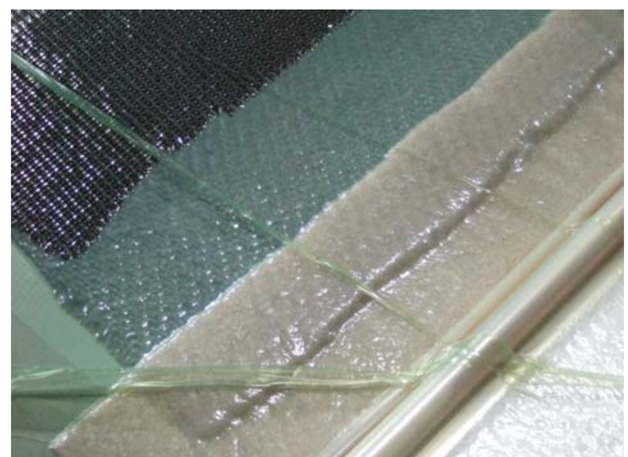

Cara Plastics
Manufacturing Partner
DynaChem
Georgetowne IL

First I-Beam from Soy and Jute!

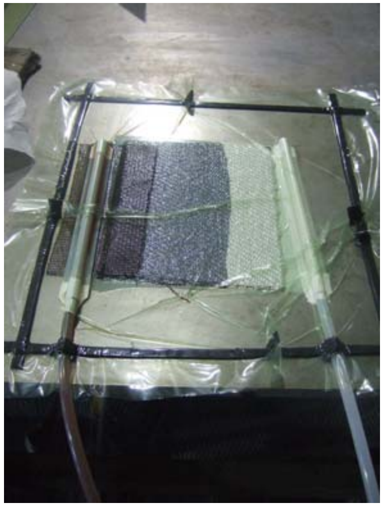
Robert McDowell Justin Alms Peter Yonko

Dr Julie Soden, UOU Belfast
& Prof Richard Wool & Researchers, CCM Delaware
July 2008



Dr Julie Soden, UOU Belfast
& Prof Richard Wool & Researchers, CCM Delaware
July 2008



3D Woven Flax Mats

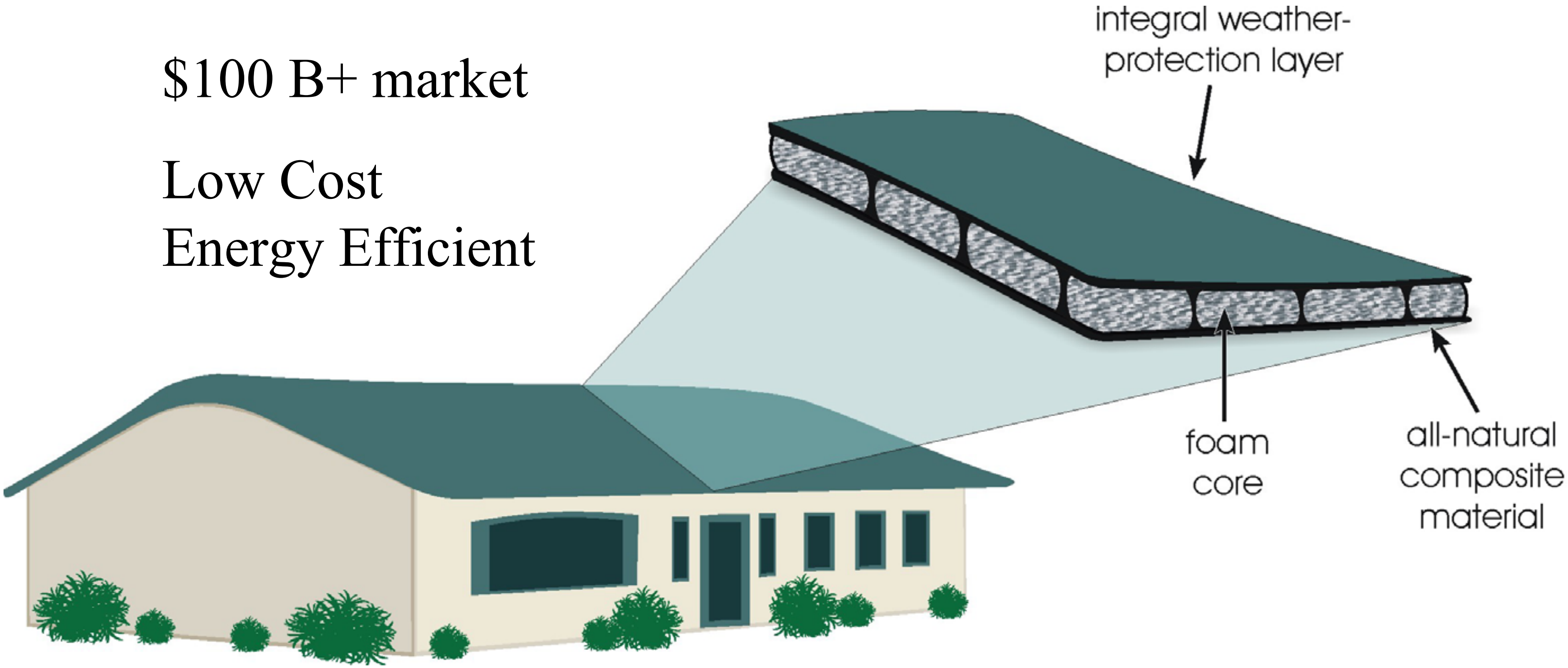
The Problem

The Solution-Monolithic Roof

Newsweek Oct 27 2003, T. Shenton, M. Dweib and R. P. Wool
Architectural Record Nov 2003, Royal Institute British Architects, 2004
R.P. Wool et al (2006-Patent pending)

$100 B+ market

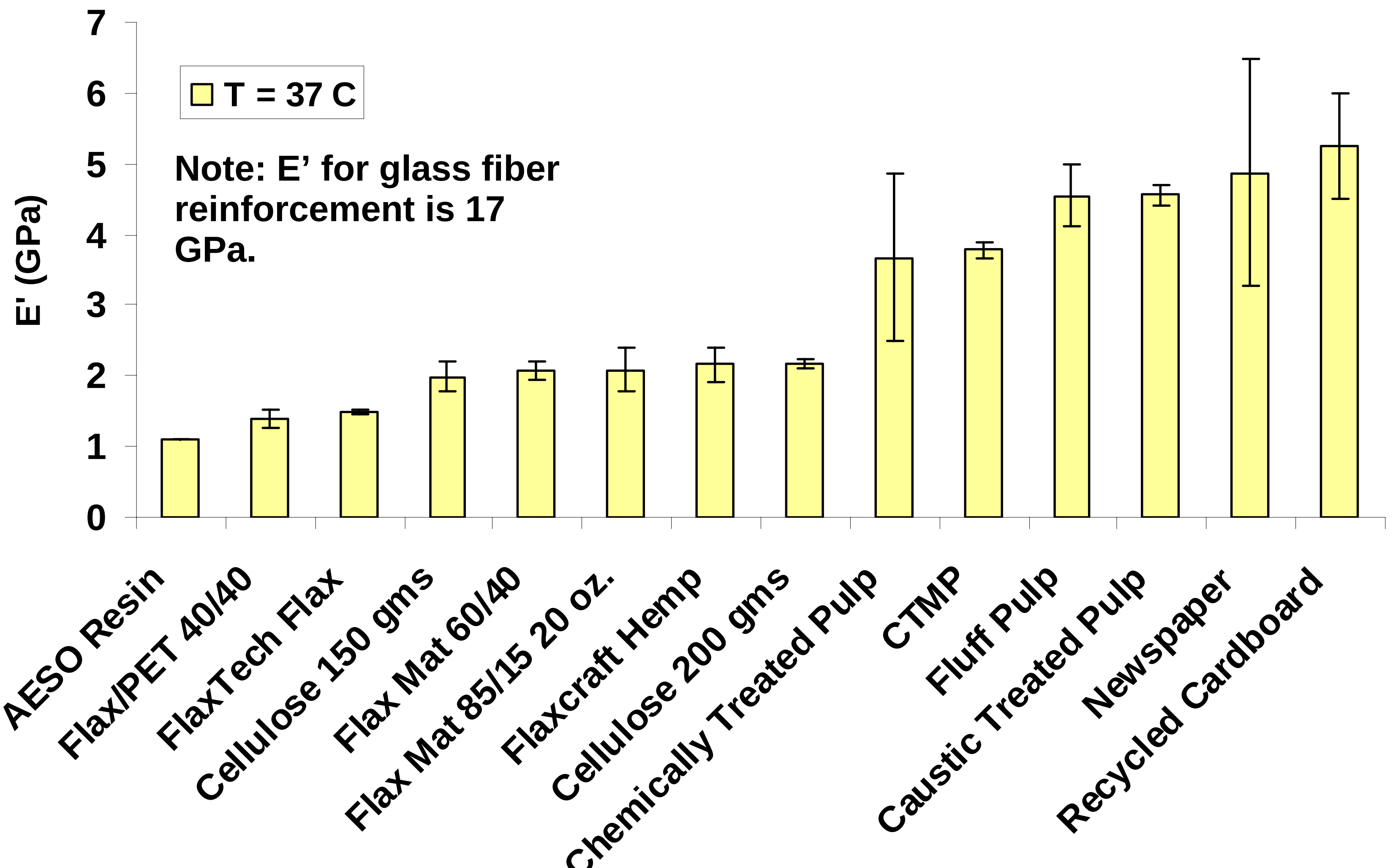
Low Cost
Energy Efficient



Optimal Solution: Solar Panels + Hurricane Resistance-in progress
Benefit ~ 30 Quads/yr

Very Low Cost Composites for Housing

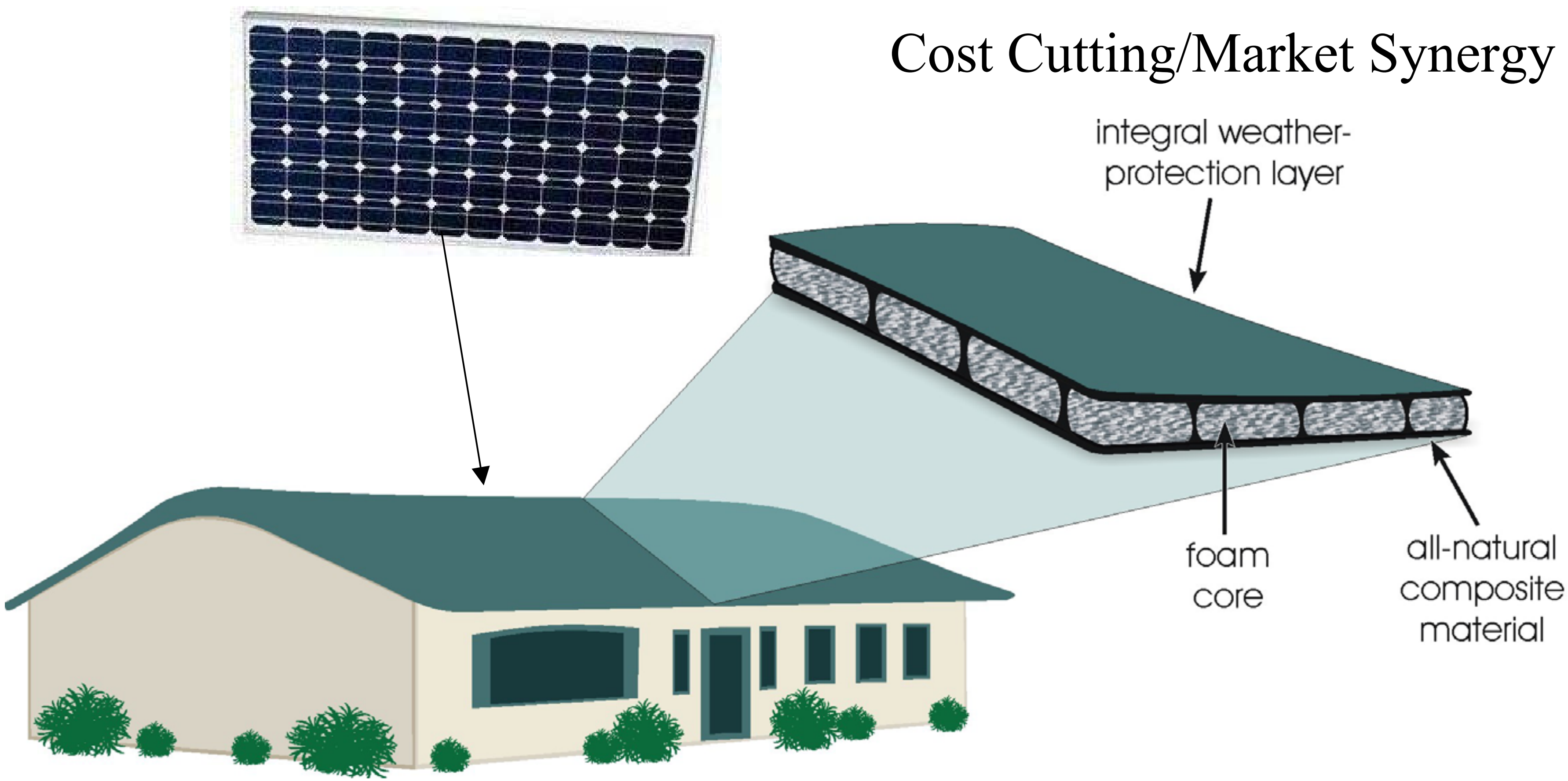
PROPERTIES: DMA 3-Point Bending Test



Solution for USA Energy needs: Need 92 million for energy independence and offset Global Warming

US has124 million roofs; 1.3 million new per year

Cost Cutting/Market Synergy



Nominated for the Richard Branson Virgin Global Warming Solutions Award

Bio-Based Content = 83%. Recycled Content = 50%

The sky is the limit!

Soy based Solid Rocket Propellants

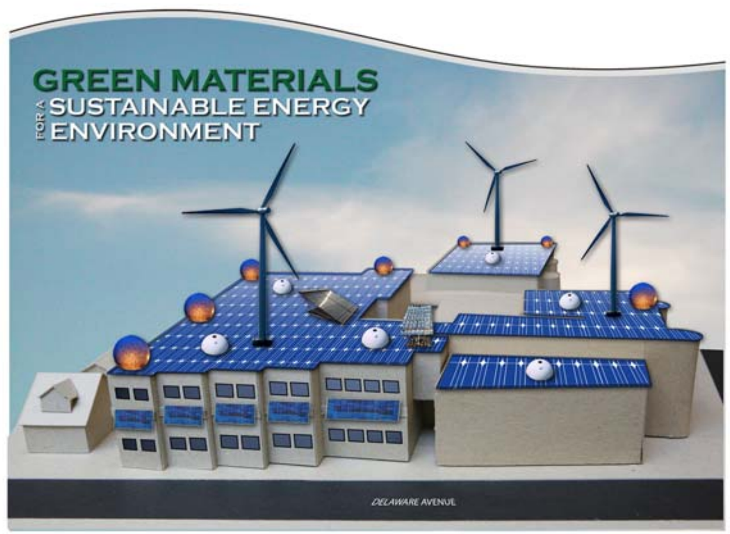
National Security

ICBMs and Rogue Missile Interceptors

Next Step? GEM Center:

Green Materials for a Sustainable Energy Environment

The focus of GEM is the development of advanced bio-based materials in support of renewable energy (Solar, Wind, Hydrogen)



DREAM TEAM

UD,Yale, KSU, BU, Ulster, U Manitoba, DynaChem, Dow, DuPont, Boeing, CIRO S. Africa, Istanbul, CCM, Risoe, Vestas, Siemens, Bluewater, Pickens: Institute for Solar Energy, Environmental Policy-, NREL, NASA