SAND2020-2263C

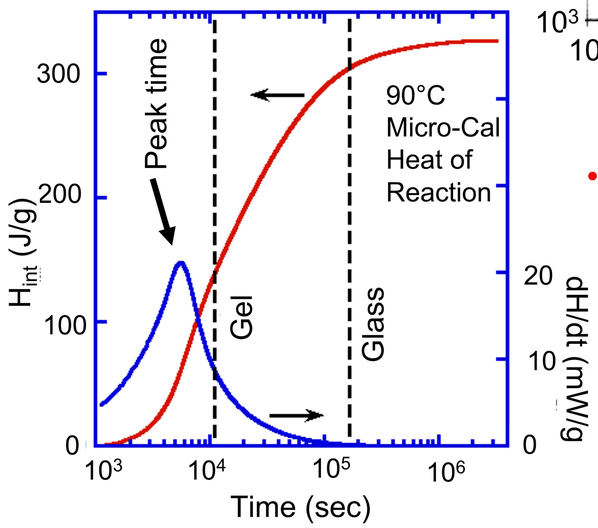
Gelation of DGEBA epoxy in the presence of a tertiary amine above and below the ceiling temperature

J.D. McCoy, C.T. House, J.M. Kropka* *New Mexico Tech, Socorro, NM; *Sandia National Labs, Abq, NM*

Introduction

- DGEBA is reacted with diethanolamine (DEA).
- DEA secondary amine + epoxide -> adduct (30 min 70°C)
- Gelation by zwitterion-initiated add. rxn (24 hrs, 70°C for "full" cure)
- Cures above ~80°C display a "ceiling temperature" effect.
- This Study: gel point determined over a wide range of temperatures.
- Low T, gel point from bubble viscometer.
- High T, gel point from parallel plate rheometer.
- Gelation at 42±3% extent of reaction for all T.
- Network structure is step-growth like.
- Agreement with Carothers Theory of gelation.

Relation to Calorimetry



Carothers Gelation Theory

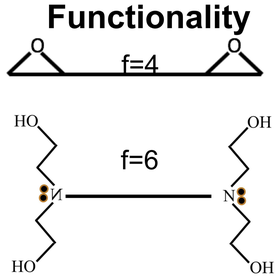
f_{avg}=0.21*6+0.79*4=4.42

Extent of Reaction at gel point=2/f_{avg}=**0.45**

Total Heat of reaction =350J/g

Heat of reaction at gel point =0.45*350J/g=**157J/g**

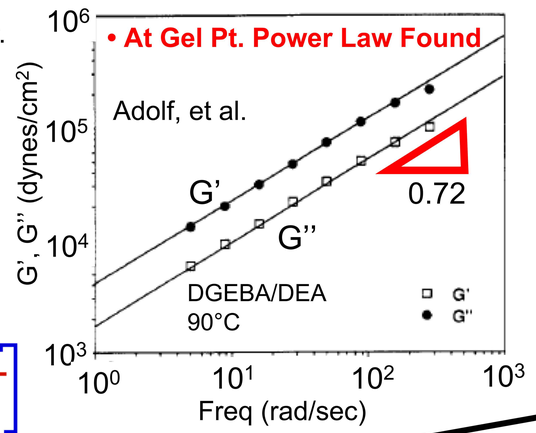
Functionality



Previous Work

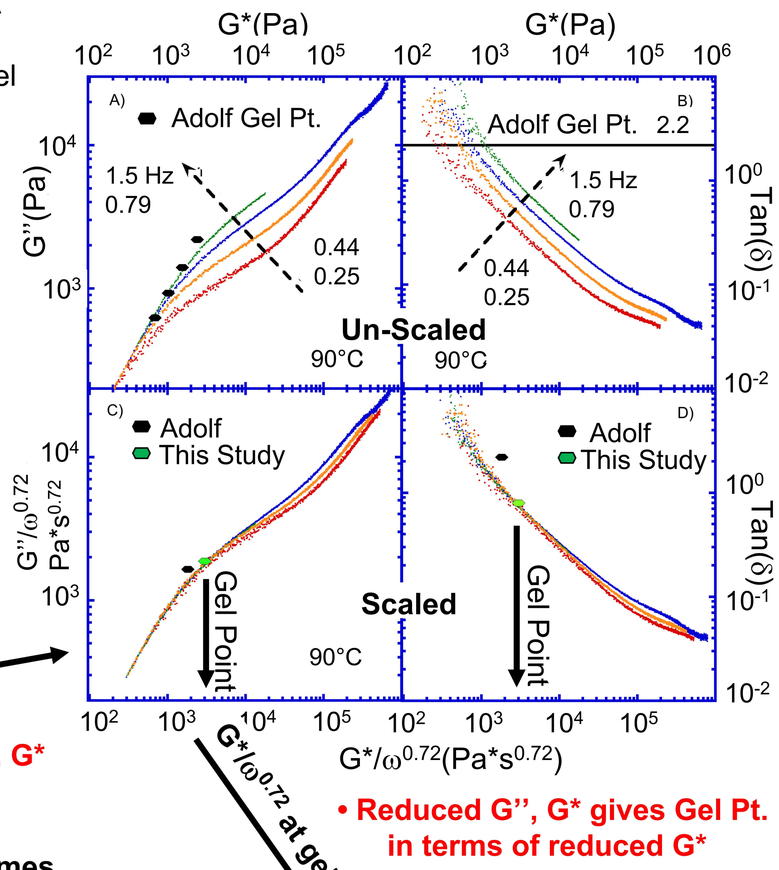
Rheology on DGEBA/DEA

- Adolf and coworkers [3,4,5]
- Moduli powerlaw in frequency at gel
- Power of 0.72 for DGEBA/DEA
- G''/$\omega^{0.72}$ vs.G*/$\omega^{0.72}$ same for all ω at gel
- Find G* '/$\omega^{0.72}$ at gel and then t_{gel}



• Adolf result used to scale G'', G*

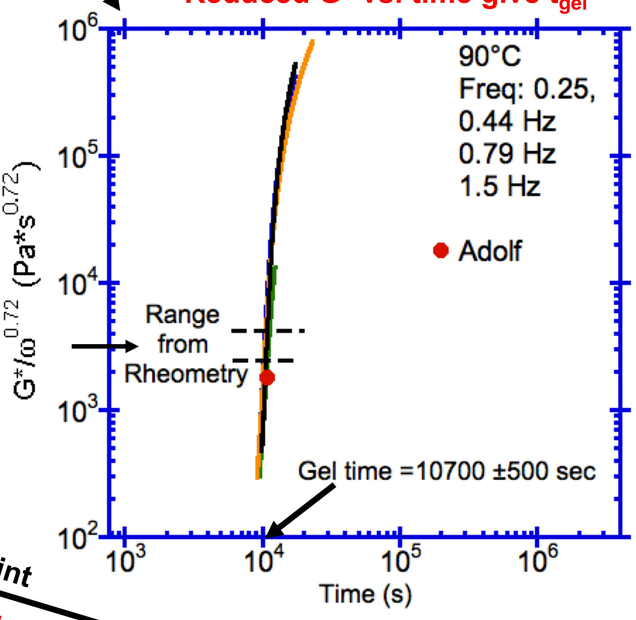
Parallel Plate Rheology during Cure



• Reduced G'', G* gives Gel Pt. in terms of reduced G*

G*/$\omega^{0.72}$ at gel point

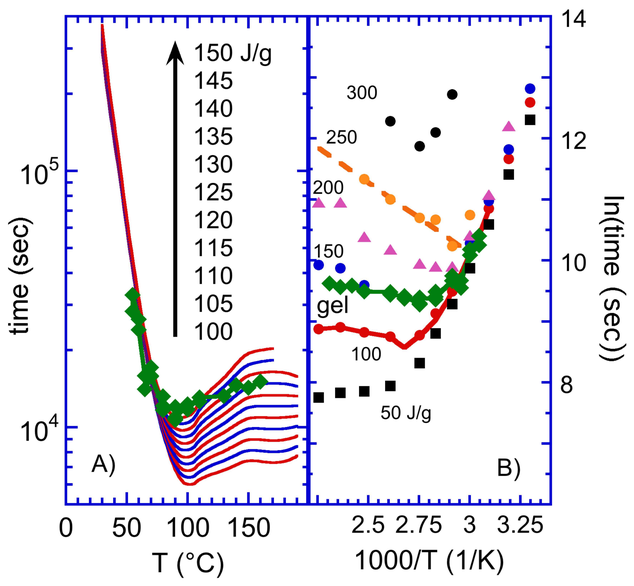
• Reduced G* vs. time give t_{gel}



t at gel point

• Combine with Bubble Results

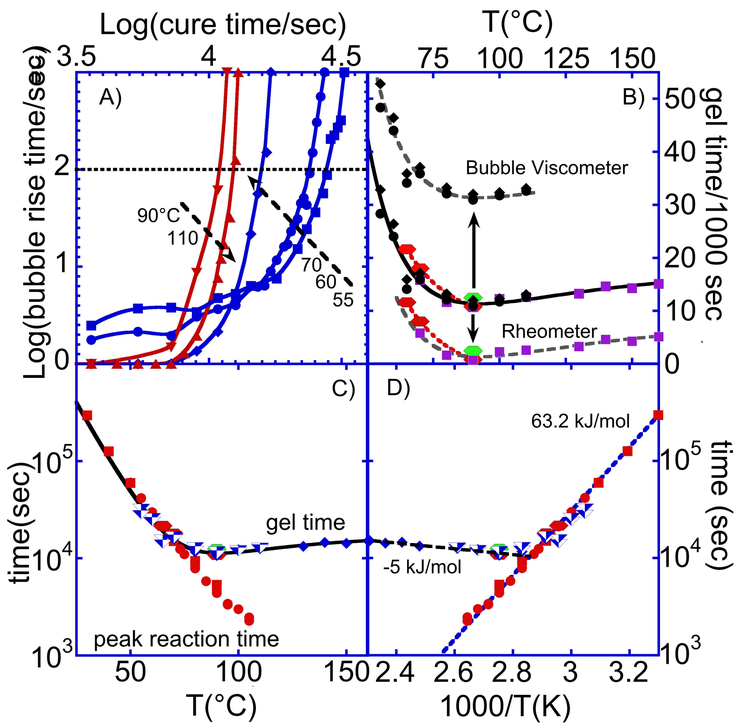
Iso-conversional times



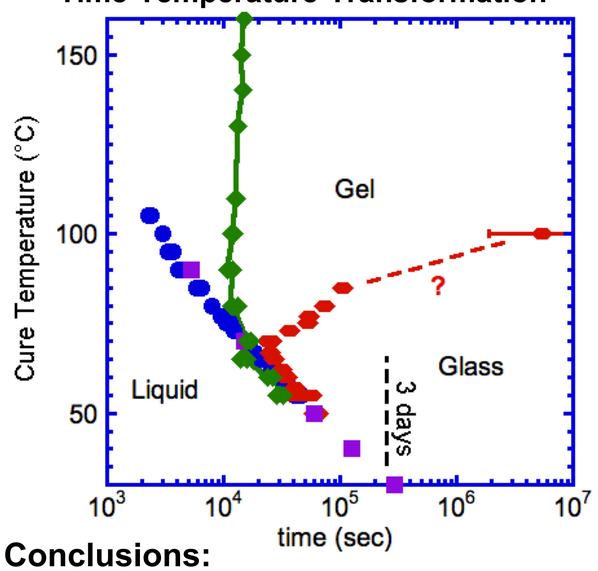
• t_{gel} compared to Calorimetry gives extent of reaction at Gel

• Extent of reaction at Gel agrees with Carothers

Bubble Viscosity



Time-Temperature-Transformation



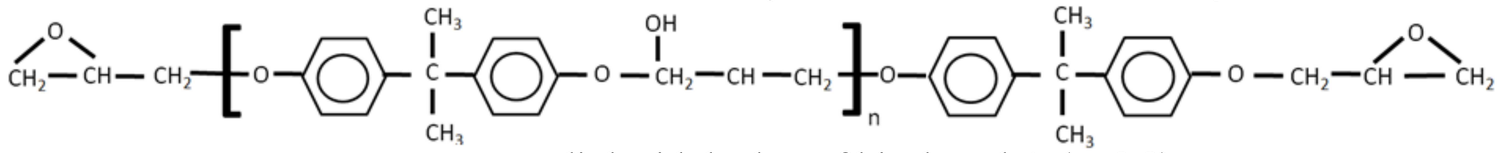
Conclusions:

- DGEBA/DEA gel point at 42±3% for all temperatures
- Agrees with Carothers prediction of 45%
- Confirms step-growth-like network structure
- Bubble viscosity in agreement with rheology
- New analysis method for rheology – plotting reduced moduli
- Gel time tracks negative effective activation energy above ceiling T
- Time-Temperature-Transformation (TTT) diagram results.

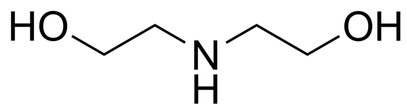
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525

Background Information:
Gelation of DGEBA epoxy in the presence of a tertiary amine

J.D. McCoy, C.T. House, J.M. Kropka*

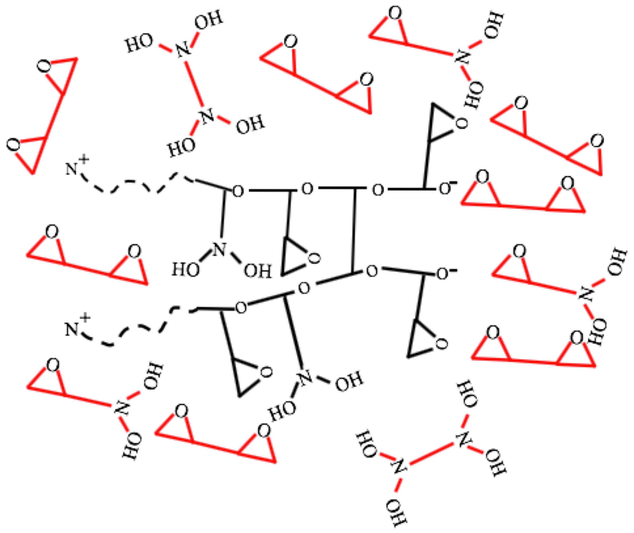


diglycidyl ether of bisphenol A (n~0.2)

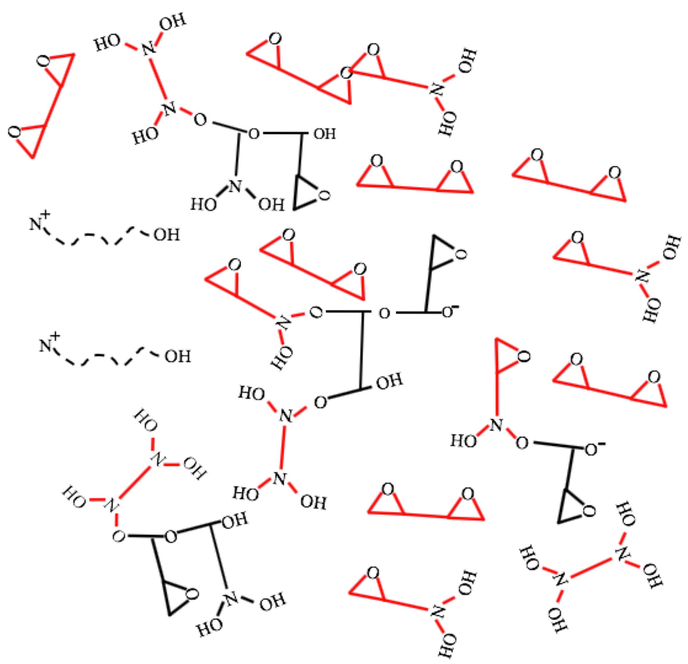


diethanolamine (DEA)

Effect of Proton Transfer on Network Structure



Anionic chain-growth without proton transfer
A few large clusters Chain-Growth-like

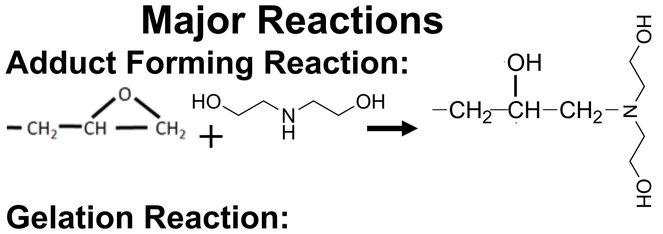


Anionic chain-growth with proton transfer
Many small clusters Step-Growth-like

Proton transfer
- Distributes reactive sites
- Makes Network Step-Growth-like [2,6]
- Increases extent of cure at gelation
- Makes Carothers Theory applicable

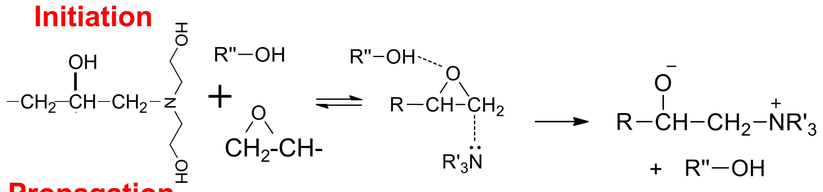
Major Reactions

Adduct Forming Reaction:

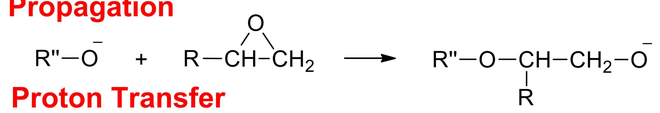


Gelation Reaction:

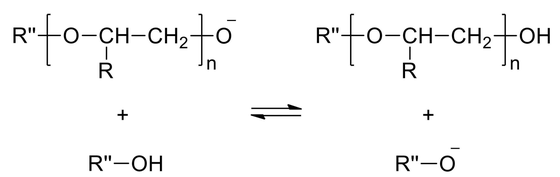
Initiation



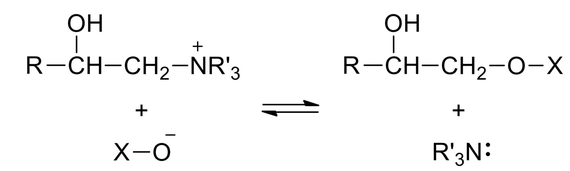
Propagation



Proton Transfer

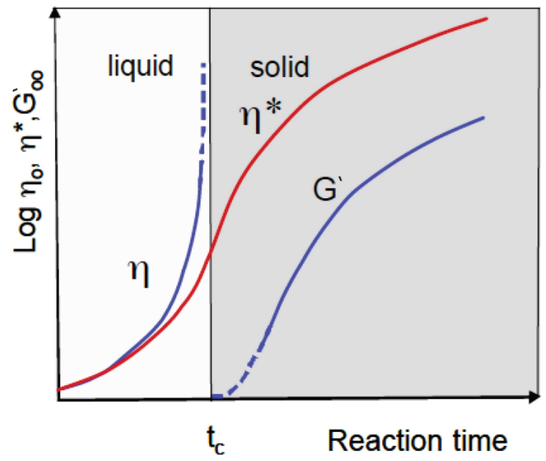


Termination



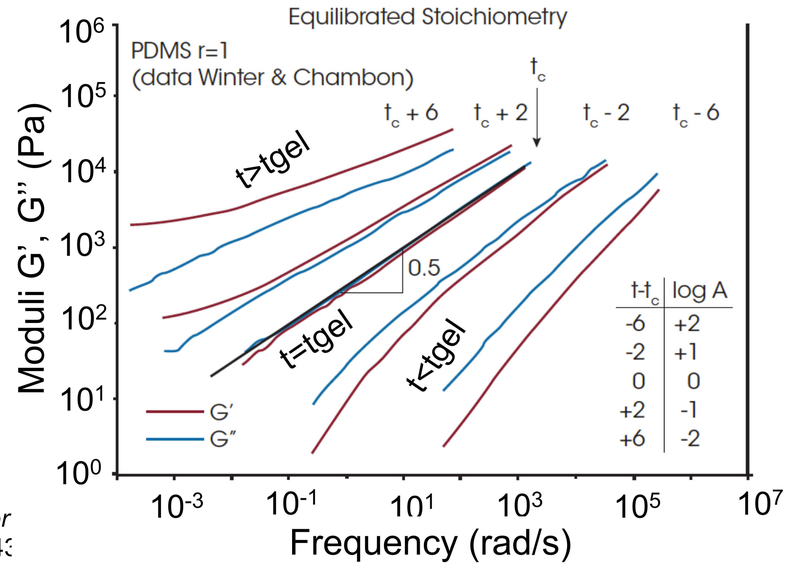
Bubble Viscometer [7]

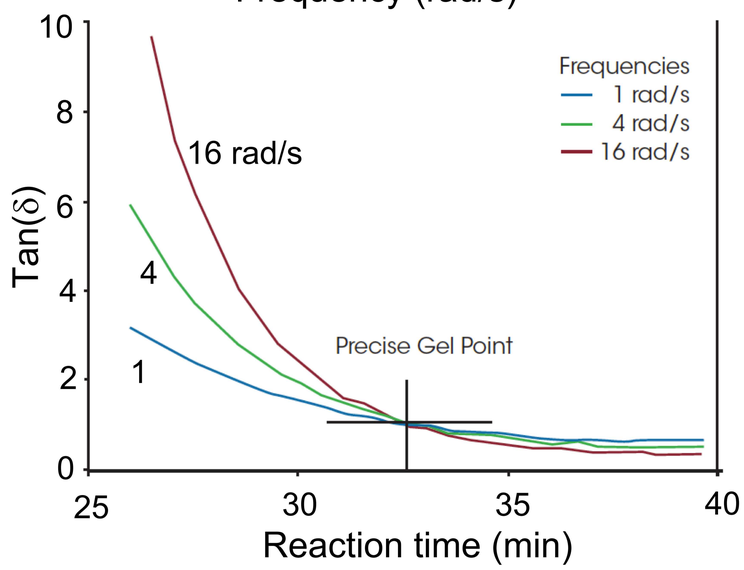
- Viscosity (bubble viscometer used here with viscosity proportional to bubble rise time.



Dynamic Oscillatory Rheology [7]

- Storage and loss moduli should both follow same powerlaw for frequency the gel point.
- Tan(δ) should cross at gel point for different frequencies.





References

[1] J.D. McCoy, W.B. Ancipink, C.M. Clarkson, J.M. Kropka, M.C. Celina, N.H. Giron, L. Hailesilassie, N. Fredj, *Cure mechanisms of diglycidyl ether bisphenol A (DGEBA) epoxy with diethanolamine*, Polymer 105 (2016) 243-254

[2] J.D.McCoy, W.B.Ancipink, S.R.Maestas, L.R.Draelos, D.B.Devries, J.M.Kropka, *Reactions of diglycidyl ether of bisphenol A (DGEBA) epoxy cured with diethanolamine: Unusual dependencies on temperature and extent of reaction and implications to network structure*, Thermochimica Acta 671, 149 (2019)

[3] J.E.Martin, D.Adolf, J.P.Wilcoxon, *Viscoelasticity of near-critical gels*, PRL 61, 2620 (1988)

[4] D.Adolf, J.E.Martin, J.P.Wilcoxon, *Evolution of structure and viscoelasticity in an epoxy near the sol-gel transition*, Macromolecules, 23, 527 (1990).

[5] D.Adolf, J.E.Martin, *Time-cure superposition during crosslinking*, Macromolecules 23, 3700 (1990).

[6] X.Fernandez-Francos, W.D.Cook, J.M.Salla, A.Serra, X.Ramis, *Crosslinking of mixtures of diglycidylether of bisphenol-A with 1,6-dioxaspiro 4.4 nonan-2,7-dione initiated by tertiary amines: III. Effect of hydroxyl groups on network formation*, Polymer International, 58, 1401 (2009).

[7] A. Franck, TA Instruments, Thermosets and Structural Adhesives, RH007