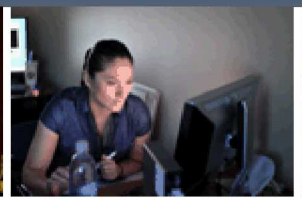
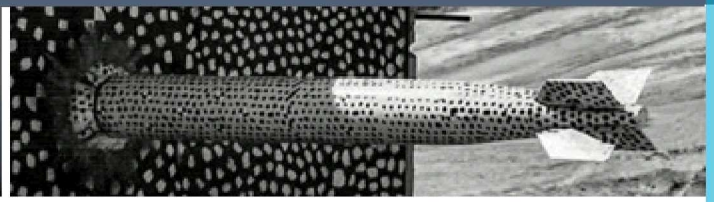
SAND2018-10076PE

ASSESSING THE NEED FOR REQUALIFICATION OF AN EPOXY SYSTEM





PRESENTED BY

Margaret House, mentored by Jamie Kropka

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & 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.

Agenda

Requalification

- Initial motivations
- Project plan

Legacy Material

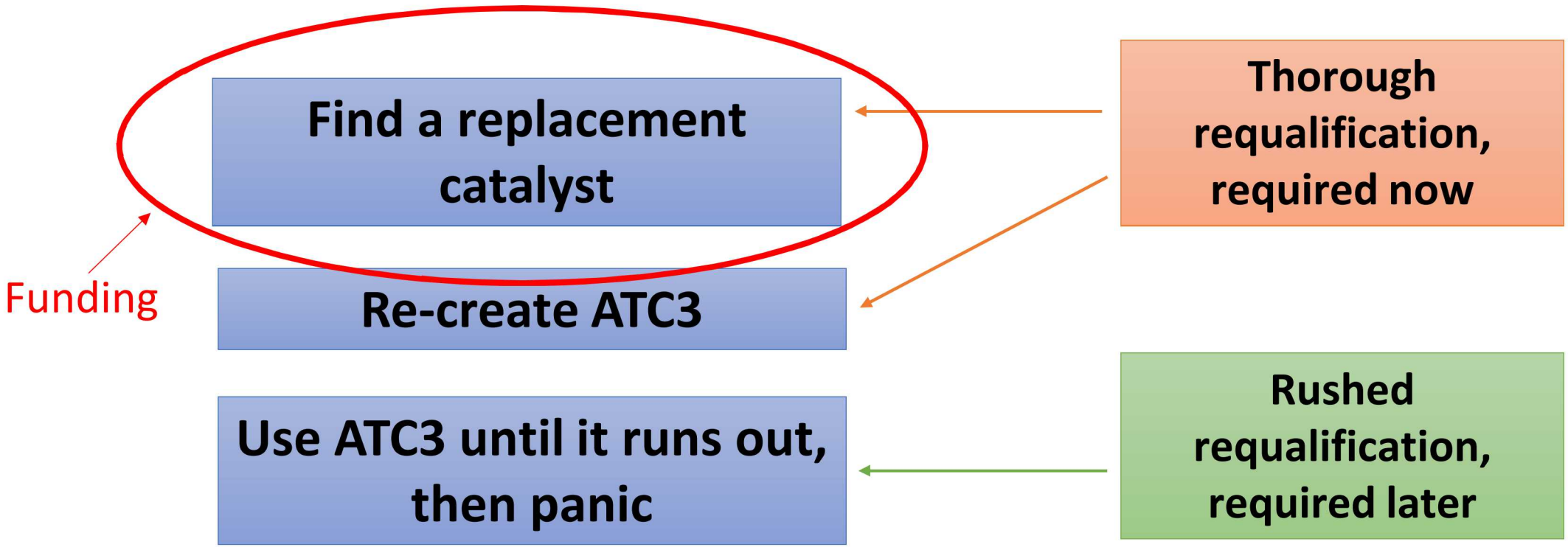
- Review constituents and ratio of reactive groups
- Assess current cure schedule and recommend options to simplify
- Compare currently made ATC-3 epoxy with 1987 reported properties

Project Results

Conclusions

Requalification of Epoxy System

- Epoxy-anhydride-alcohol system accelerated by chromium-based ATC3 catalyst
- ATC3 catalyst no longer being produced
- MUST requalify system if changed at all



How can we convince the engineering team to requalify now with a replacement catalyst?

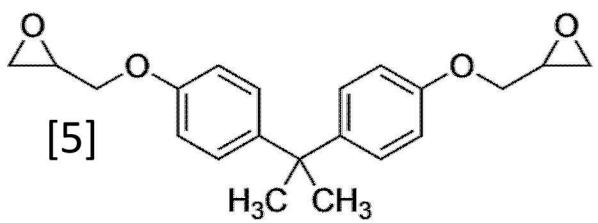
Current Material Characteristics

- Catalyst
  - Composition
  - Hazards
  - Cost
- Mix
  - Stoichiometry
- Processing
  - Pot life
  - Cure time
- Materials Properties
  - Modulus

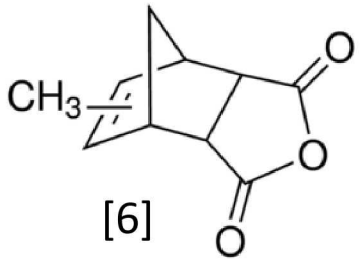
Encapsulant Constituents

Resin + Anhydride + Alcohol + Catalyst

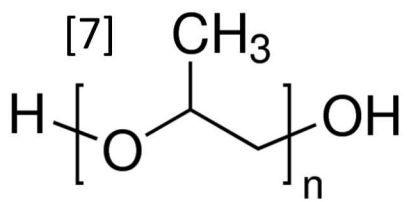
DGEBA
Epon 828



Nadic Methyl Anhydride HY 906

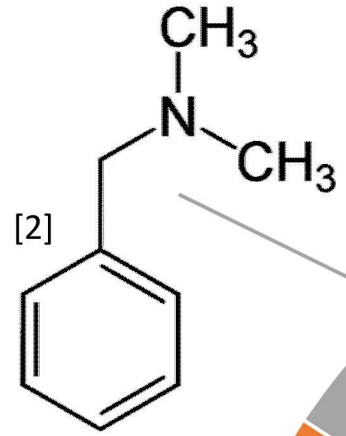


Polypropylene Glycol 1025 (“flexibilizer” [1])

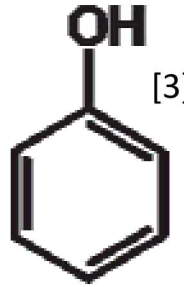


ATC-3

What is ATC-3?



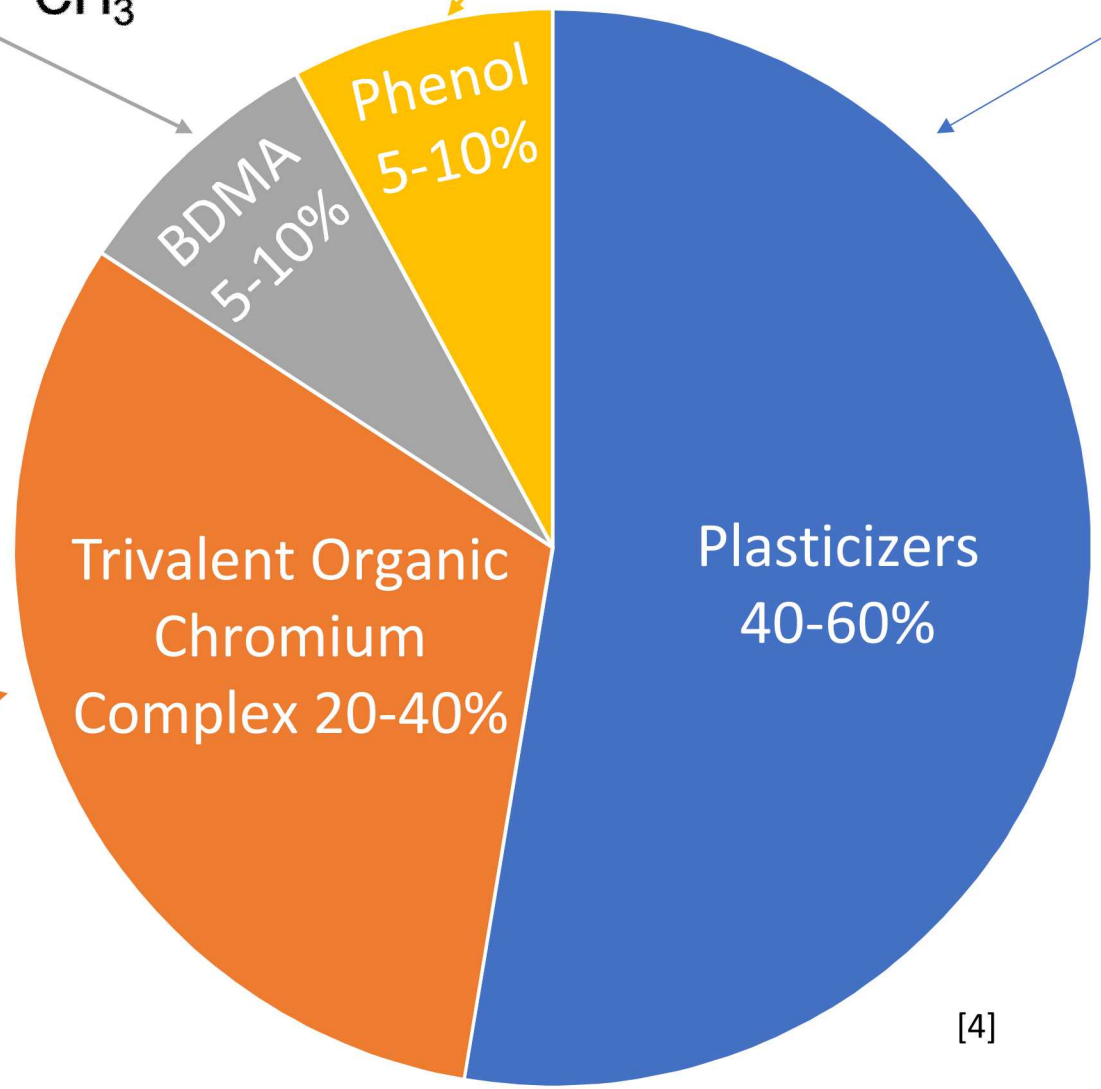
[2]



[3]

Essentially fillers

RCRA Material



[4]

Baseline Encapsulant Stoichiometry

828	50
NMA	42
1025	20
ATC-3	3
total	115

828 equivalent weight ~ 188 g/eq

NMA equivalent weight = 179 g/eq

PPG equivalent weight = 500 g/eq [5]

[1]

Resin Reactive Groups **Curative Reactive Groups**

50/188 eq 828 $\stackrel{?}{=}$ 42/179 eq NMA + 20/500 eq PPG 1025

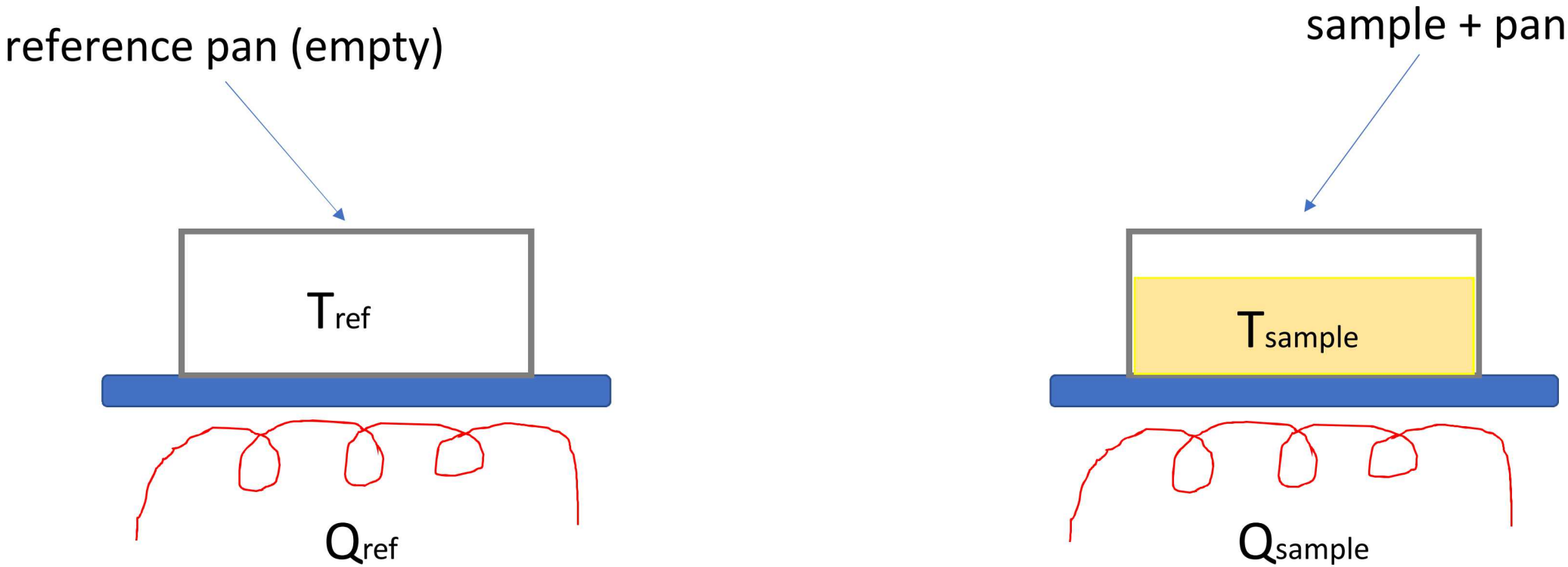
0.266 eq epoxide < 0.275 eq curative

Excess Curative Makes Encapsulant more Susceptible to Remaining Small Molecules that Could Outgas Over Time

Experimental Methods

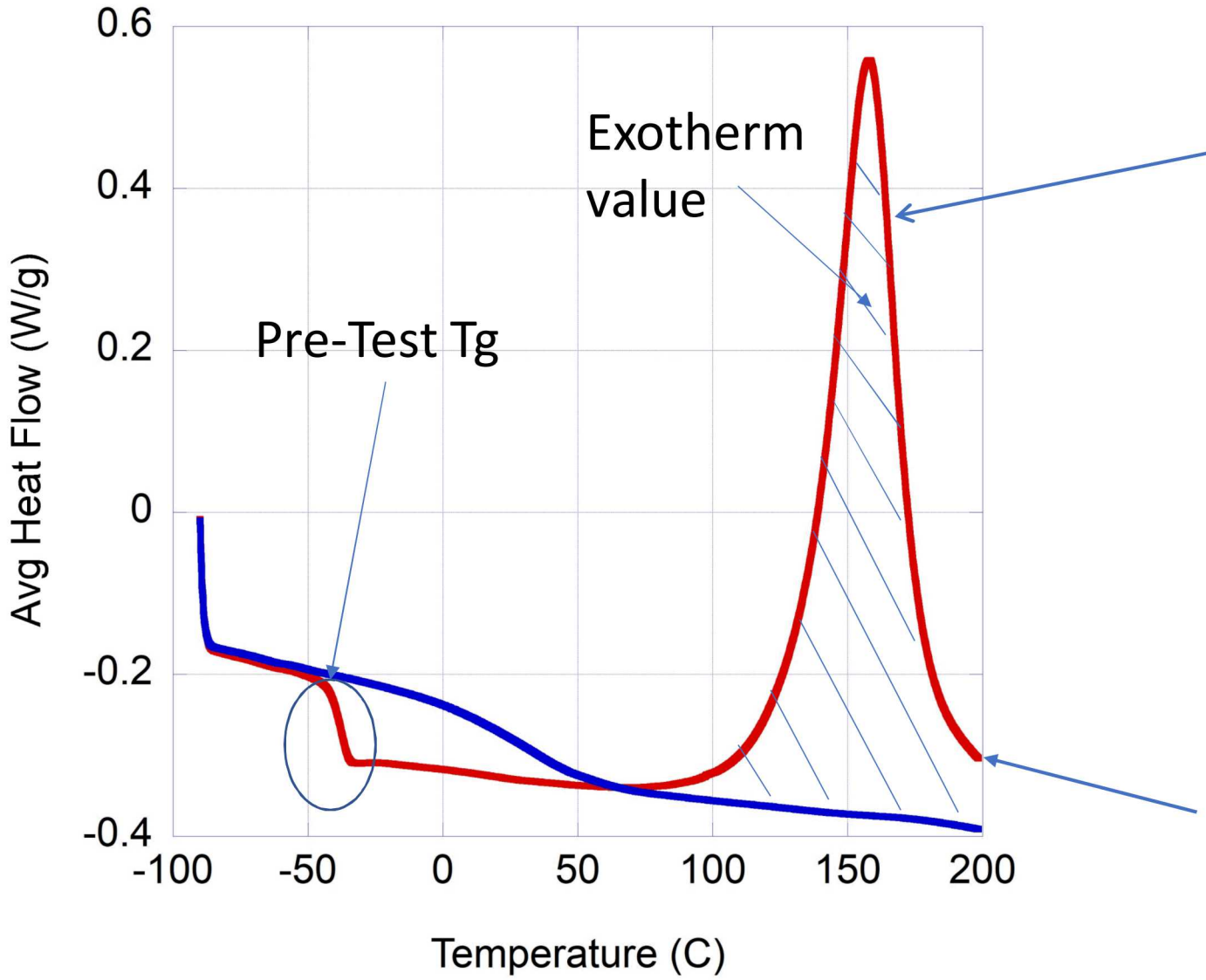
- Choose ingredient concentrations based on legacy paper [1]
- Batch at RT
- Deposit directly into pans and freeze at -50C
- Legacy cure schedule [1] performed in Q2000 DSC
  - 6 hours at RT (25C)
  - 6 hours at 71C
  - 12 hours at 80C
  - 2 heat/cool cycles from -90C to 200C at 10C/min

Differential Scanning Calorimetry



Tref=Tsample; measure heat flow difference (Q_{ref}-Q_{sample}) throughout test

Data Analysis

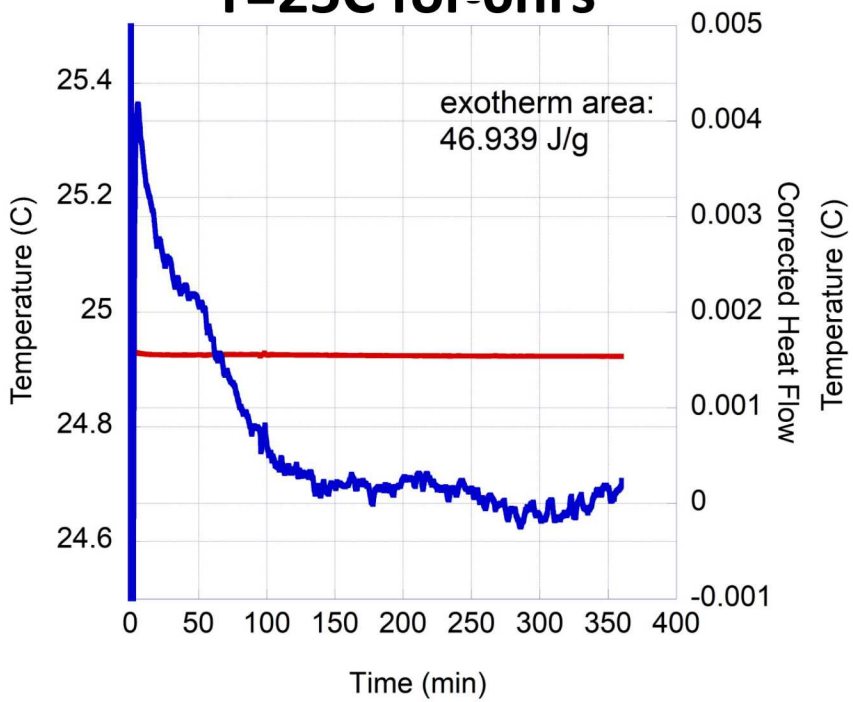


Q_{ref}-Q_{sample} large due to reaction occurring

Q_{ref}-Q_{sample} "baseline" because reaction is done

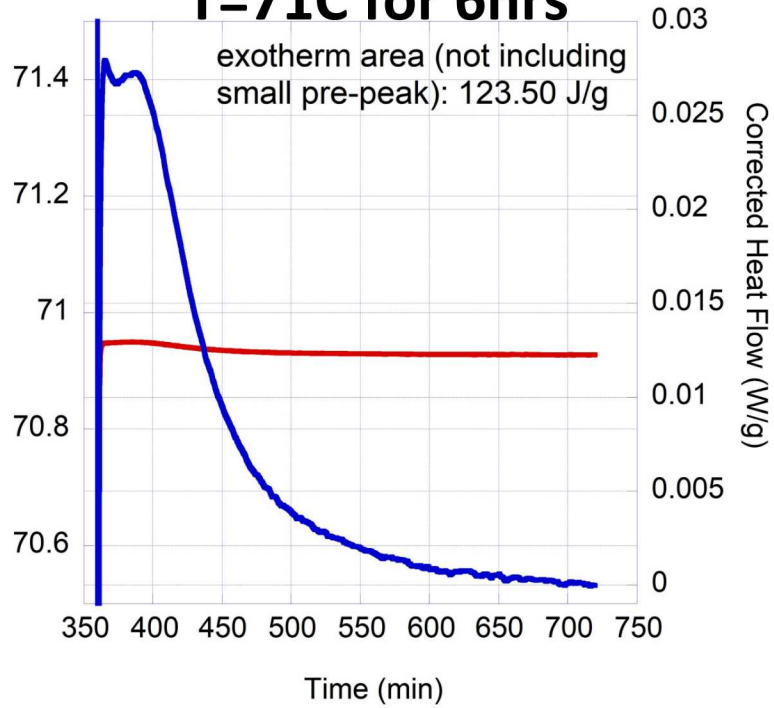
Reaction Progression- Legacy Cure

T=25C for 6hrs



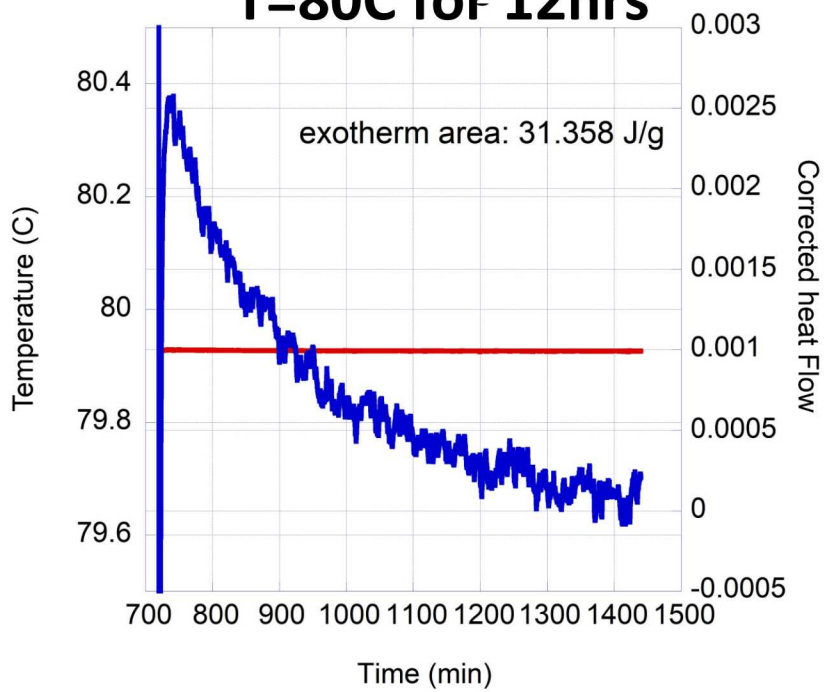
2-3 hours sufficient at 25C

T=71C for 6hrs



Bulk of cure accomplished at 71 C

T=80C for 12hrs



Superficial cure for the next 12 hours at 80 C

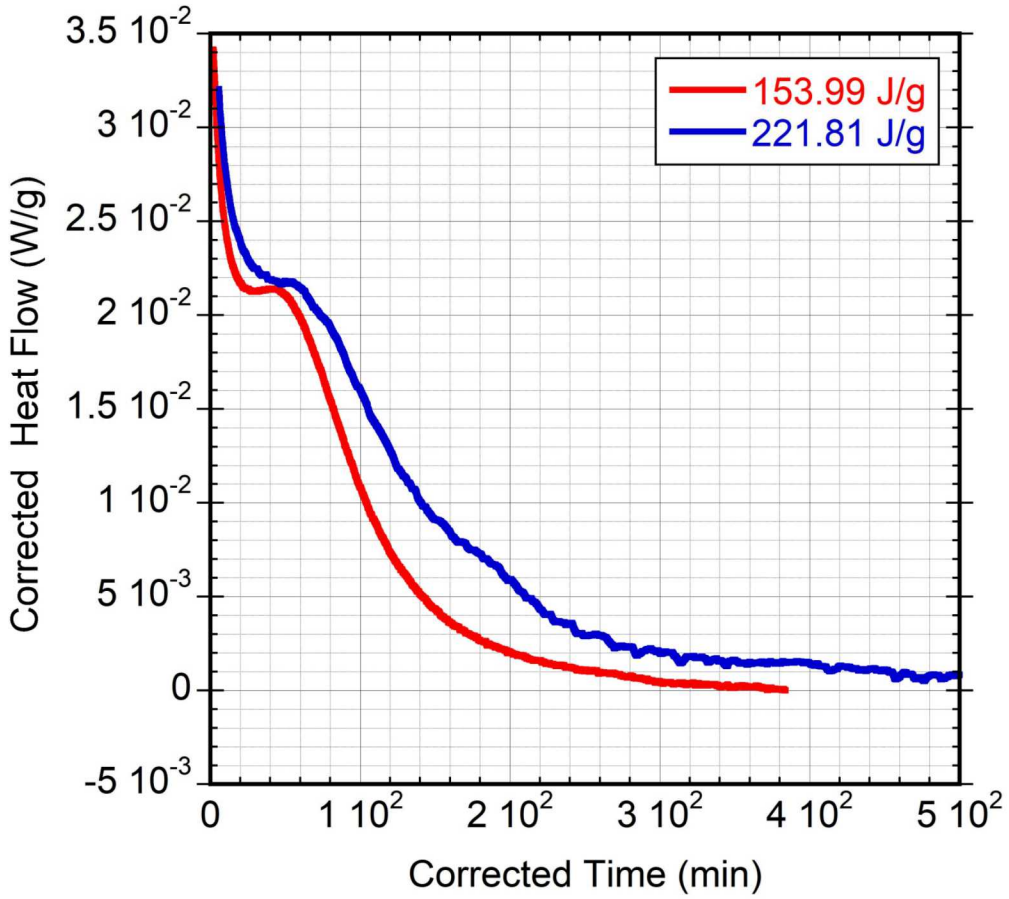
Total exotherm from all stages of cure: **~200 J/g < 250 J/g** (expected for 95-120 kJ/mol epoxy [17])

Findings:

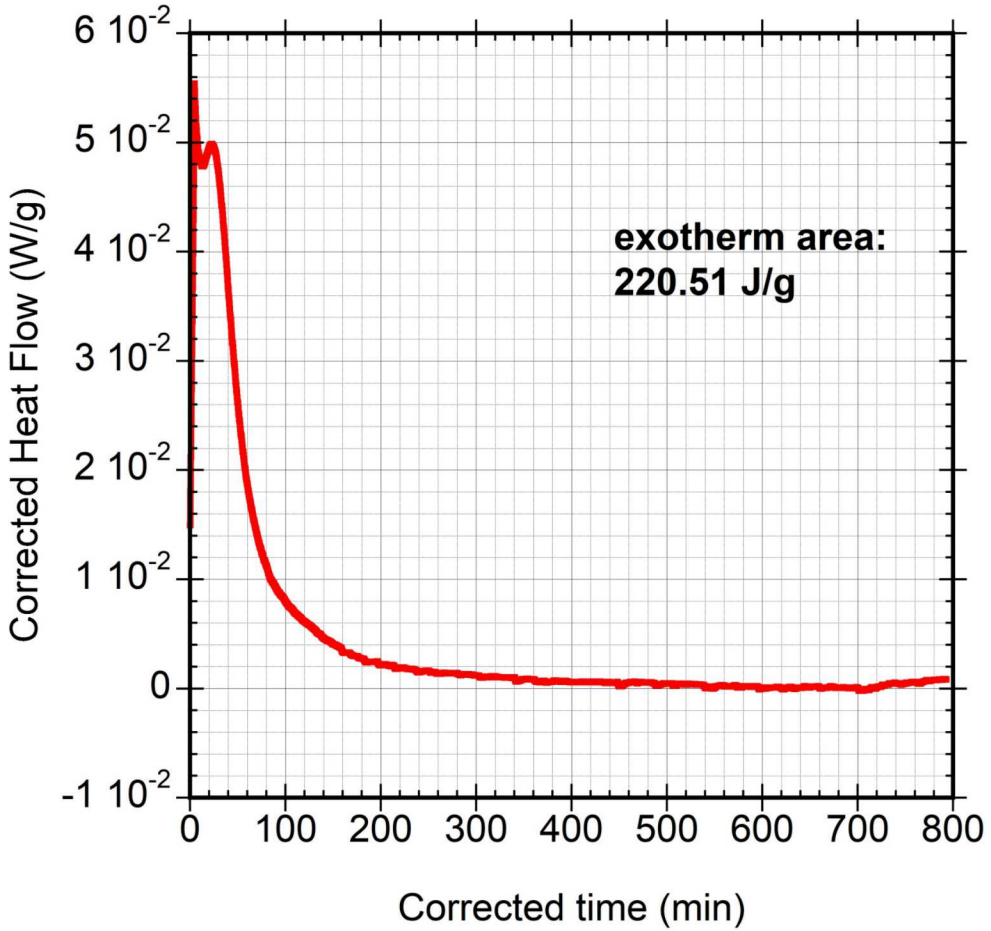
- Encapsulant contains remaining reaction potential (not all epoxide has reacted)
- Opportunities exist to reduce time of cure

ATC-3 Isothermal Cure

T=70°C Cure



T=80°C Cure

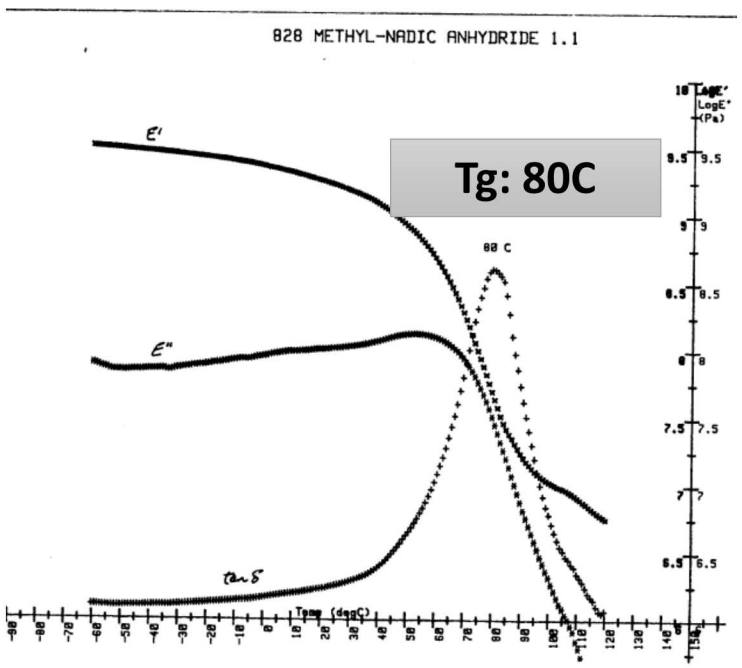


Findings:

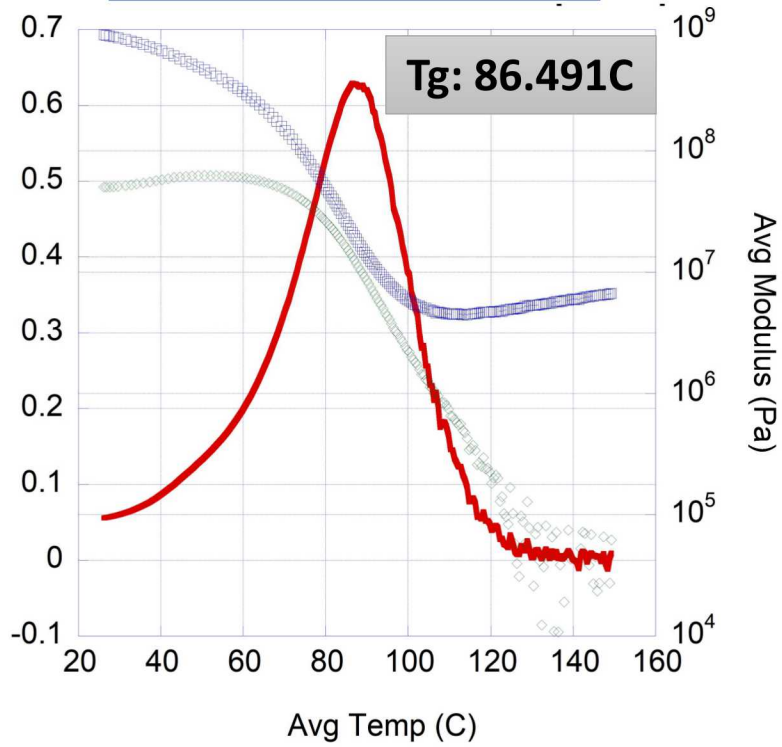
- Isothermal Cure at 70°C for 9-12 hours may be sufficient
- Isothermal Cure at 80°C for 8 hours may be sufficient

Effect of Cure Schedule on Mechanical Properties

Wischmann 1987 [1]

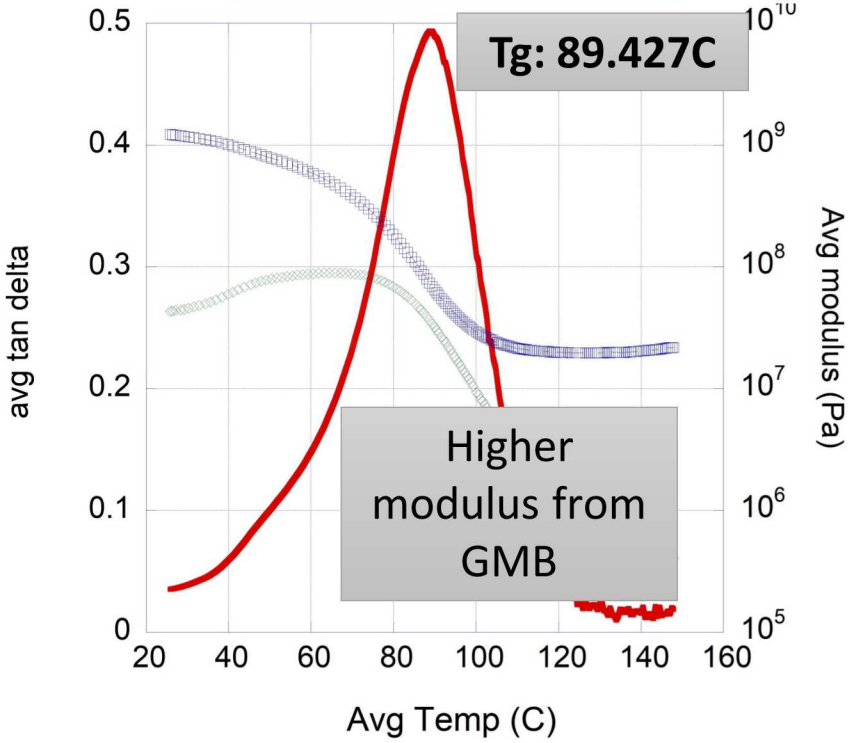


15 hours at 70C



Shorter cure at 70C equally effective

Legacy Cure



What We Concluded and What Happened

Our experiments showed…

- Current material not fully reacted- risk of small molecule diffusion
- Current cure schedule too long
- ATC3 catalyst can be re-synthesized, but replacements are much cheaper
- Replacement catalysts lead to higher Tg's and modulus, indicative of more complete reaction

What was decided

- Presentation to project realization team (PRT)
- Replacement catalysts feasible
- System won't have to be overhauled
- Requalification may start soon, but it will take 5+ years

Lessons Learned and Final Remarks

- Even when you have all the data on your side, it is hard to convince people to change!
- In presentations, meet the audience where they are at and speak to what they care most about
- Overall successful in showing the need for requalification and outlining a path forward
- Still waiting on projects for FY19

References

[1] Wischmann K.B., “A Compatible Encapsulant for Explosives.” *SAND87-2087C*, **1987**.
[2] https://en.wikipedia.org/wiki/Dimethylbenzylamine#/media/File:Benzyldimethylamine.svg
[3] https://en.wikipedia.org/wiki/Phenol_extraction#/media/File:Phenol2.svg
[4] “ATC-3.” *DAR*, **2004**.
[5] https://en.wikipedia.org/wiki/Bisphenol_A_diglycidyl_ether
[6] https://www.sigmaaldrich.com/catalog/product/aldrich/235431?lang=en&region=US
[7] https://www.sigmaaldrich.com/catalog/product/aldrich/202304?lang=en&region=US

Thank you!