SAND2015-9000C

A New High Voltage Elastomer- No Compromises

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Original Goal-Find a non-TDI castable PU with favorable processing

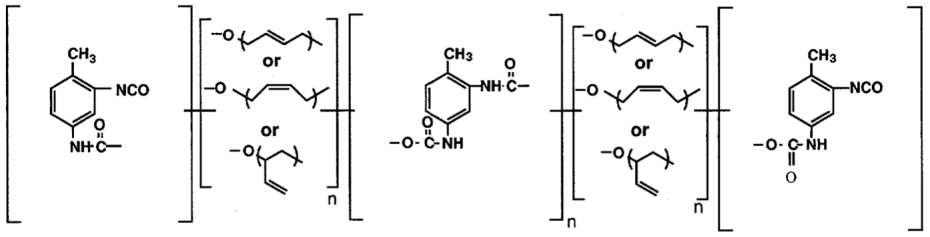
- New Goal
  - Find a TDI-free replacement for EN-7 polyurethane encapsulant that meets or exceeds electrical, mechanical, and processing characteristics of EN-7.
  - Use a commercially available formulation or readily available ingredients requiring only mixing (no synthesis) and room temperature processing.
  - Allow more options for external potting of cables and connectors with high voltage requirements. Limited number of vendors that are willing to process EN-7 due to presence of TDI.

Background: Conathane EN-7

- Encapsulant for cables and connectors
- Excellent properties
  - Electrical, mechanical
    - High voltage applications
  - Processing
    - Liquid reagents, but 15 minute potlife
- TDI: suspected carcinogen, highly volatile sensitizer

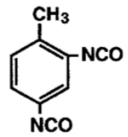
Mixing ratio
A:B = 100 : 18.8

Part A (isocyanates):

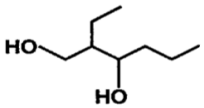


TDI-capped polybutadiene

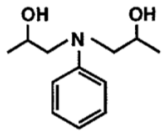
+ ~10% free TDI:



Part B (polyols):



DEH



Voranol 220-530

+ catalyst

Previous Efforts to Develop Castable Polyurethanes

- EN-7 was actually a replacement for Adiprene L100/MOCA (used prior to 1973).
  - MOCA is a carcinogen, not great HVB

- Proposed alternatives:
  - 1984 Caruthers (KCP): Adiprene L100/Cyanacure
  - 1993 Wilson (KCP): Airthane PET90/Ethacure 300
  - 1995 Myers (SNL/NM): Adiprene L100/Ethacure 300
    Airthane PET90/Cyanacure

Require warm processing

Desired Properties

- Physical
  - T_g below STS
  - Low outgassing
  - Good aging and materials compatibility
- Mechanical
  - Shore A hardness ~90
  - Good adhesion
- Electrical
  - Exceptional dielectric properties (HVB)
- Processing
  - Commercially available constituents
  - All components liquid at room temperature
  - Free of TDI
  - 30-60 minute pot life at room temperature
  - Room temperature cure in 24-48 hr (shorter at higher temperature)
  - Low viscosity

Background: Arathane 5753

- Based on MDI (not TDI)
- Common in aerospace industry
  - Dielectric breakdown strength ~14 kV/mm
    - (EN-7: ~30 kV/mm)
  - Aging and compatibility
    - Meets NASA requirements for outgassing in critical environments, e.g., high vacuum/outer space
    - Humidity resistance
  - Shore A hardness of ~55-60
    - (EN-7: ~90-95)
  - Favorable processing
    - Liquid components at RT
    - RT cure in 24 hours

New TDI-free formulation (funding provided by RTBF)

- Arathane 5753 properties are improved by addition of a short-chain diol (DEH):
  - Matches dielectric breakdown strength and hardness of EN-7
  - Does not affect processing
  - DEH= 2-ethyl-1,3-hexanediol or dihydroxyethylhexane

Formulations (by mass)			
Name	EN-7	Arathane 5753	Arathane 5753 HVB
	PART-A	PART-A	PART-A
Arathane 5753A	—	20	61.05
EN-4	100	—	—
	PART-B	PART-B	PART-B
EN-7	18.8	—	—
Arathane 5753B	—	100	100
DEH (2-ethyl-1,3-hexanediol)	—	—	20

Polyurethane Elastomer Property Summary

Property	EN-7	Arathane 5753	Arathane 5753 HVB
Physical			
T_g (°C)	−77	−69 *(lit)*	−64 (rheo)
CTE (ppm/°C)	168 *(exp & lit)*	170 *(lit)*	143
Outgassing total mass loss[2] (%)	0.251 ± 0.011	0.673 ± 0.017	0.659 ± 0.014
Mechanical			
Hardness, Shore A	94	60	90
Tensile strength (MPa)	8.0	2.0	12
Elongation (%)	220	210	150
Tear strength[3] (lbf/in)	430 ± 30	84 ± 6	230 ± 52
Electrical			
Breakdown strength[4] (kV/mm)	30.0 ± 0.6	14 *(lit)*	29.1 ± 2.7
Processing			
Pot life[5] (min)	10-15	~30	25-30

AN1

High Voltage Breakdown

Material	Breakdown Voltage (kV)	Breakdown Strength (kV/mm)
EN-7	31.4 ± 0.6	30.0 ± 0.6
Arathane 5753 HVB	29.7 ± 2.9	29.1 ± 2.7

AN2

- The data were obtained from Exova on 6/10/2013 (ASTM D149).
- Ramp rate: 500 V/s.
- Temperature: 23±2°C.
- Approximate specimen thickness: 1.0 mm.
- Three specimens of each material were tested.
- Reported values are means ± standard deviation.

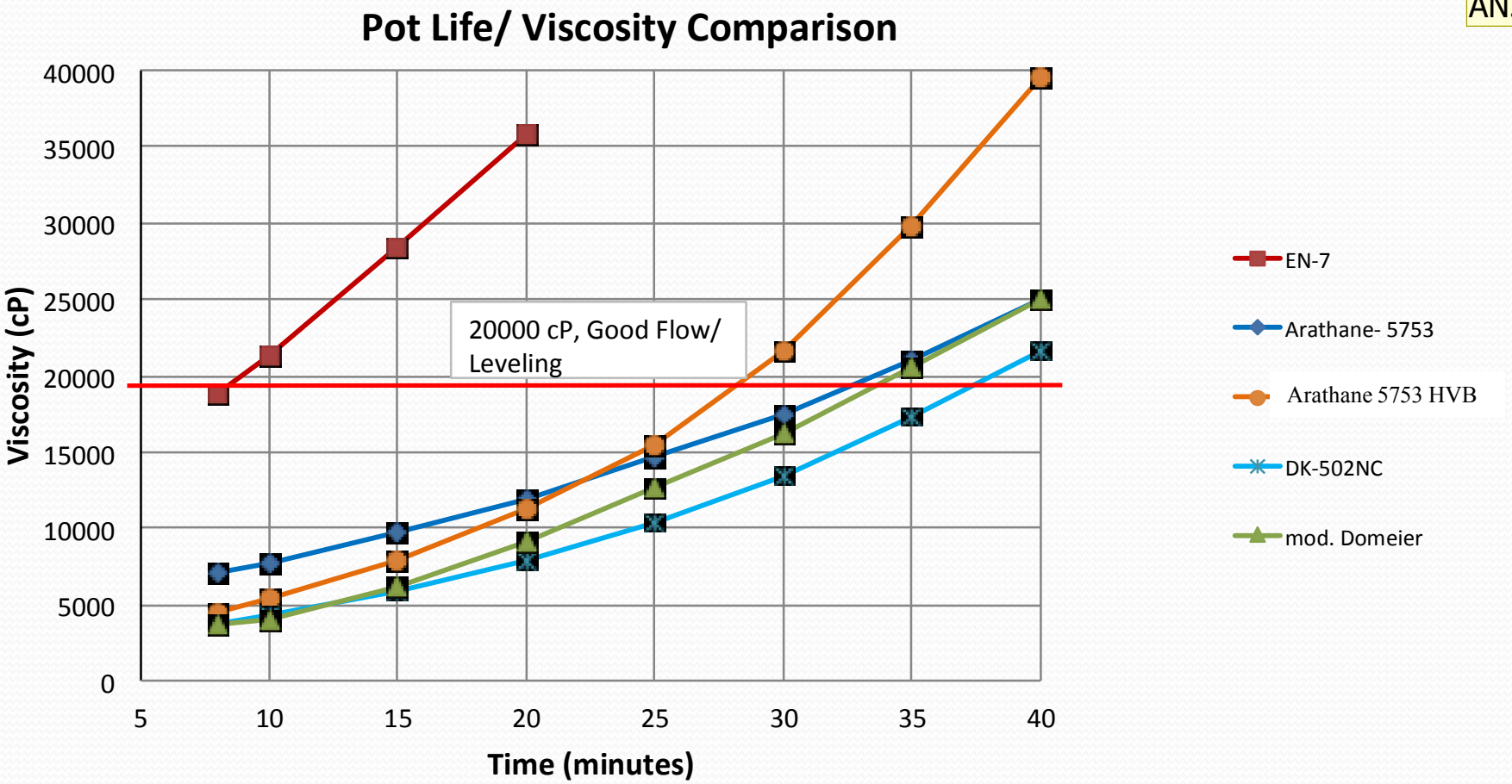
Slide 9

AN1 April Nissen, 12/1/2014

AN2 This is the first time the Domeier formulation is mentioned. Is this worth keeping in the presentation? If yes, some more detail about the formulation should be included. LIkewise for the following two slides which also include this material.
April Nissen, 12/1/2014

Viscosity

AN3



EN-7 is much faster than the technical data sheet indicates (30 min)

Slide 10

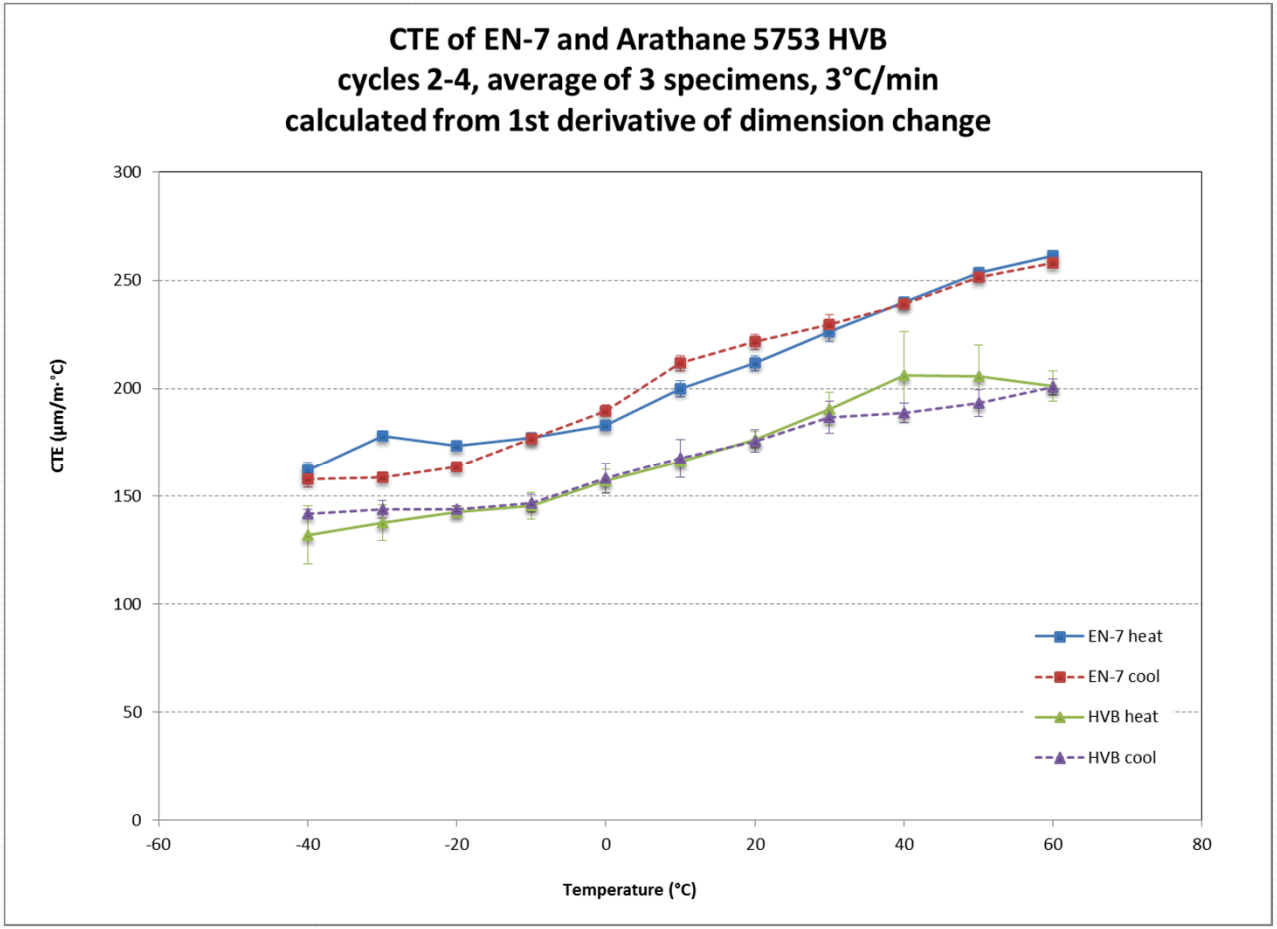
AN3 To be consistent with other slides, "mod. Domeier" should be listed as "R45HTLO + DEH".
April Nissen, 12/1/2014

Outgassing-Meets NASA specifications

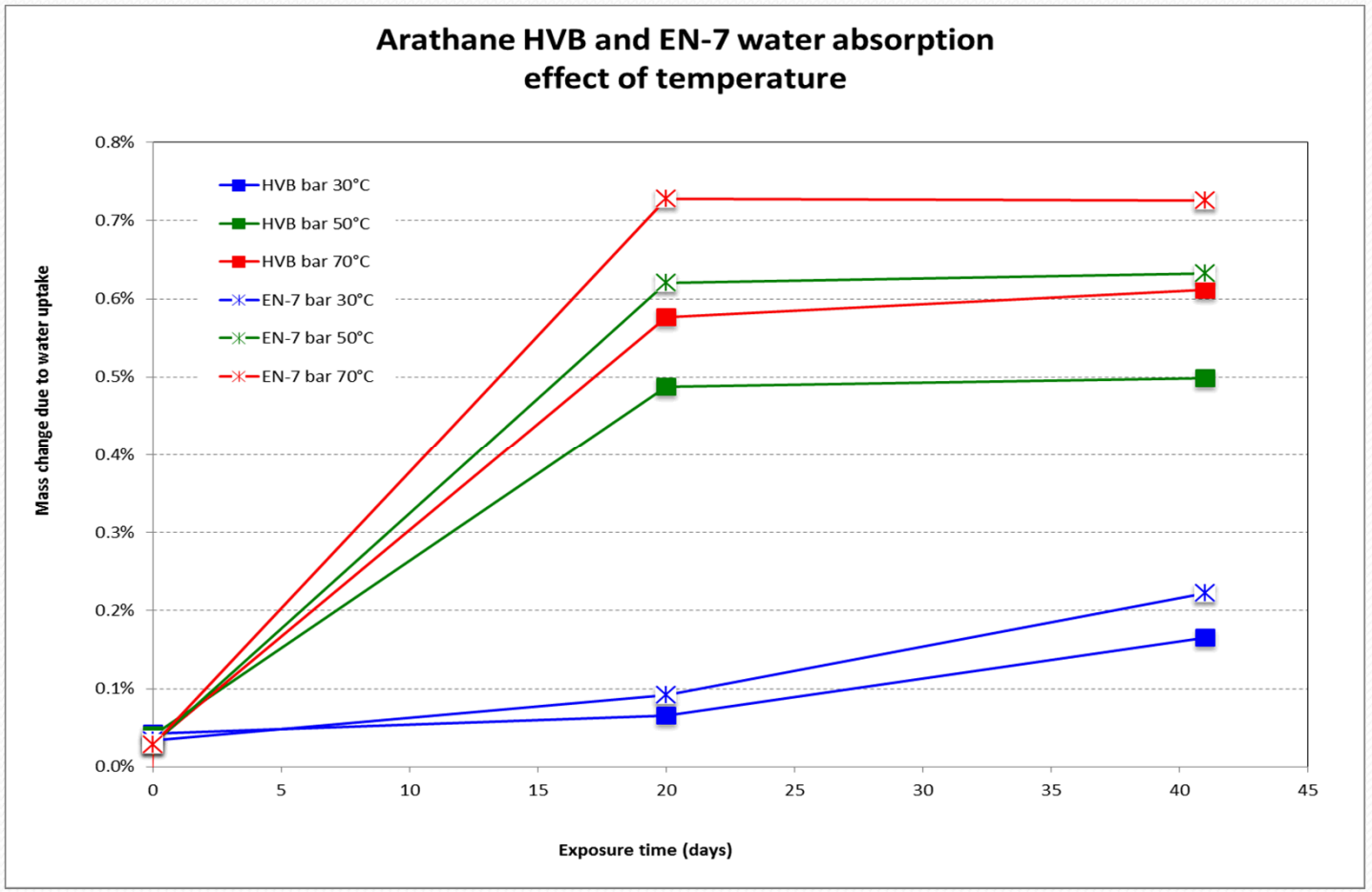
Material	TML (%)	CVCM (%)	WVR (%)
EN-7	0.251 ± 0.011	0.013 ± 0.003	0.113 ± 0.004
Arathane 5753 HVB	0.659 ± 0.014	0.006 ± 0.002	0.115 ± 0.009

- The following data were obtained from Exova on 6/24/2013 (ASTM E595).
- Historically, Total Mass Loss (TML) of 1.00% and Collected Volatile Condensable Materials (CVCM) of 0.10% have been used as screening levels for rejection of spacecraft materials.
- Water vapor regain (WVR) data was also collected.
- Three specimens of each material were tested.
- Reported values are means ± standard deviation.

Slightly lower CTE than EN-7



EN-7 absorbs a little more water than Arathane 5753 HVB



- Higher temperature samples saturate faster
- Water reservoir in 30C chamber went dry <20 days

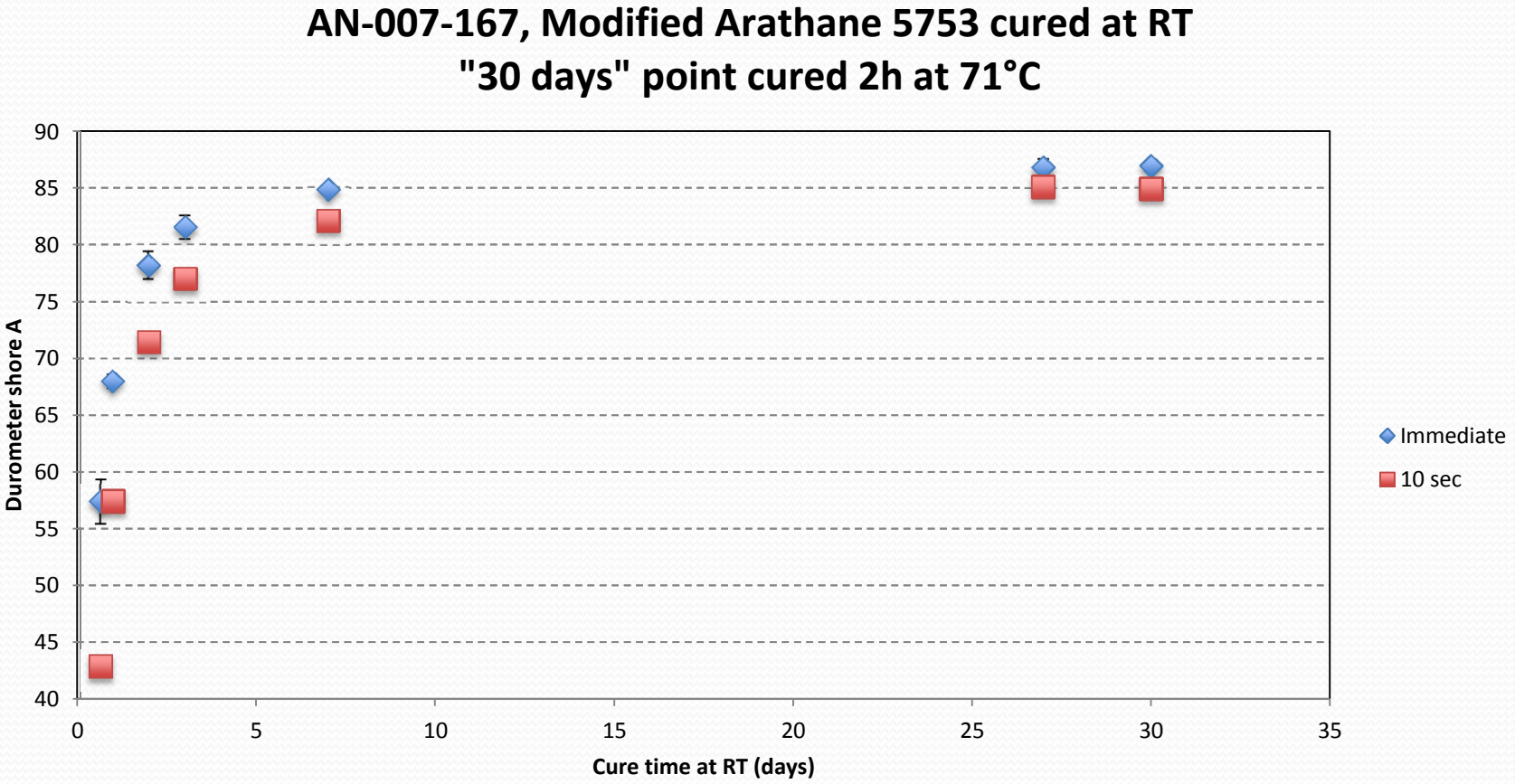
Thickness

All = 0.125” thick

Cure Shrinkage

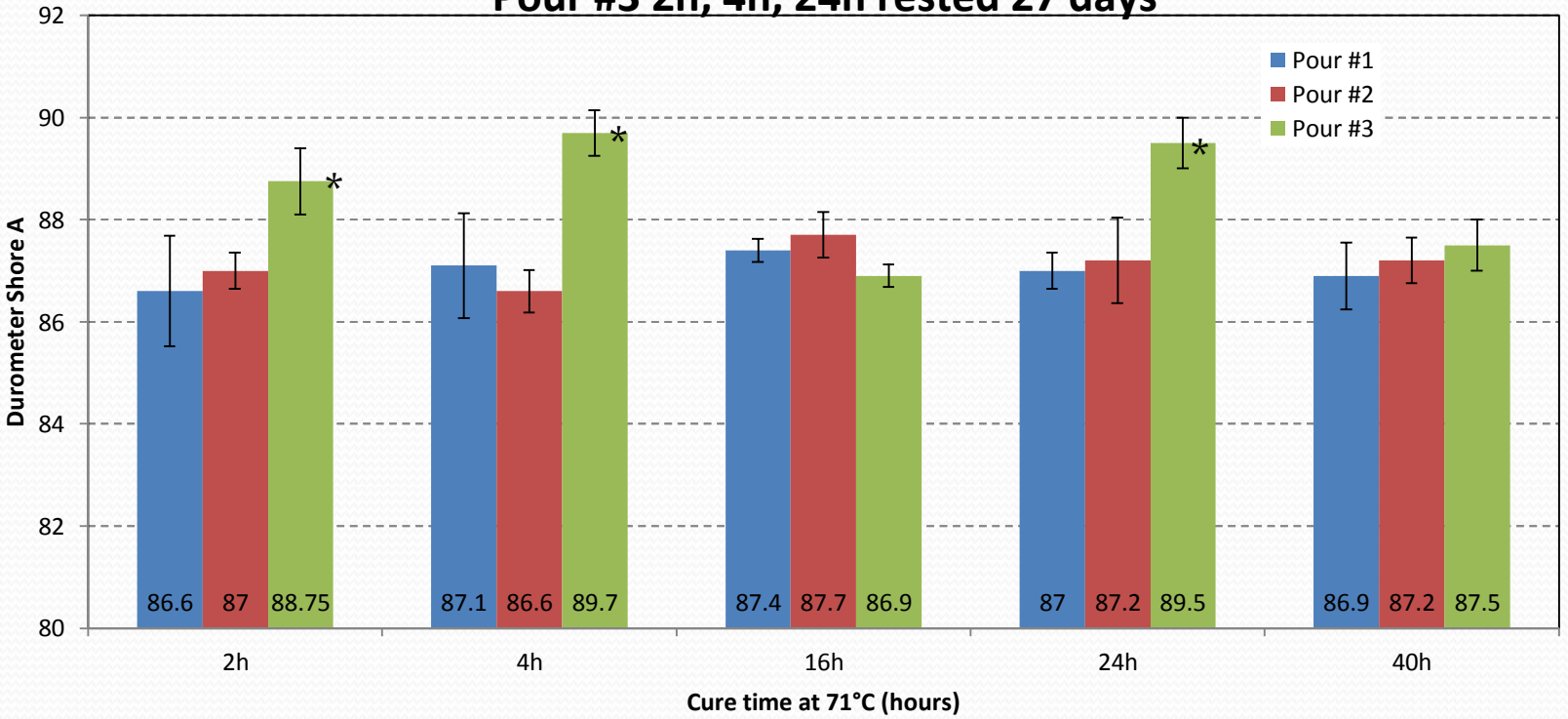
- The volumetric shrinkage from mold to post-cure was measured
  - 2 samples
  - Mold 3.58 cm dia, 1.28 cm tall
  - Mold preheated to 71C for 2 hrs
  - Cure: 15 min at RT, 4 hrs at 71C
- Volumetric shrinkage of 5.1% and 6.0%, for an average of **5.6%**
- Repeating with EN-7

Material appears cured after 7 days at room temperature

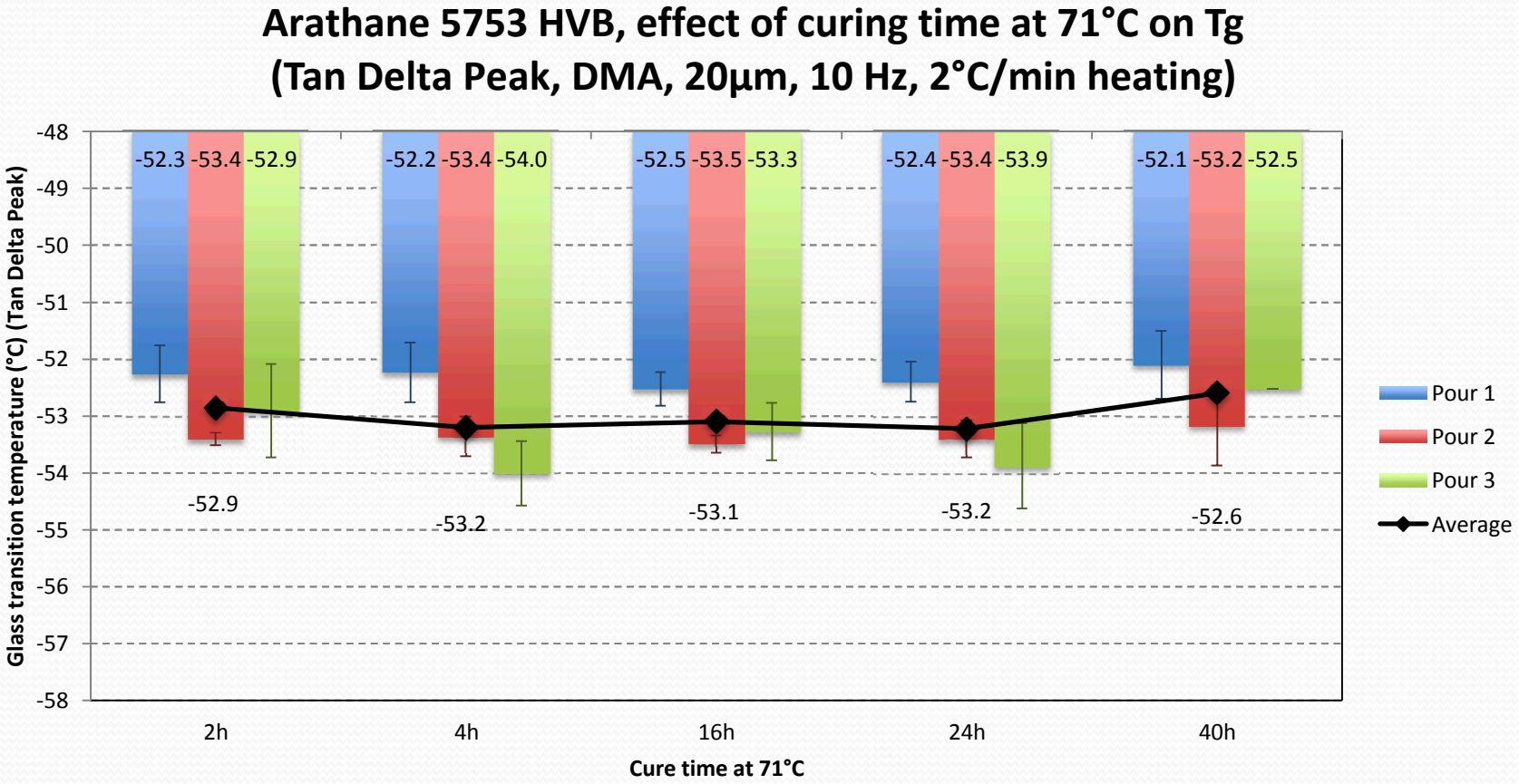


Or cured after 2 hours at 71°C

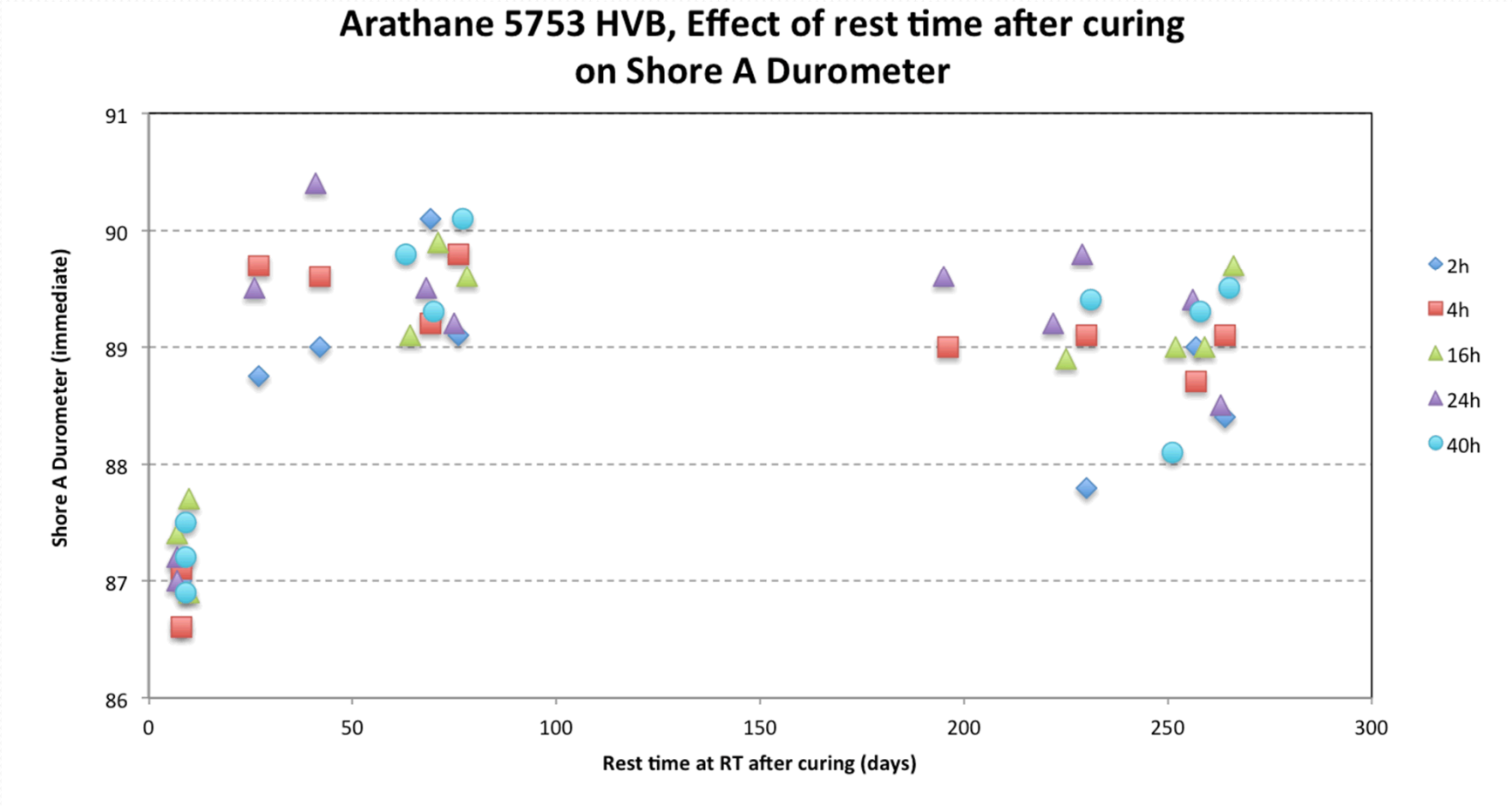
Modified Arathane Elastomer, Durometer Shore A (immediate)
as a function of cure time at 71°C
note: most samples rested 7-9 days before measurements
***Pour #3 2h, 4h, 24h rested 27 days**



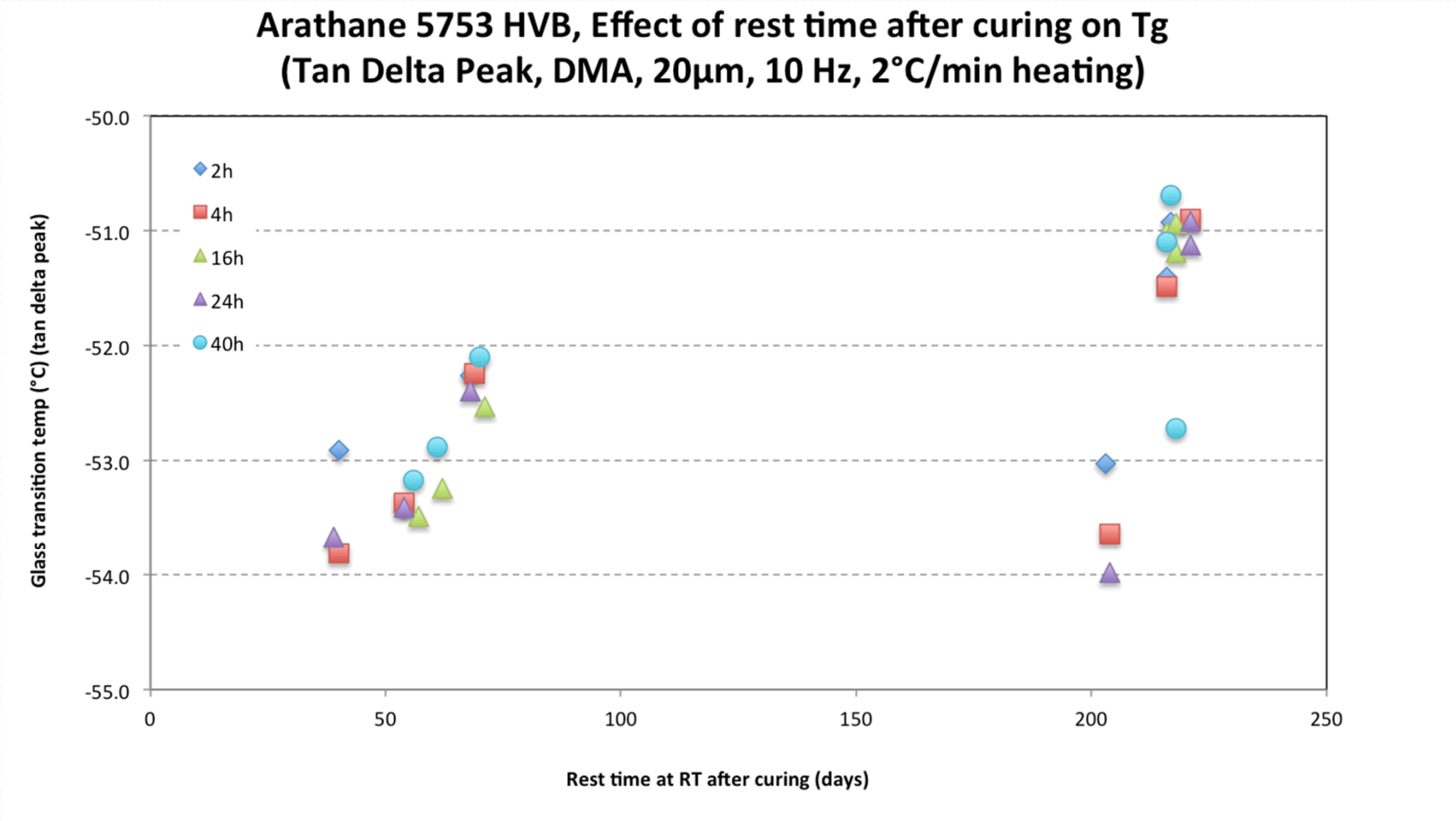
Tg data also indicates material is cured after 2 hours at 71°C



Might be a little something going on as the samples sit around in air?

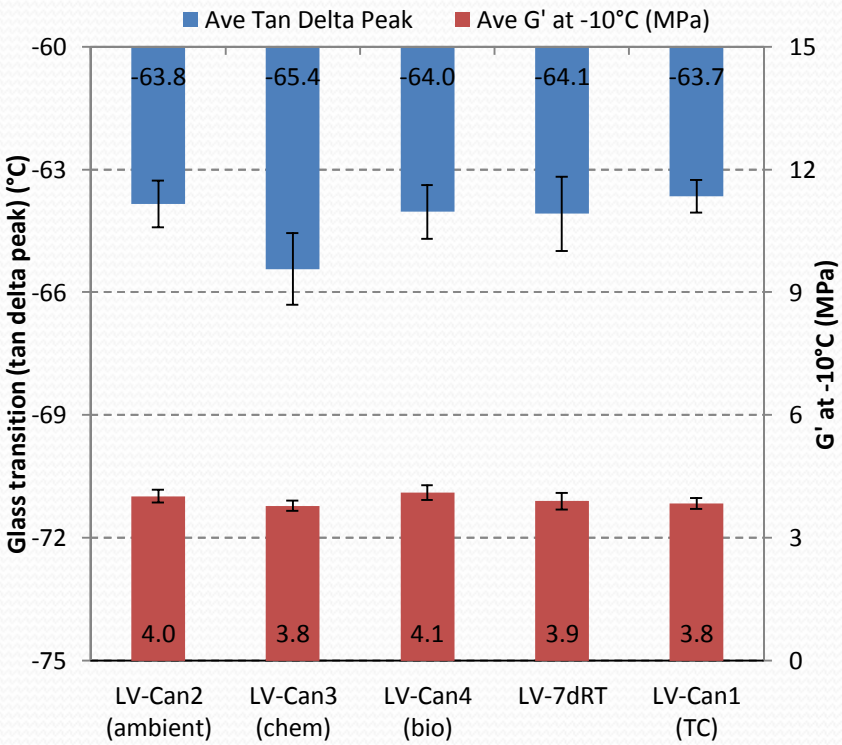


No change in Tg during exposure to lab air need to determine effect on HVB

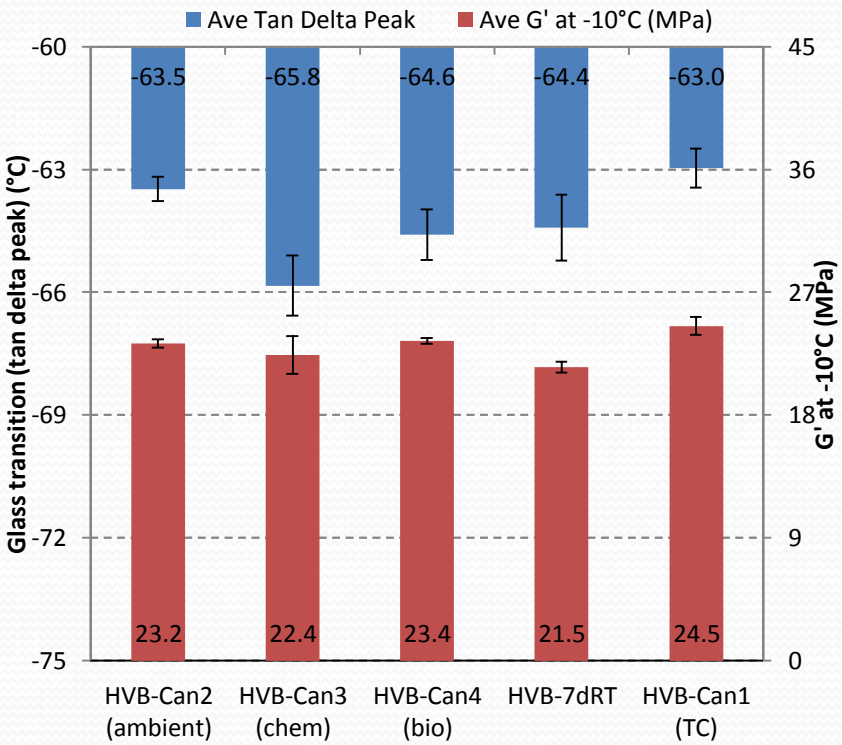


No changes observed in 6 month small-core aging samples

Arathane 5753



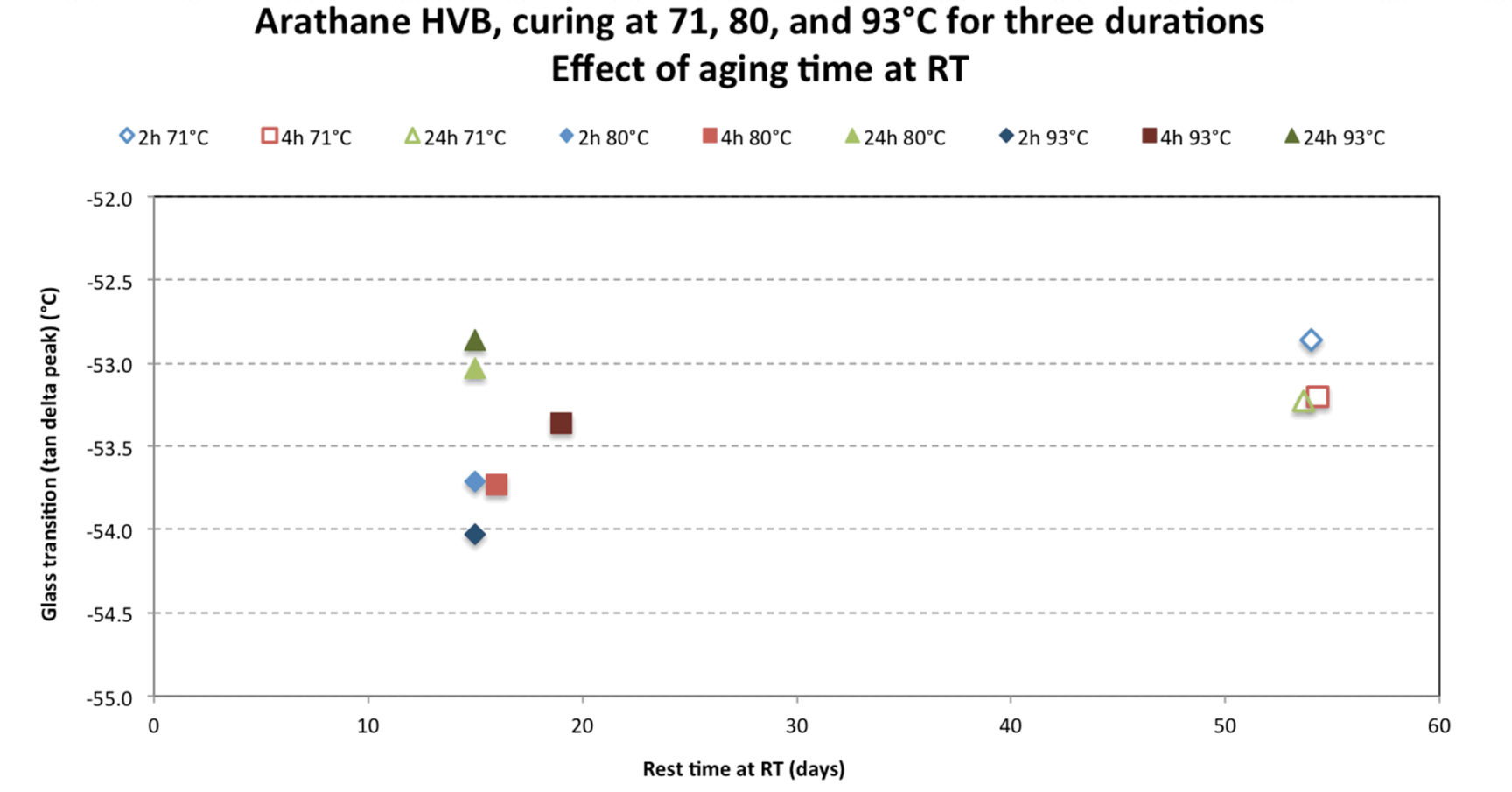
Arathane 5753 HVB



Rheometer rectangular torsion, 0.005% strain, 1 Hz, 2°C/min heating

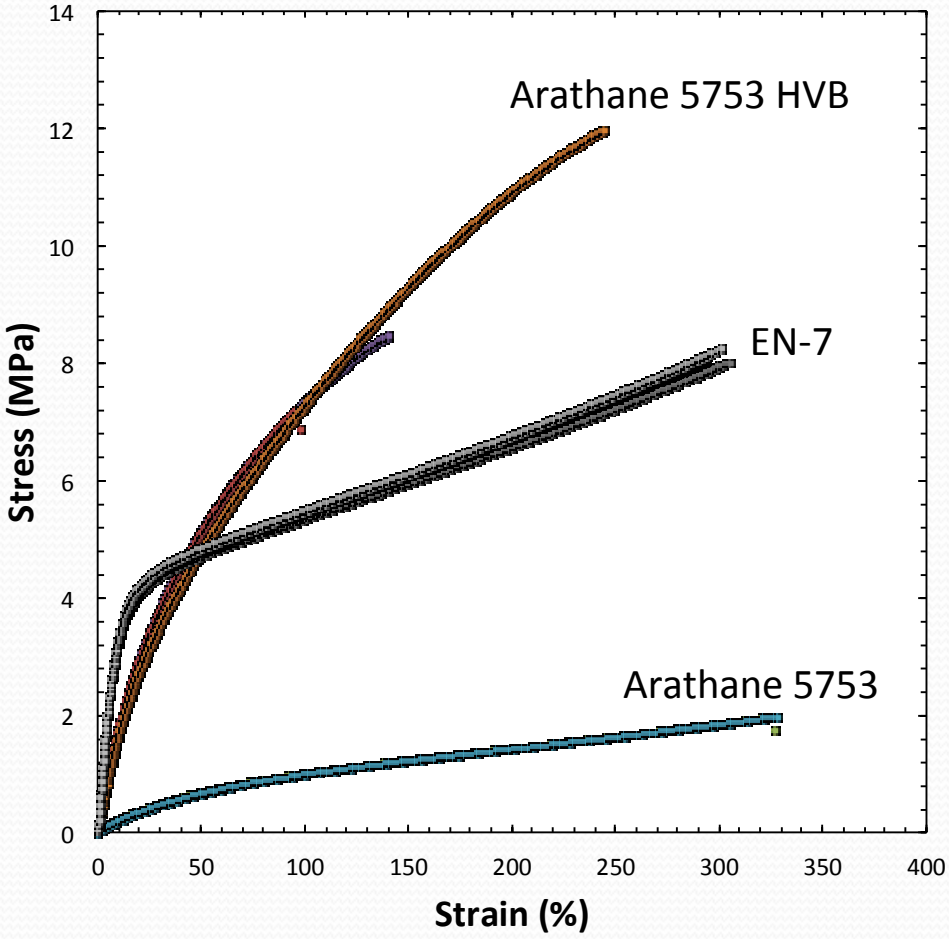
Curing at elevated temperatures does not appear to affect T_g

- Comparison after 50+ days rest

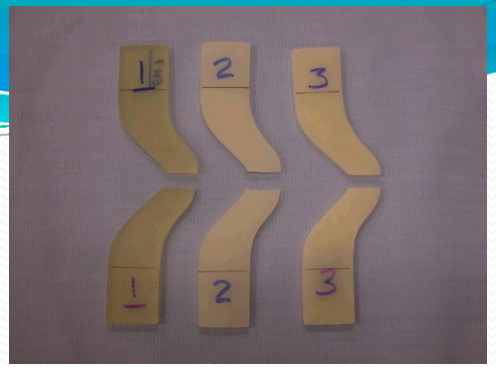


Tests in Tension

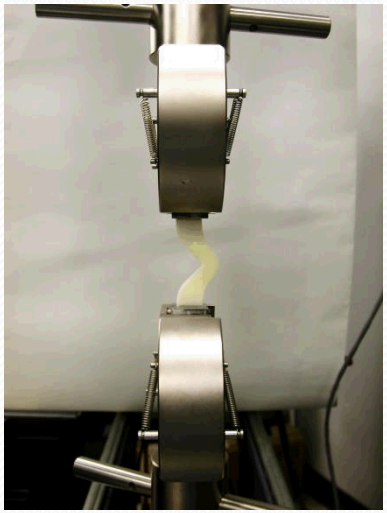
- Addition of diol stiffens Arathane 5753, reduces elongation
- Measurements of modified Arathane appear less consistent, but could be due to flaw sensitivity of the test

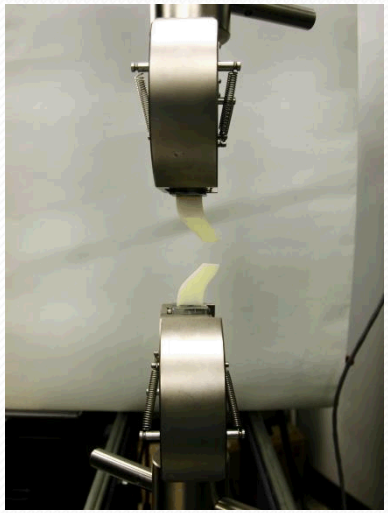


Tear Strength (ASTM D624)

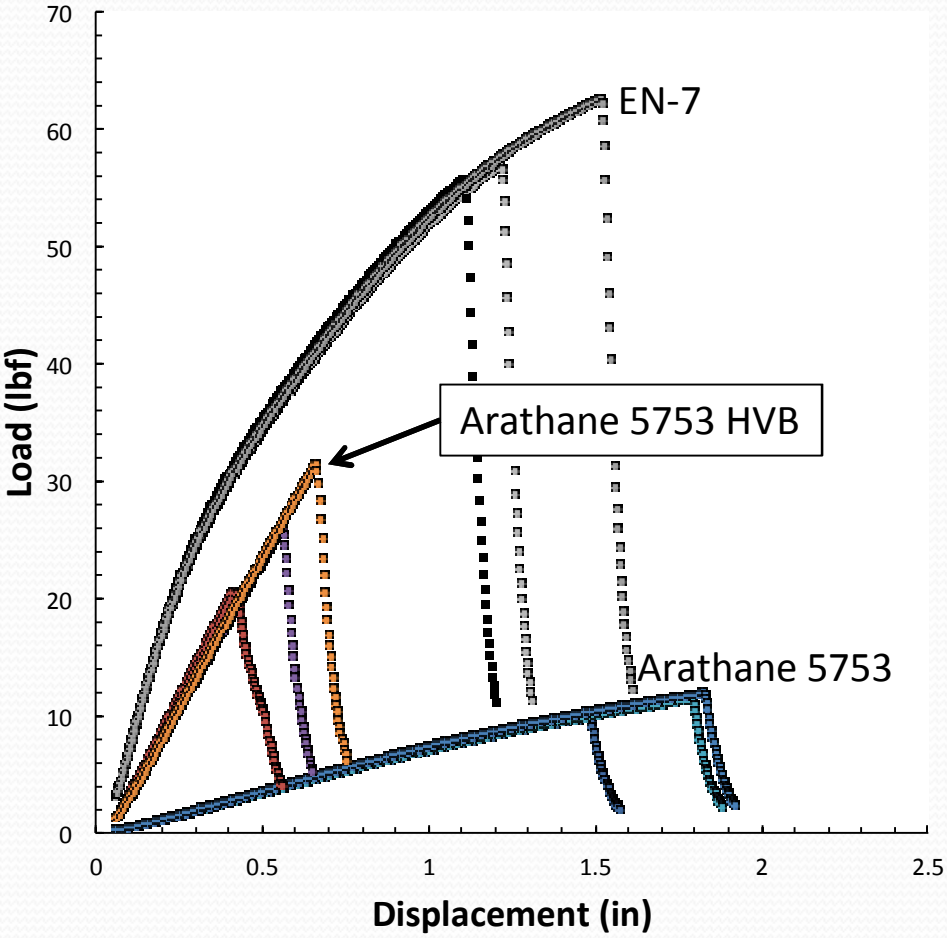


- Arathane-based formulations have lower tear strength than EN-7

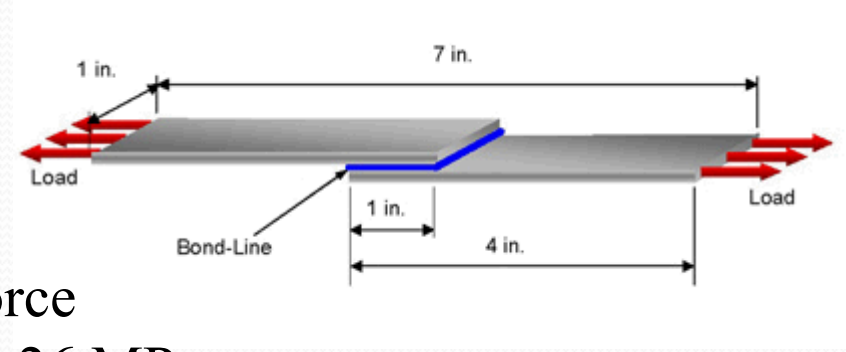




Above: modified Arathane



Lap Shear Adhesion Testing



- Arathane 5753
  - Average peak load: 123 ± 17 Kg-force
  - Average peak shear stress: 1.88 ± 0.26 MPa
- Arathane 5753 HVB
  - Average peak load: 347 ± 55 Kg-force
  - Average peak shear stress: 5.27 ± 0.83 MPa
- All cohesive failures observed
  - Not a good indicator of adhesion strength
- Single lap shear, using 4”x1” Al 6061-T6 coupons, Alodine coated, with a 1” overlap (area of bond = 1 sq in)
- 3 specimens per adhesive
- 0.5 wt% of 0.005” glass beads added to each adhesive to ensure a minimum bond line
- Each specimen cured at RT for 24 hours in fixture, then 6 days at RT (bagged)

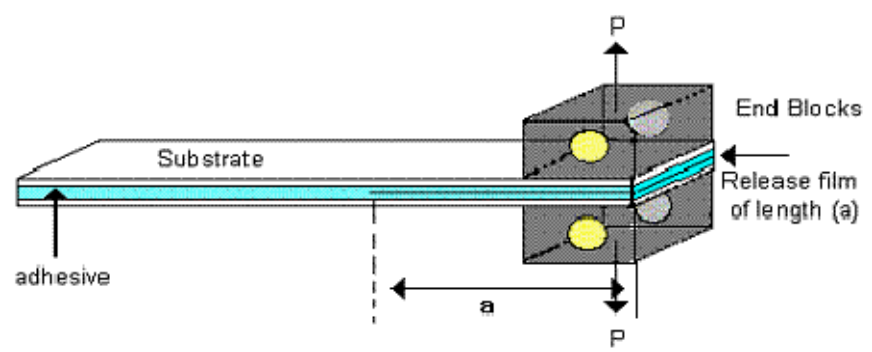
Aging Plans (compare to EN-7)

- Adhesion (DCB)
  - Considering thick PU butt tensile test for PEEK (Zamora)
- Durometer
- Volume Resistivity
- Mass
- Outgassing (SPME)
- Tg (rheometry)

- Aging Conditions
  - Air RT
    - 0, 3, 6, 12, 24, 48 weeks
    - Subset for lap shear: 0, 12, 48 weeks
  - N2 RT
    - 3, 6, 12, 24, 48 weeks
    - Subset for lap shear: 12, 48 weeks
  - N2 50°C
    - 3, 6, 12, 24, 48 weeks
    - Same for lap shear
  - N2 105°C
    - 2, 4, 8, 16, 32 days
    - Same for lap shear

DCB Adhesion testing

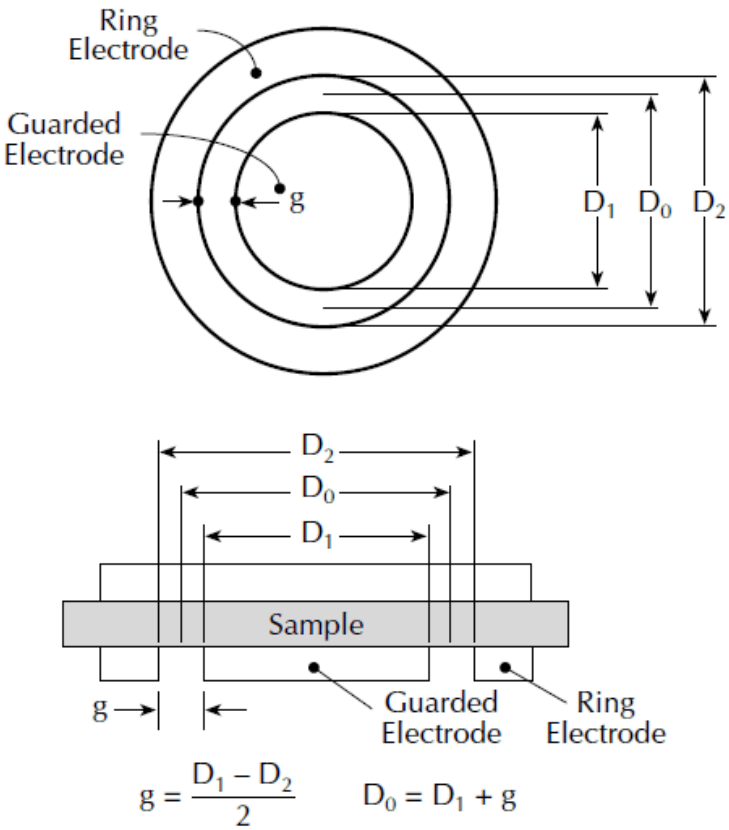
- PEEK: RTP 2205 HF Black, 0.125”
  - 0.125 x 7.5 x 4” (50) ordered from RAM Inc
  - Single use, 3 per condition/duration, 3 durations
  - Total: 36 per material (144 coupons)
    - Surface prep: IPA wipe/bakeout
    - Pre-crack
- Al: Aluminum 6061
  - 0.125 x 1 x 4” (300) ordered from Metal Samples
  - Single use, 5 per condition/duration
  - Total: 75 per material (300 coupons)
    - Surface prep: IPA wipe/bakeout
    - Pre-crack
- May add Nylon

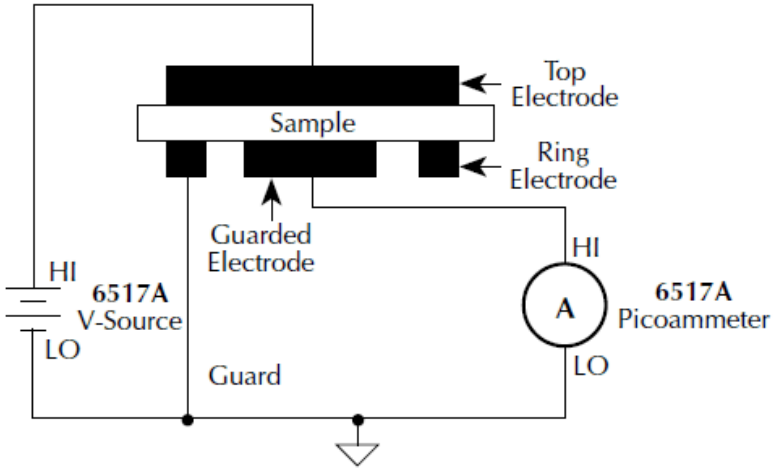


High Resistance Measurements using Keithley's Model 6517B Electrometer High Resistance Meter and the Model 8009 Resistivity Test Chamber

- Need to modify safety case prior to use

Volume resistivity measurement technique





- From Keithley Instruments

Conclusion

- Arathane 5753 HVB shows promise as replacement for EN-7 (and other castable elastomers)
- Straightforward processing
  - Free of TDI
  - Commercially available constituents
  - All components liquid at room temperature
  - Improved pot life
- Desired properties
  - High voltage breakdown strength is comparable to EN-7
  - Passes NASA outgassing requirement

Future Work

- Aging
- Adhesion
- Cure shrinkage
- Self adhesion?
- Small Core
- Asked Sandia to not pursue a patent
- Advertise to the public
- Convince Huntsman to make as a new product
- Find new customers!