Using DSR reference fluid to verify DSR

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Introduction – Purpose of Presentation

1. Review the history and intended use of the reference fluid as it is used in ASTM D7175 and AASHTO T 315
   - ✓ Cannon Viscosity Standard N23700000SP is recommended
2. Provide a comprehensive characterization of the reference fluid through two experiments:
   a. Experiment 1 - Measurements in Newtonian region of behavior
   b. Experiment 2 - Measurements in viscoelastic region where fluid is used in ASTM D7175 and AASHTO T 315
3. Correct some basic misunderstandings
4. Offer recommendations on proper use of fluid based on characteristics of the fluid and its intended use

1. Historical and Intended Use

- DSR test method was developed expecting that manufacturers would supply “calibration” fixtures
- Reference fluid was suggested as alternative - AASHO T 315

  “9.5.1 *Verification of Torque Transducer*—Verify the calibration of the torque transducer using a reference fluid ….. be within 3 percent ….. indicates that the torque transducer is not in calibration.”

  “A1.2.5 When tested at 10 rad/s, the reference fluid should only be used between 58 and 64°C.” (*No strain specified*)

  “Cox-Merz empirical rule ….. following approximation” $G^*/\omega = \eta$

  G^* = the complex modulus,

  ω = the angular frequency in radians/s, and

  η = the shear-rate independent capillary viscosity as reported

  “A1.3.1 ….. measurements where the phase angle approaches 90°”

Initial Study Justifying Use of Fluid

- Round robin test program sponsored by NEAUPG in 1997[a]
  - ✓ Viscosities were calculated using from Cox-Merz rule and compared to Newtonian viscosities reported by Cannon
  - ✓ In-depth rheological characterization was not performed
  - ✓ Fluid was assumed to be linear as claimed by supplier of fluid
- Findings from NEAUPG Round Robin
  - ✓ Restrict use to 10 rad/s and 10% strain at 58°C and 64°C
  - ✓ At 58°C and 64°C Round Robin results showed a 3% difference between reference viscosities and Cox/Merx viscosities

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[a] Interlaboratory Test Program to Determine the Precision of the SHRP Performance-Based Asphalt Binder Tests, Anderson et al., Advanced Asphalt Technologies, 1997

NEAUPG Round Robin Test Results

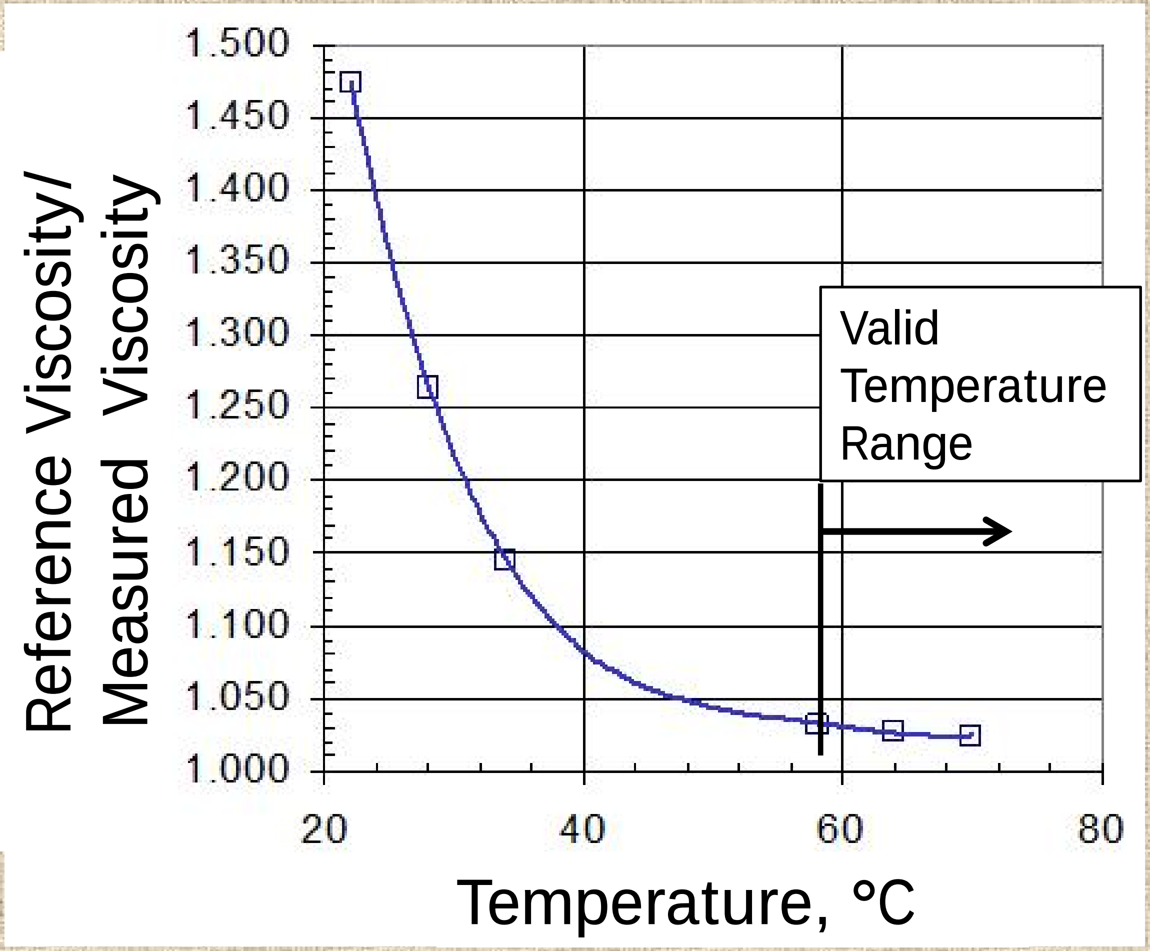
Estimated vs. Measured Dynamic Viscosity
14 Laboratories with replicate measurements
25 mm plate - 10 rad/s – 10% strain

Temperature,° C Plate (mm)	Estimated[a] using Cox-Merz Rule η* (Pa-s)	Measured with DSR: η* (Pa-s)	Ratio: Measured/ Estimated
70° C (25mm)	1.77	1.73	1.02
64° C (mm)	2.58	2.51	1.03
58° C (mm)	3.82	3.71	1.03
34° C (8mm)	23.3	20.4	1.15
28 °C (mm)	39.4	31.2	1.26
22 °C (mm)	68.9	46.7	1.47

[a] Viscosity reported by manufacturer divided by frequency, 10 rad/s.

Reference vs. Measured as f(T)

- Recommend testing at 64°C
- Errors become large at lower temperatures
- Binder flows from plates at higher temperatures



2. Fluid Properties Reported By Cannon

- Cannon Instrument Company produces a series of viscosity standards with a wide range of viscosities.
- Prepared by blending different batches of polybutene polymer with different molecular weight.

"Most cannon standards are hydrocarbon oils produced from mineral oil base stocks, polyalphaolefins or polybutenes …. Because most Cannon standards are Newtonian liquids, their viscosity is independent of shear rate and shear stress. However, viscous heating may cause high viscosity standards to appear non-Newtonian by effectively lowering their viscosity when measured a high shear rates. "

- Standards are reported as being Newtonian but shear rates for reported viscosities are not given

Measurement of Complex Viscosity, η^*

- Assuming only viscous response, $\eta^* = G^*/\omega$

  Substituting, $G^* = 2Th/4\pi r^4\Phi$

  $\eta^* = Th/2\pi r^4\Phi\omega$

where:

T = Torque applied to specimen, N-m

h = Specimen thickness, m

Φ = Angular rotation, rad

r = radius of test specimen, m

ω = frequency, rad/s

- If we assume other variables are accurately known uncertainty lies with measurement of torque, T

Items that might affect accuracy of DSR measurements using fluid

- Measurement temperature
  - ✓ Always verify DSR thermometer before using fluid
- Fluid expiration date
  - ✓ Do not use beyond expiration date – check label
- Heating the fluid
  - ✓ Heating can cause it to deteriorate
  - ✓ Use proper storage temperatures
- Improper test specimen preparation
  - ✓ Incorporation of bubbles can reduce measured value
  - ✓ Gap and improper bulge – good laboratory technique
- Each of above easily controlled with proper laboratory procedures

Viscosity Reported for Fluid

- Reference fluid meets the precision specifications of ASTM D445/446 and ISO 3104/3105
  - ✓ Traceable to National Institute of Standards and Technology
- Manufactured and/or certified in Cannon's ISO 9001 registered and A2LA-accredited laboratory.
  - ✓ An A2LA laboratory is accredited for technical competence in the field of calibration including viscosity standards in accordance with ISO/IEC 17025.
  - ✓ All calibrations are based on capillary viscometers using the procedures detailed in ASTM D 2162

Conclusion – Viscosity standard is measured very accurately and is NIST traceable and reported values are not in question.

Sidebar - how is viscosity of reference fluid determined?

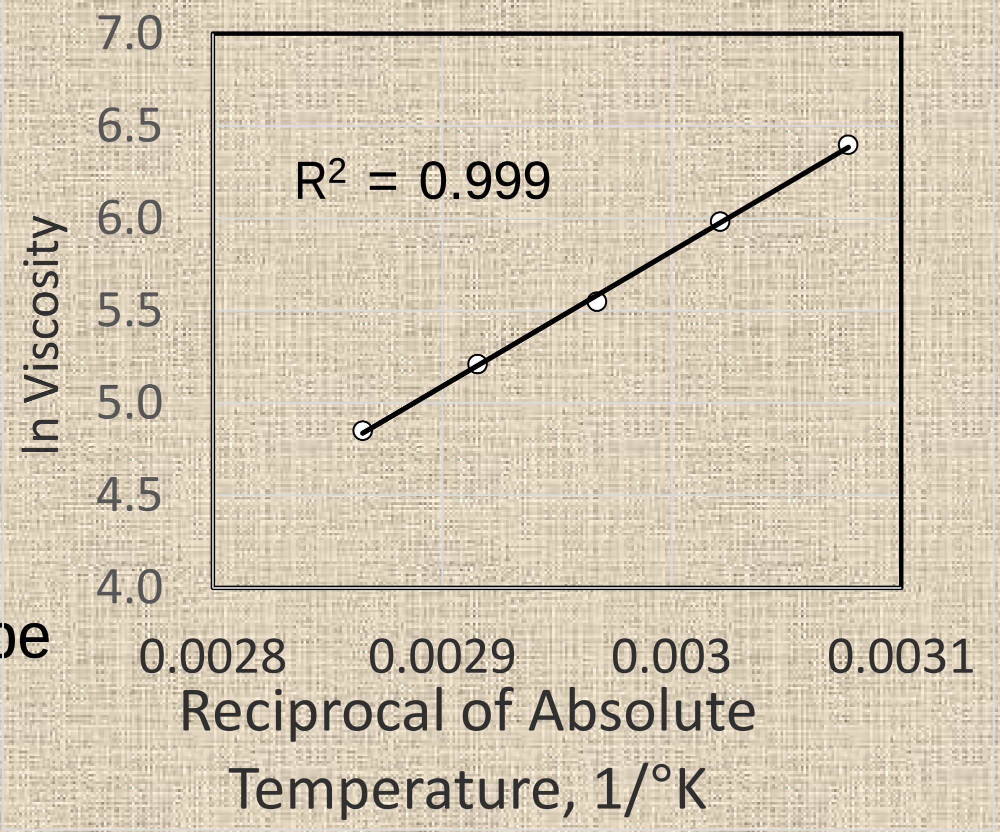
- Reference values determined with capillary viscometer in region of Newtonian flow
  - ✓ Viscosity independent of shear rate
  - ✓ Shear rate is NOT given on reference fluid container
- When reference fluid is calibrated supplier must exercise same cautions used when DSR measurements are made
  - ✓ Stay in Newtonian (linear) region
  - ✓ Avoid shear thinning (non-Newtonian region)
  - ✓ In capillary experiment limits defined by temperature and shear rate

Variables Affecting Viscosity Measurement

- Quality of test specimen – bubbles, trimming and gap
- Temperature control – should not be issue
- Viscosity of fluid – temperature, shear rate, and handling
  - ✓ Fluid temperature affects torque generated but does NOT affect operation of DSR
  - ✓ Measurement at different temperatures of NO value
- Proper operation and calibration of software
  - ✓ Torque and angular rotation
- Conclusion: Reference fluid cannot be used to validate torque transducer and measurement at single torque level (single temperature) is sufficient

Arrhenius Plot – Newtonian Viscosities as Reported By Cannon

- Viscosities plotted as ln viscosity vs. reciprocal of absolute temperature should be linear if fluid is Newtonian
- Linear with $R^2 = 0.999$
  - ✓ Implies it is Newtonian
- Activation energy from slope
  - ✓ E_a = 61 kJ/mole
  - ✓ Relatively high value indicative of a branched polymer
  - ✓ E_a for branched PE is 55 kJ/mole



3. Remaining Questions

- What questions remain relative to use of the viscosity standard as a reference fluid for D7175 and T315?
  - ✓ Can the reported values be replicated with the DSR in region of Newtonian flow?
    - Validate our experimental results
  - ✓ What is the Newtonian flow region?
  - ✓ Can we explain the 3% offset in NEAUPG Report?
  - ✓ Are the claims that self heating or machine compliance are responsible for measurement anomalies correct?
  - ✓ How should the fluid be used to take best advantage of it's properties and DSR validation needs?
- Proceed to testing in viscoelastic domain

Experiment 1: Measured vs. Reported Viscosities in Newtonian Region

- Instrumentation and geometry
  - ✓ Kinexus DSR with 25 mm parallel plate and 1 mm gap
- Three modes of loading at small strains:
  - ✓ Creep Mode
    - Steady state viscosities at 5 Pa
  - ✓ Constant strain rate
    - Steady state viscosities at 0.1 s^{-1} shear rate
  - ✓ Oscillatory mode
    - Viscosities estimated using Cox-Merz Rule
    - 0.1 rad/s and 0.03% strain
- Cox-Merz viscosities were within 0.6% of reference values
  - ✓ Verified Newtonian region and agreement with reference values

Data Summary: Values Reported by Cannon Compared to Cox-Merz Values

DSR using 25 mm parallel plate, 1.0 mm gap

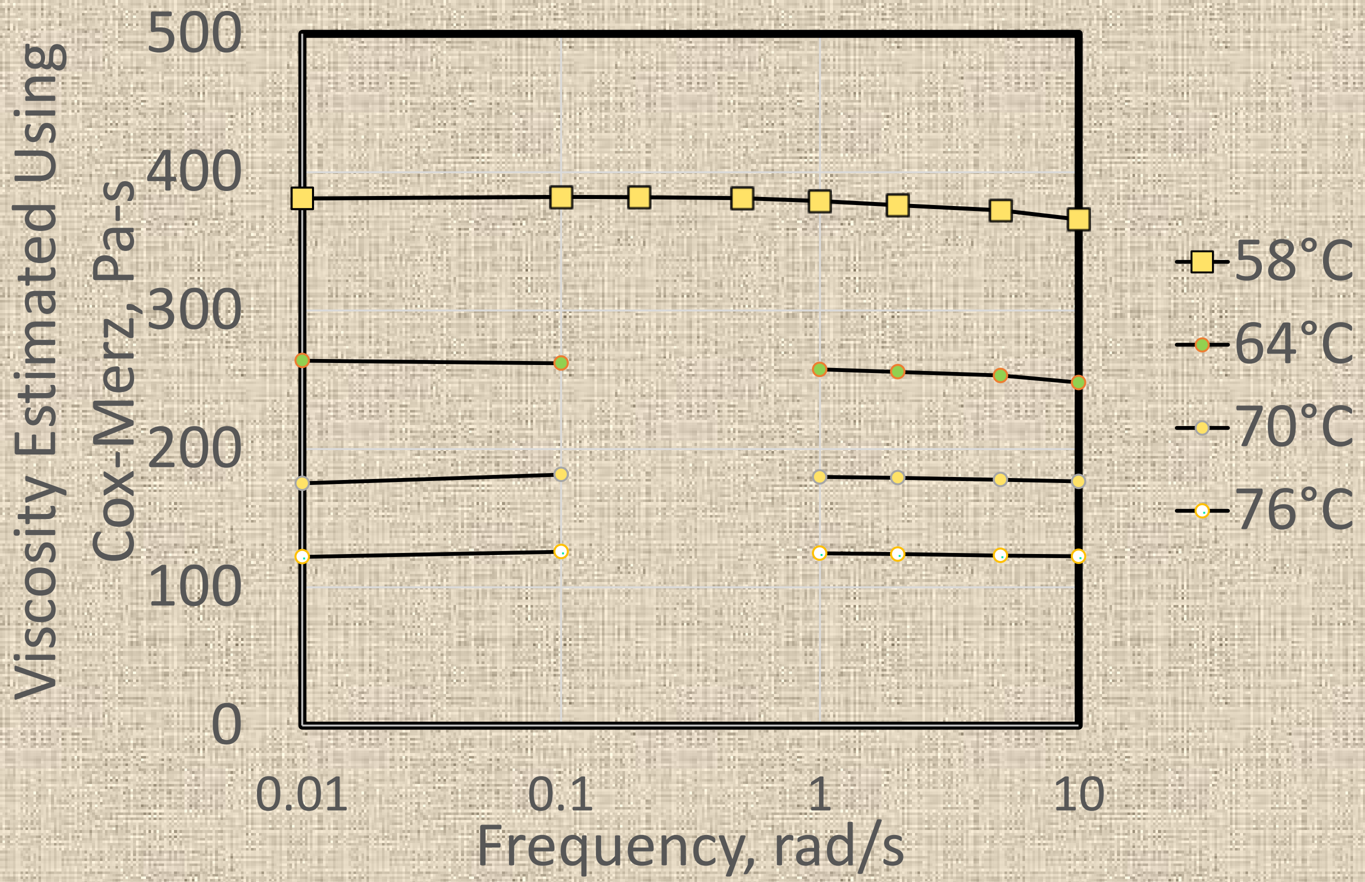
Temperature, °C	52	58	64	70	76
Bottle Value, Pa-s	600	396	257	183	128
1. Creep, DSR, Pa-s	601	396	259	190	127
Percent Difference	*0.0*	*0.1*	*1.0*	*4.0*	*-0.3*
2. Constant Rate, DSR, Pa-s	610	382	264	182	130
Percent Difference	*1.7*	*-3.4*	*2.7*	*-0.7*	*1.5*
3. Oscillatory[(A)], Pa-s	597	401	252	179	128
Percent Difference	*-0.5*	*1.4*	*-1.8*	*-2.1*	*0.5*
Average 3 Tests	603	393	258	184	129
Average Percent Difference	*0.4*	*-0.6*	*0.6*	*0.4*	*0.6*

[(A)] Oscillatory viscosities at 0.1 Hz, 0.03% Strain

Experiment 2: Measurements in Viscoelastic Region

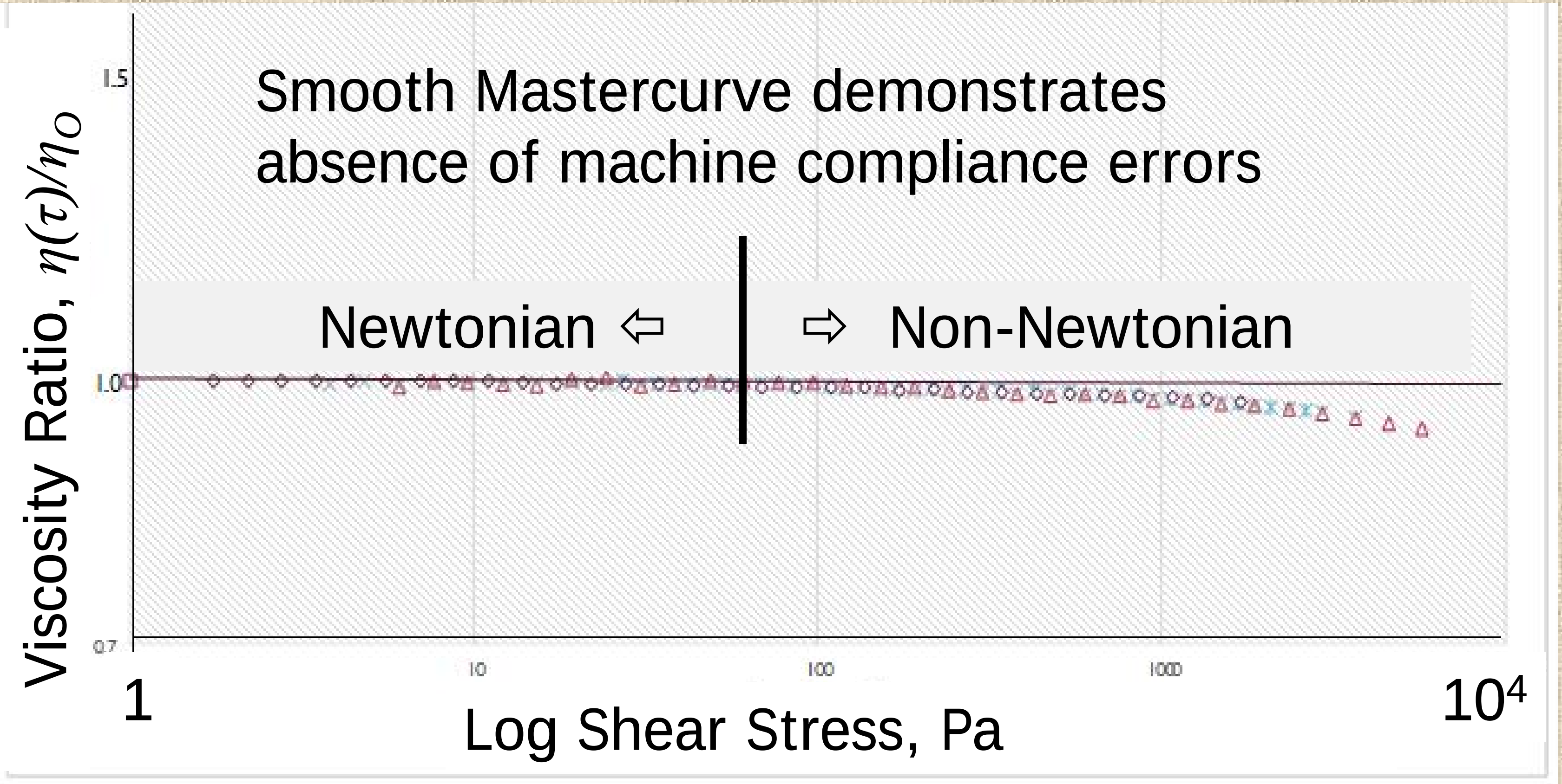
- Viscosity measurements from 0.1 to 10 rad/s
  - ✓ Power law coefficients
- Frequency sweep showing viscoelastic effect
- Generalized viscosity mastercurve
- Viscosity mastercurve

Experiment 2: Dynamic Viscosities – DSR in Non-Newtonian Region



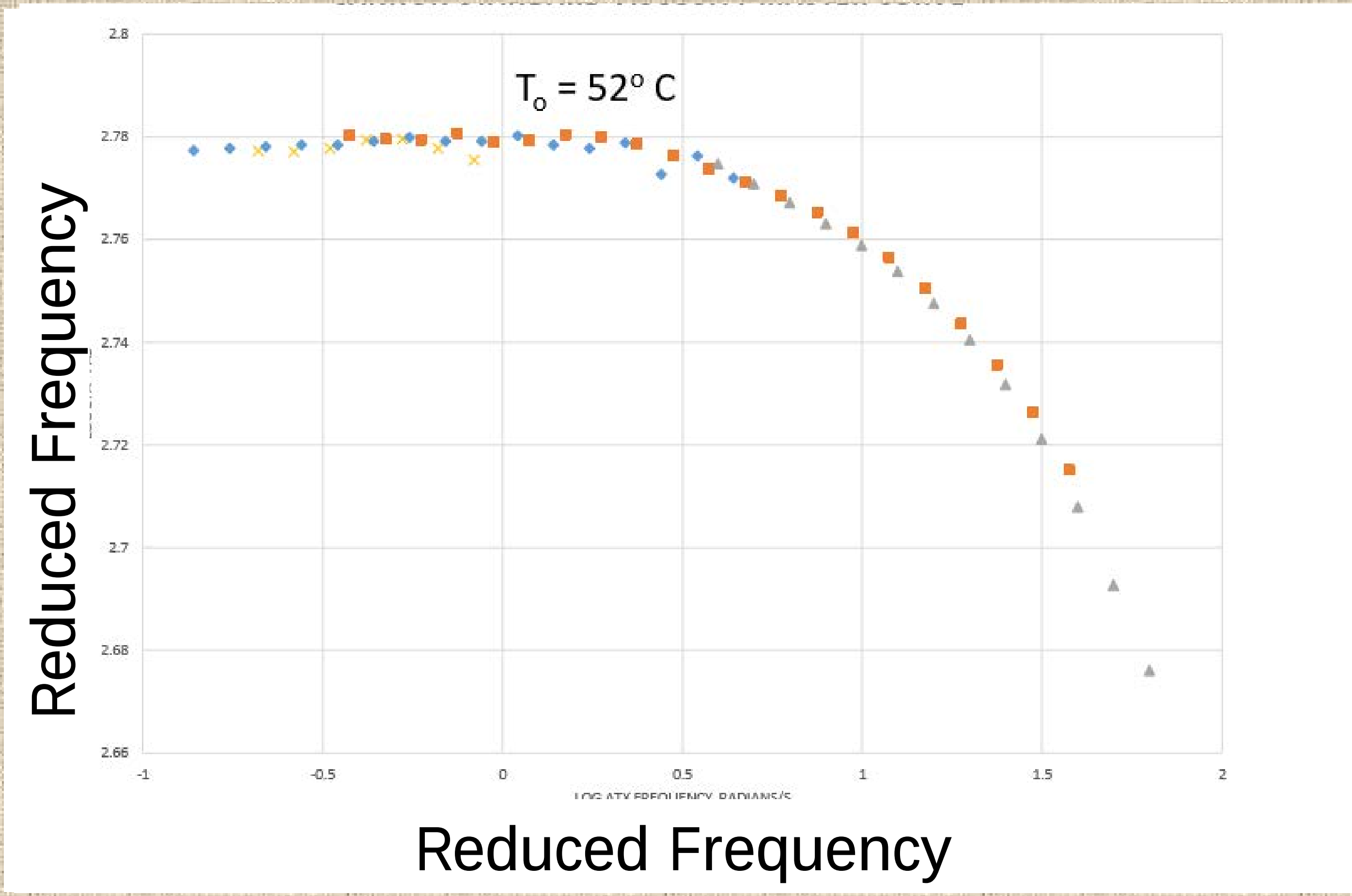
Shear thinning starting at 64°C increasing at 58°C

Temperature Invariant Mastercurve



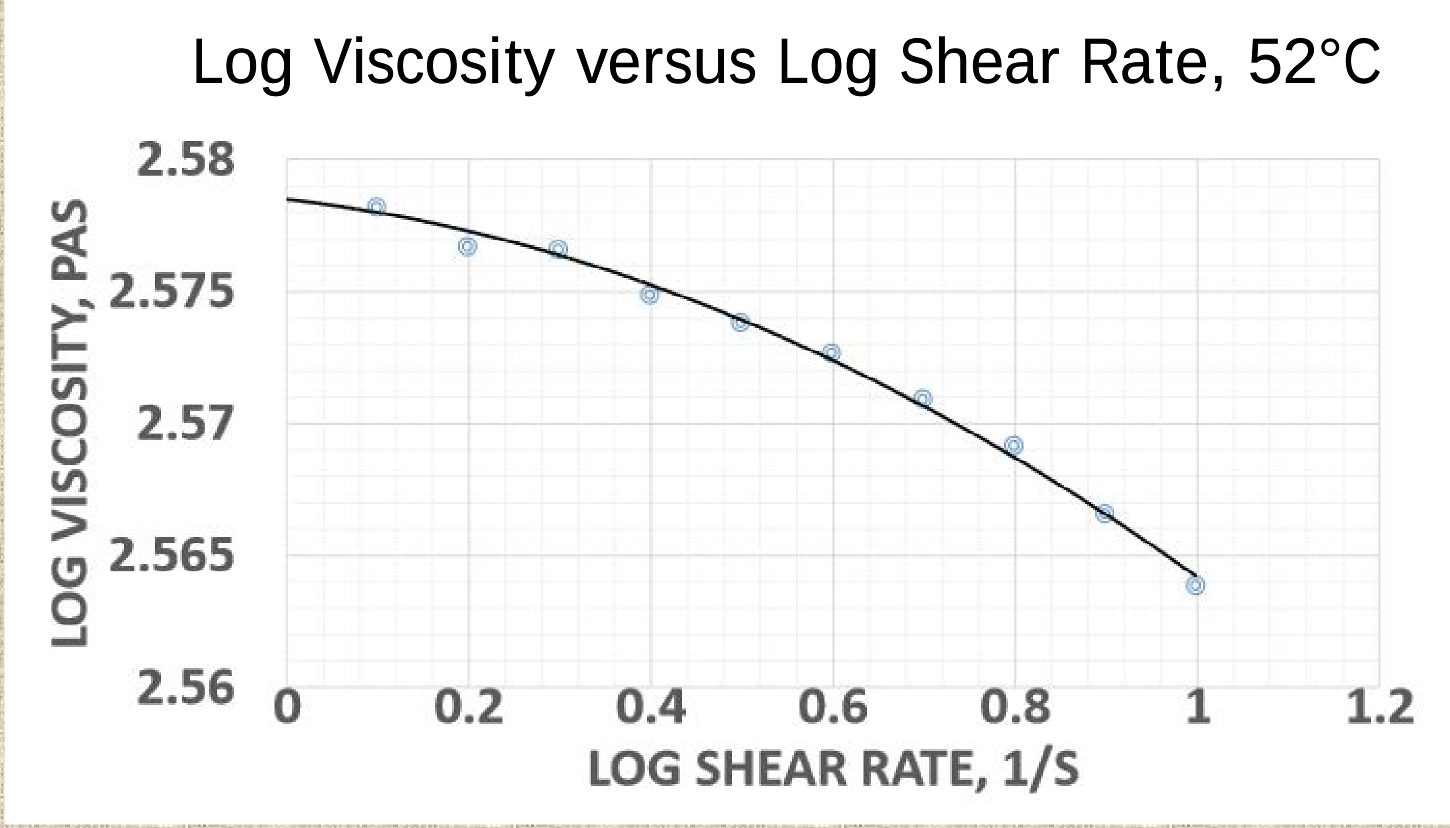
Non-Newtonian apparent when shear stress > 100 Pa

Viscosity Mastercurve, T_{ref} = 52°C



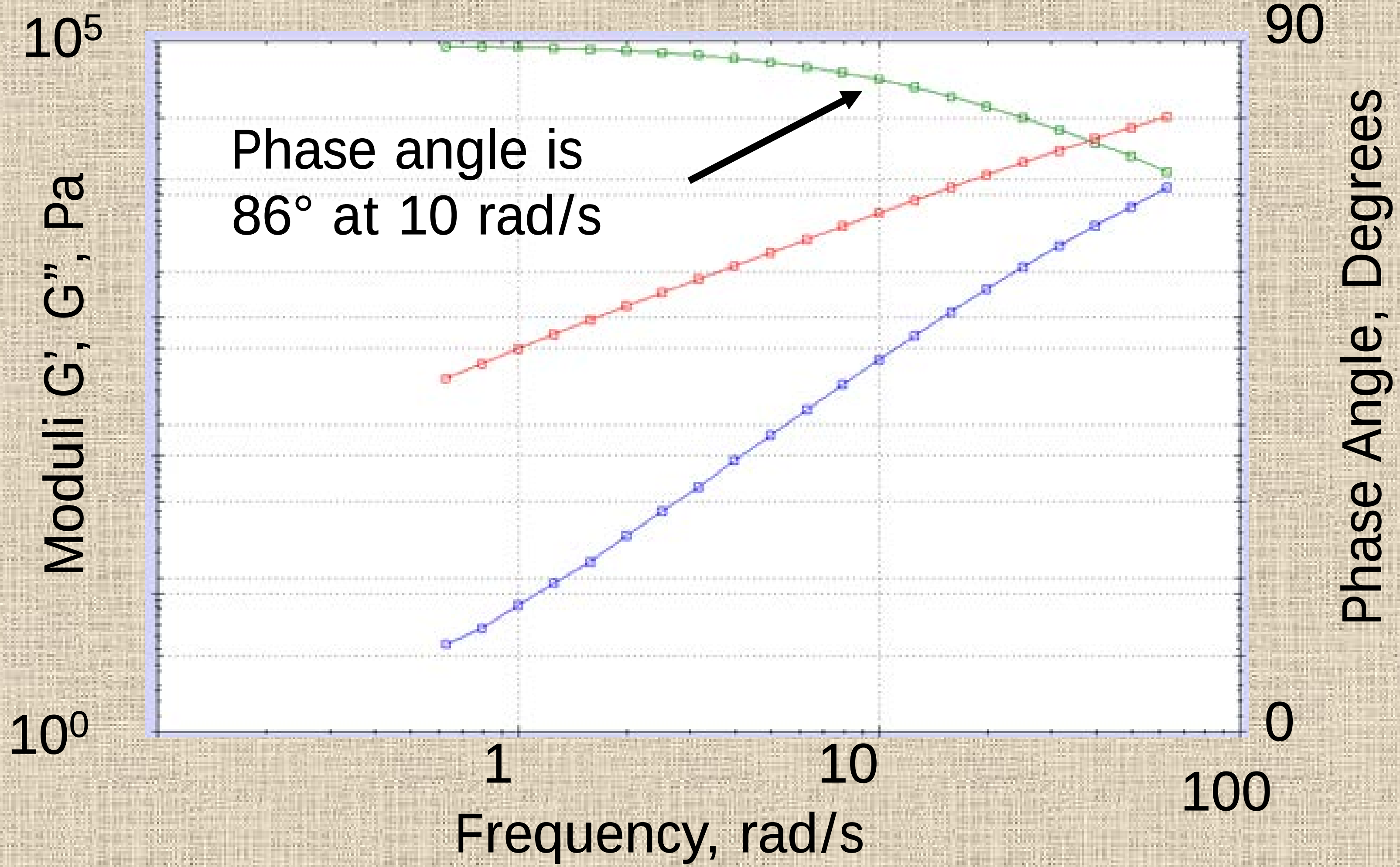
Shifted data obey WLF equation and form smooth Mastercurve verifying absence of machine compliance errors

Dynamic Viscosity vs. Shear-Rate (52°C)



- ✓ Shear rate dependency demonstrates viscoelastic nature
- ✓ Power law coefficients < 1 demonstrating shear thinning

Frequency Sweep at 52°C



Comparison of Calculated and Measured Normal Force

- Presence of normal force indicates viscoelastic behavior

Temperature (°C)	N_1 Measured (Pa)	N_1 Calculated (Pa)
52	950	995
58	423	450
64	711	813

- Based on information in preceding slides conclude without any doubt that fluid is viscoelastic and shear thinning is due to viscoelasticity

3. Flow Characteristics

- Self heating
- Instability flow

3. Flow Characteristics

- Reynolds number defines the relative importance of the viscous and inertial forces
- ✓ Re =1.66 x 10-5 ⇨ laminar flow
- Weissenberg number defines the ratio of elastic to viscous behavior
- ✓ Wi = 0.1 at 10 s-1 and 52 °C ⇨ Viscous flow dominates

Effect of Self Heating on Viscosity

- Question: Can heat generated by non-recoverable deformation cause rise in temperature sufficient to affect measured values?
- Nahme Number indicative of temperature rise caused by viscous heating
  - ✓ Na = 0.01789 ⇨ Extremely low contribution from viscous flow
- Fourier-Kirchoff Heat Flow Equation
  - ✓ Gives temperature rise at steady state caused by internal heat source
  - ✓ Temperature rise at 52°C < 0.1°C
- Conclusion: Self heating not an issue

Findings

- Reference fluid is Newtonian within limited range and measured values are in excellent agreement with reported values
- Reference fluid is viscoelastic in region where it is used in ASTM D7175 and AASHTO T 315
- Measured and reported viscosities disagree when tested at 10 rad/s and within temperatures ranging from 52°C - 76°C
  - ✓ Error small (3%) at 64°C increases as temperature is lowered
  - ✓ NEAPUG Round Robin findings were verified
- Differences between reported and measured viscosities are due to viscoelastic effects only
- Machine compliance and self-heating are non-issues

Observations

- Many factors affect values measured with DSR
  - ✓ Temperature control
  - ✓ Algorithms that calculate stress and strain
  - ✓ Specimen preparation – especially trimming
- Reference fluid measurements reflects the above and more!
  - ✓ Reference fluid CANNOT be used validate torque transducer as stated in ASTM D7175 and AASHTO T 315
- DSR fluid measurements verify *overall operation* of DSR
  - ✓ Absolutely no need to verify at multiple temperatures
  - ✓ Temperature verification should always precede DSR verification

Conclusions and Recommendations

- Viscosity standard is useful as a reference fluid
  - ✓ No intention of discontinuing use!
- Perform verification measurement at single temperature, strain and frequency
  - ✓ Modify ASTM D7175 and AASHTO T 315 to specify verification only at 60°C, 10% strain, 10 rad/s
  - ✓ Available reference fluid calibrated at single temperature (60°C) is less expensive and will curtail confusing multiple temperature validation attempts practiced by some laboratories
- Reference fluid provides a known torque that allows verification of overall operation of DSR

Conclusions and Recommendations

- Revise ASTM D7175 and AASHTO T 315 to require reference fluid viscosity as measured by DSR to be:

  (Reported value)/1.03 ± Test variability

  - ✓Test variability is unknown – 3% taken from offset as reported in NEAUPG study
  - ✓Round-robin study is needed to verify test variability
- Revise ASTM D7175 and AASHTO T 315 to require standardization when measured value falls outside limits
- Weekly reference fluid measurements should be maintained in quality control chart
  - ✓Unfortunately, for many this is a hard sell!

Conclusion

- If DSR viscosity equals reference viscosity DSR is likely working correctly and verifying that the torque transducer standardization is verified
  - ✓ Non verification does not indicate that problem lies with torque transducer – could be something else!
- If DSR viscosity differs from reference viscosity something is "wrong"
  - ✓ Could be torque transducer
  - ✓ Could be other internal DSR calibration items
  - ✓ Likely not machine compliance if strains are not small
  - ✓ Likely not temperature errors if temperature Was verified
  - ✓ Likely not specimen issues if technician is competent