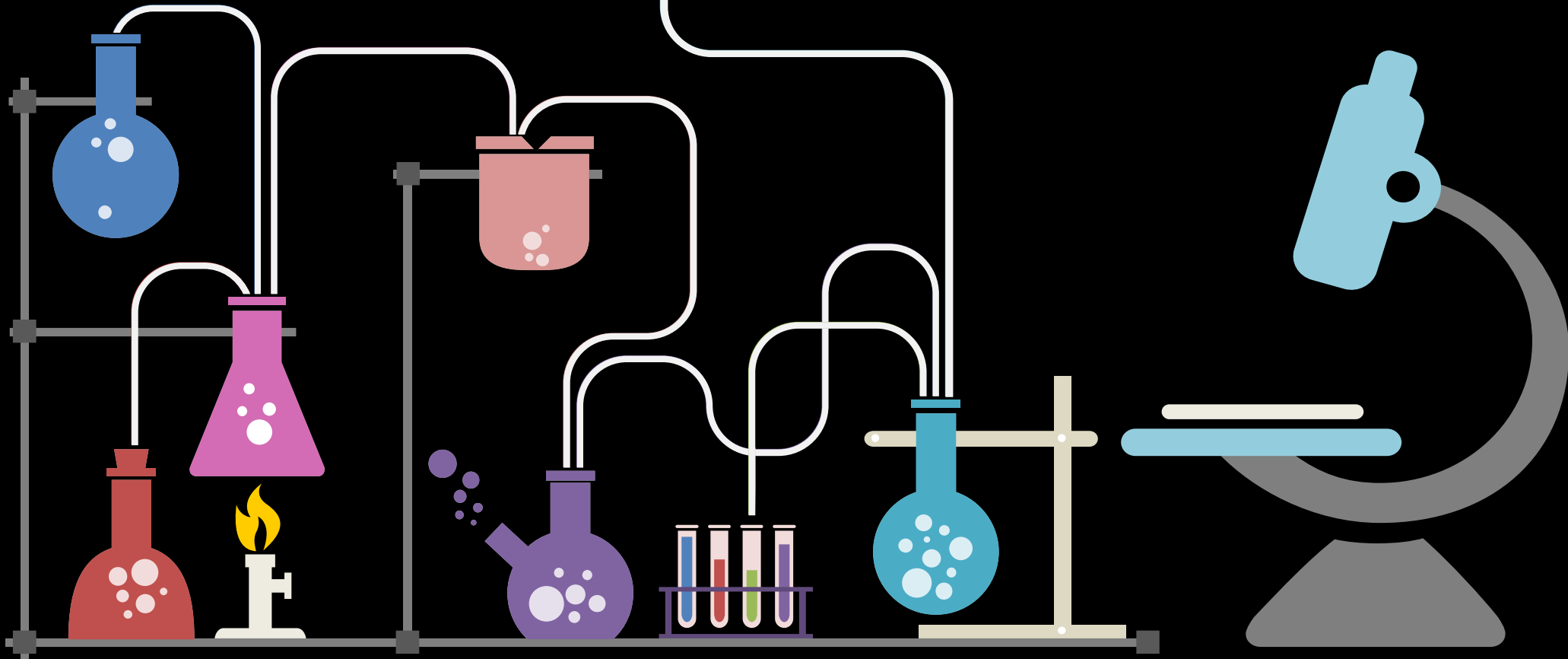


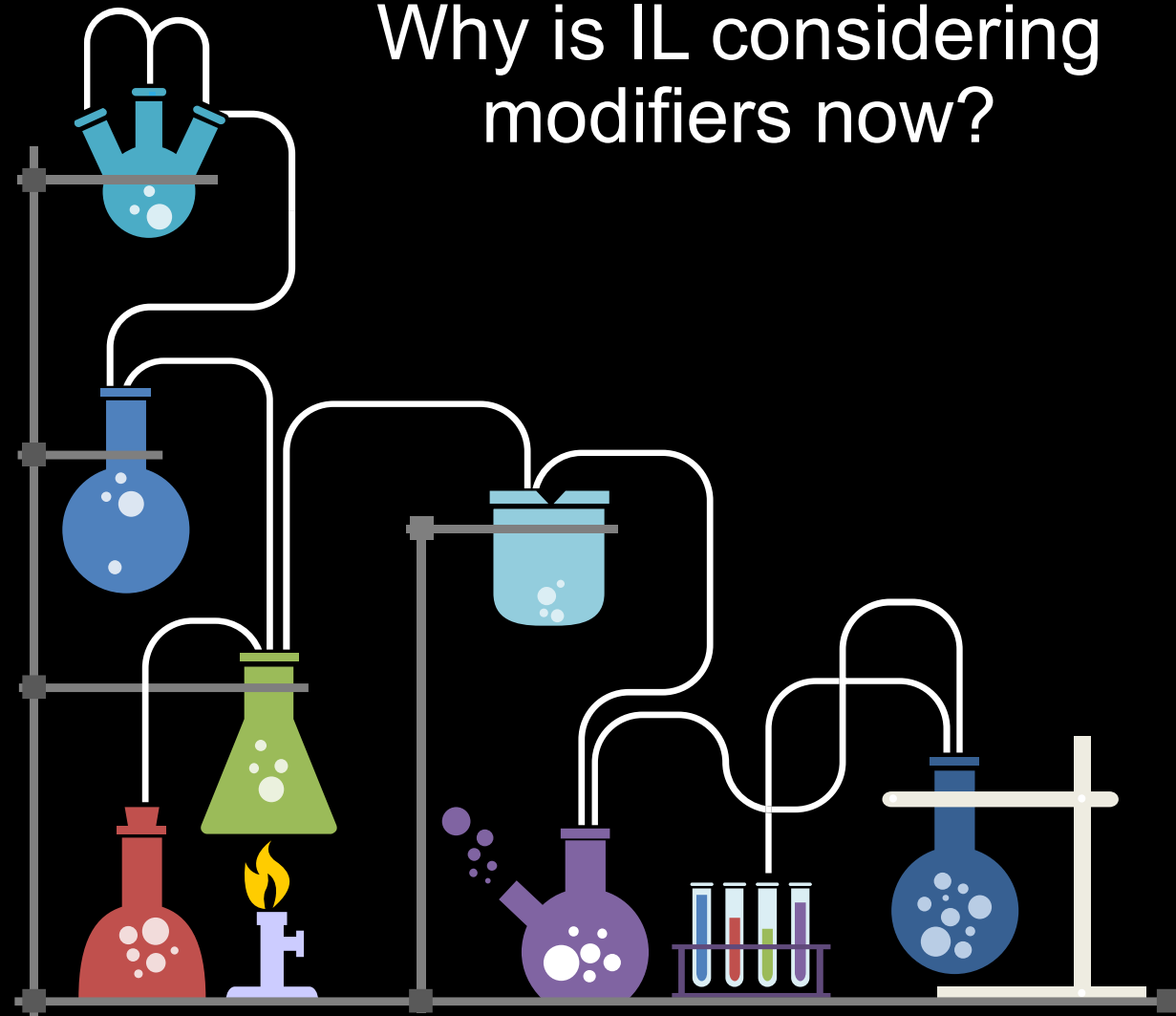


Illinois Department
of Transportation

Asphalt Binder Modification



Why is IL considering modifiers now?



- ❖ Illinois does not currently allow modification other than polymer.
- ❖ Significant change in base binder used in IL from PG 64-22 to PG 58-28.
- ❖ Need for **economic & sustainable** alternatives to achieve softer PGs.
- ❖ Can those softer grades be achieved with softening agents without a compromise?



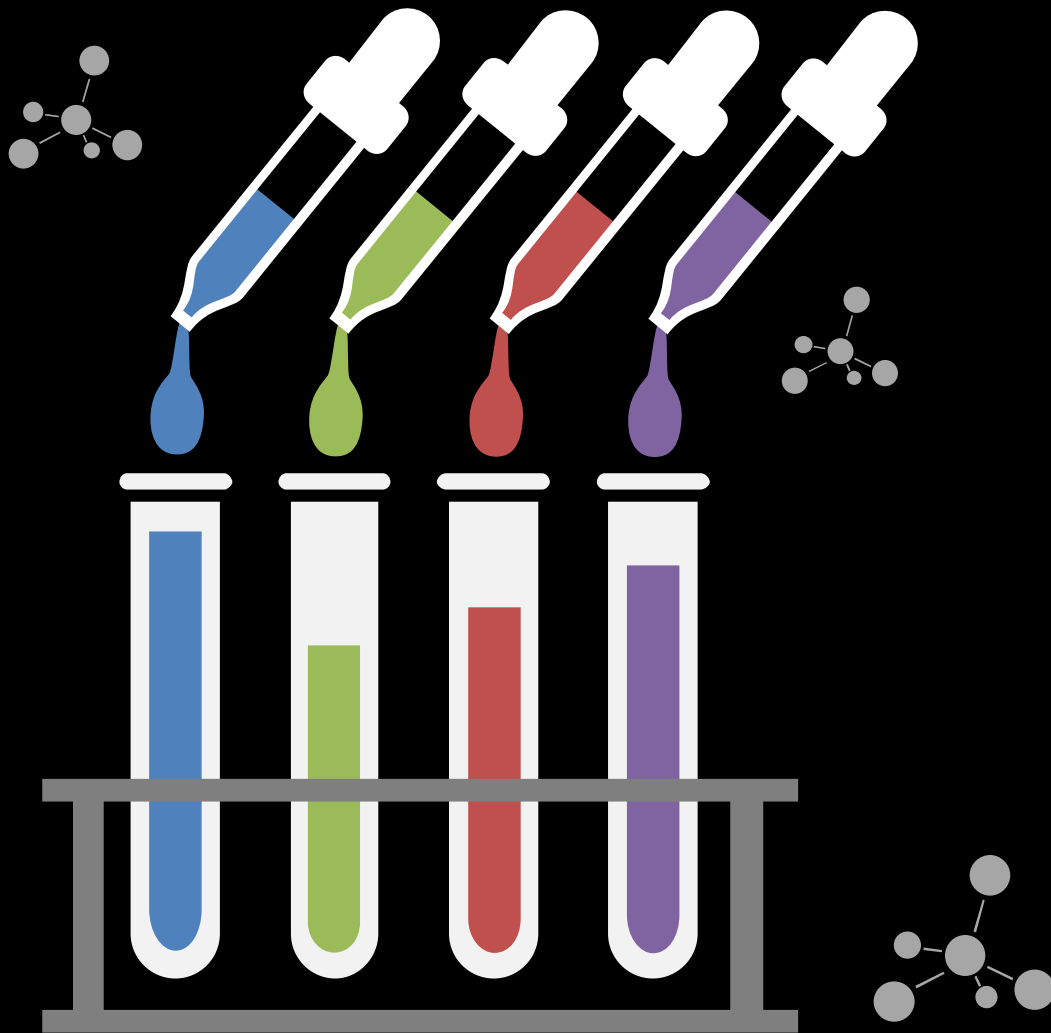
ICT Project
R27-196HS

“Rheology-Chemical Based Procedure to
Evaluate Additives/Modifiers used in
Asphalt Binders for Performance
Enhancements”

Dr. BK Sharma

Dr. Hasan Ozer

Dr. Imad Al-Qadi



Binder Chemistry



Evaluating the effect of modifiers on the binder chemistry and performance

Long Term Aging



Developing an efficient long-term aging procedure for modified binders

Modifier Chemistry



Conduct thorough chemical characterization of modifier

Validation



Validate and fine-tune the preliminary thresholds established

Rheology

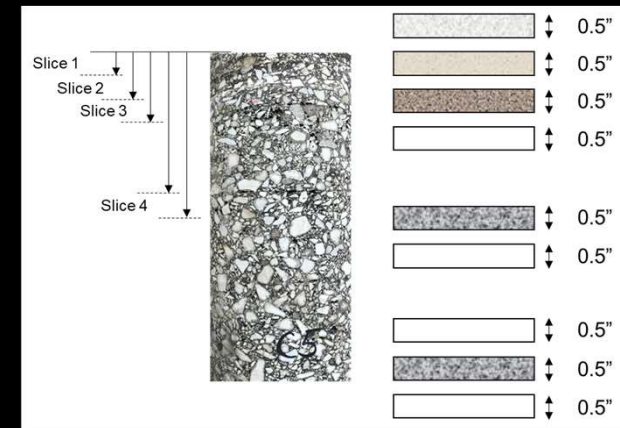
- FS (G_r , w_c , R-value)
- BBR (ΔT_c)
- LAS

- 20-hr PAV
- 40-hr PAV
- 60-hr PAV
- Modified PAV to match real time aging



Chemistry

- FTIR
- GPC
- TLC FID, SARAD
- Microscopy
- TGA/DSC

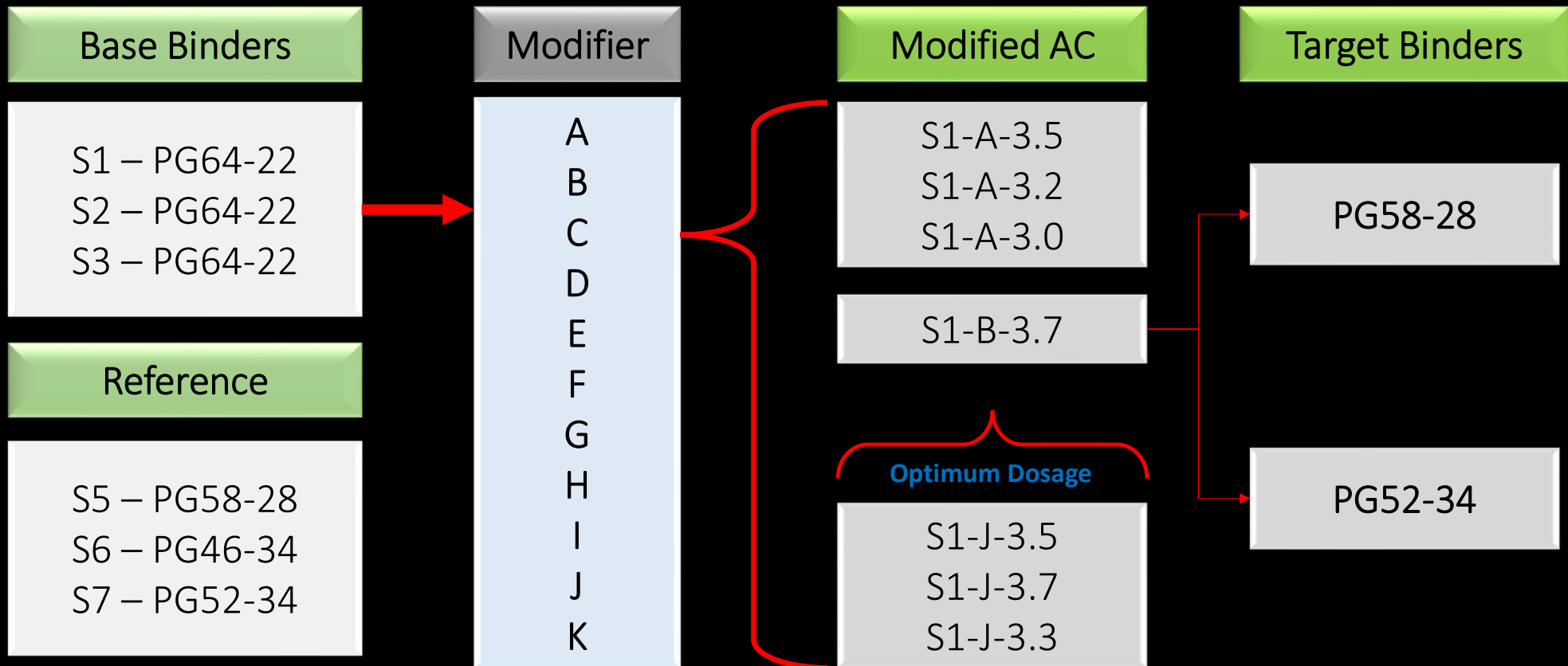


Long-Term Lab Aging

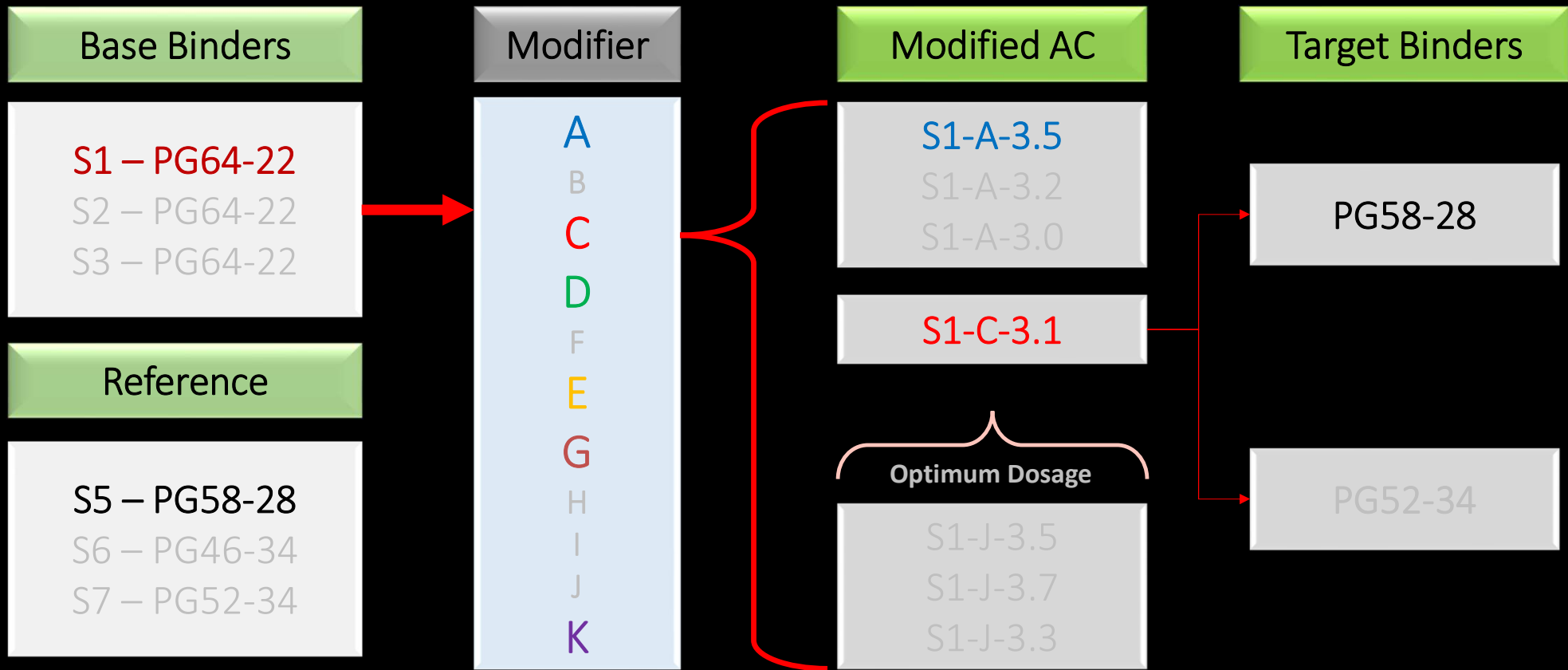
Modifiers

Modifier ID	Type	ID	Binder	Qty.
A	NA	S1	PG 64-22	110 gal.
B	Fatty acid derivatives	S2	PG 64-22	50 gal.
C	Fatty acid derivatives	S3	PG 64-22	50 gal.
D	Bio Oil Blend	S5	PG 58-28	20 gal.
E	Mod. Veg Oil	S6	PG 46-34	20 gal.
F	Mod. Veg Oil	S7	PG 52-34	20 gal.
G	Glycol Amine	S8	PG58-28	4 gal.
H	Asphalt	S9	PG64-22	4 gal.
I	Soybean Oil, Methyl ester			
J	Vegetable oil			
K	ReOB			
L	NA			

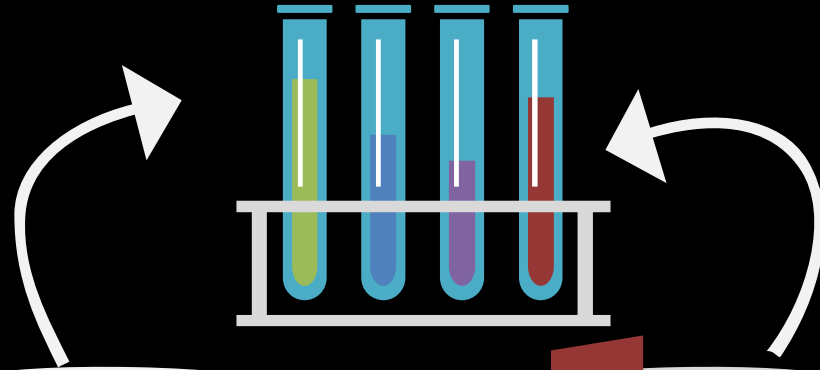
Binder Modification Matrix



Modifiers Tested



Binder Rheology



1. Base and Reference Binder

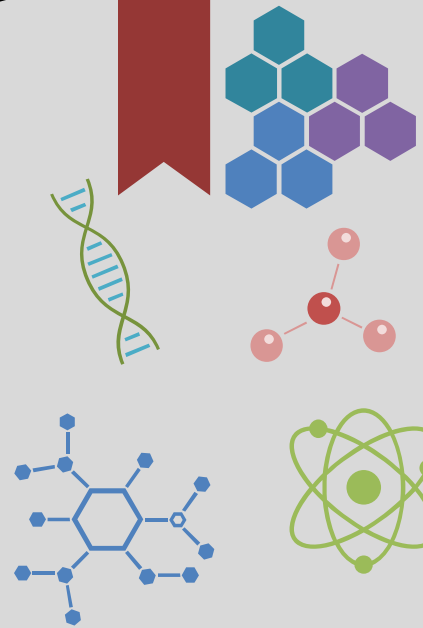
2. 11 Modified Binders

3. Optimum dosage

4. Source variability

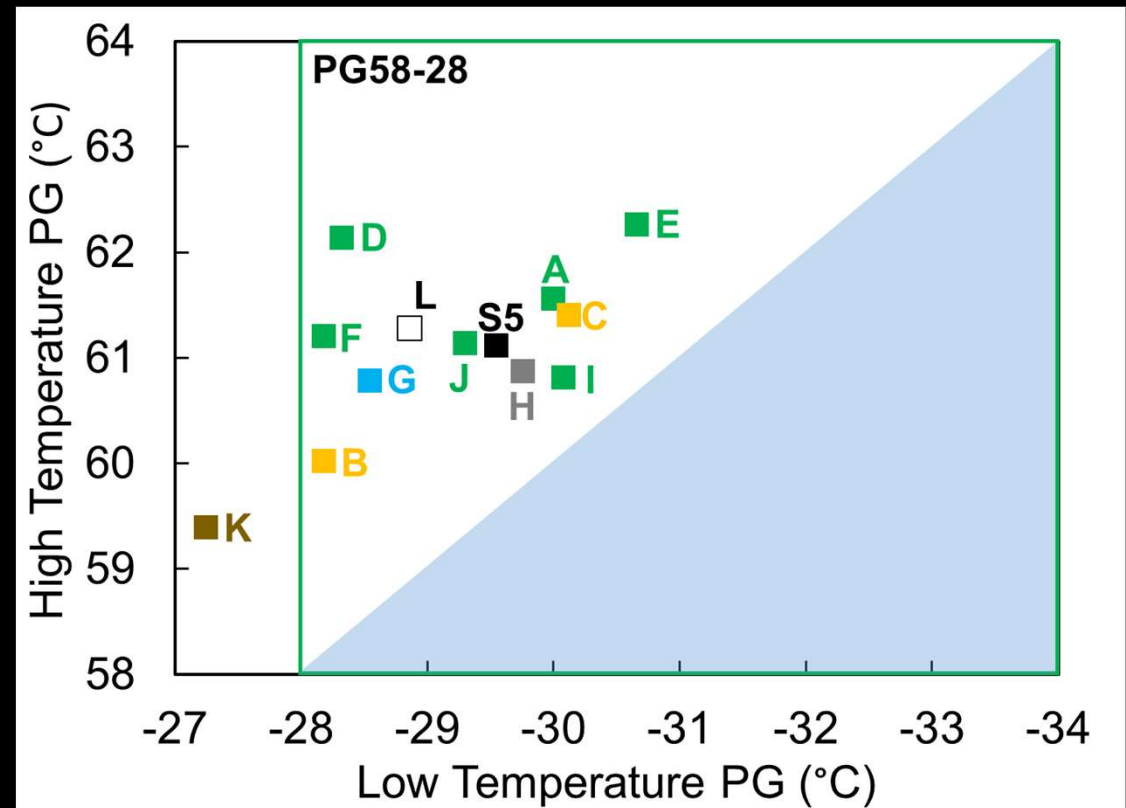
5. Other softer PGs, 52-34

Select modifiers for select aging conditions



Superpave PG Grading

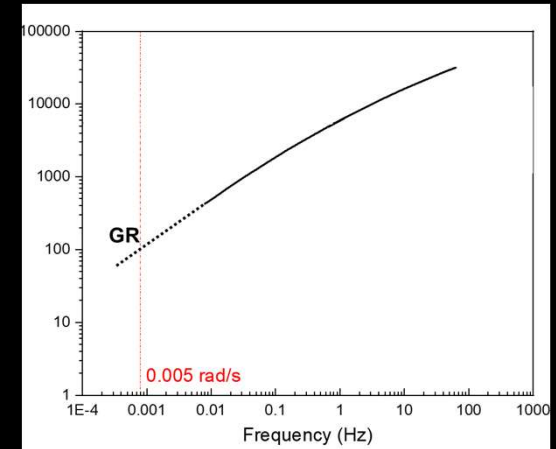
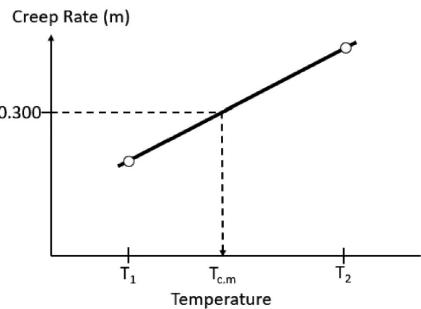
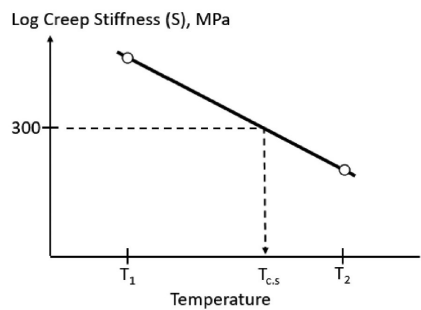
- ❖ S1 modified to 58-28s
- ❖ Modification concentrated to one region (**right**)
- ❖ Modifier **K**, ReOB **failed** to achieve 58-28 with S1
- ❖ During optimum dosage determination, modifiers will be selected to populate the **left** triangle.





Rheological Work Summary

Small-strain parameters – Low temperature



BBR: ΔT_c

Relaxation under
creep loading

DSR:

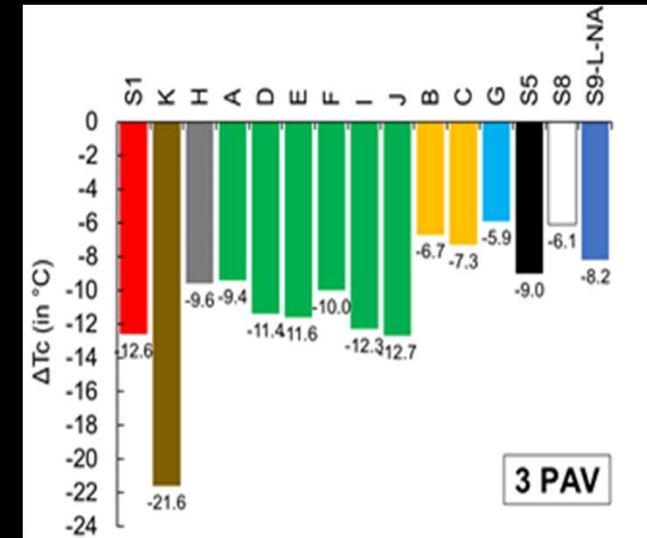
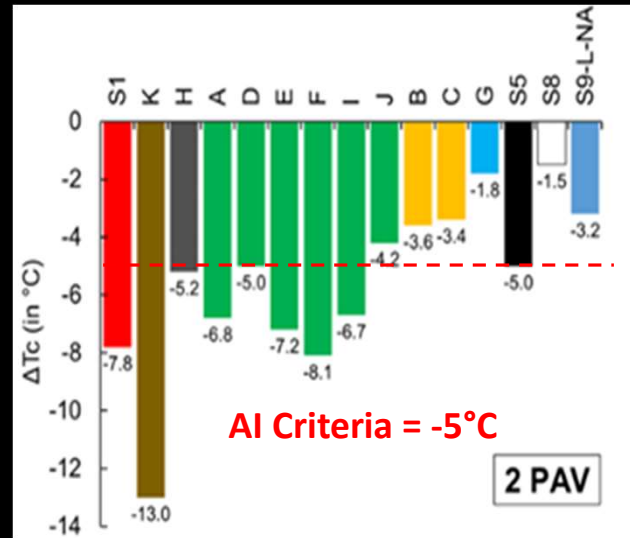
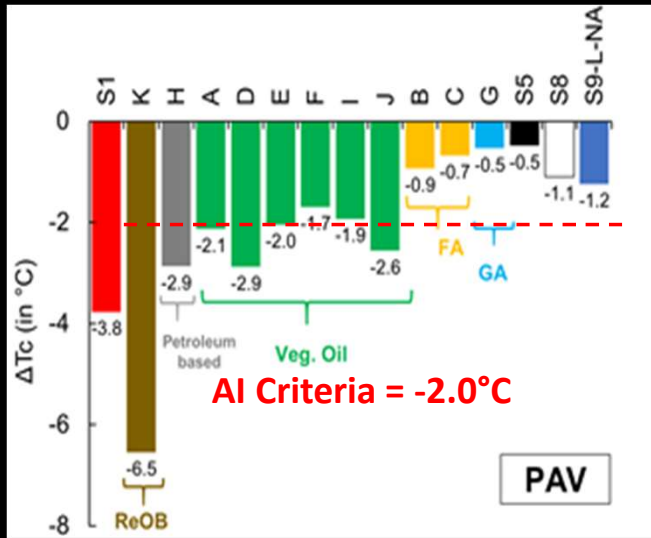
Empirical relationship to ductility

Glover-Rowe (GR)

$$GR = \frac{G^* \times (\cos \delta)^2}{\sin \delta}$$

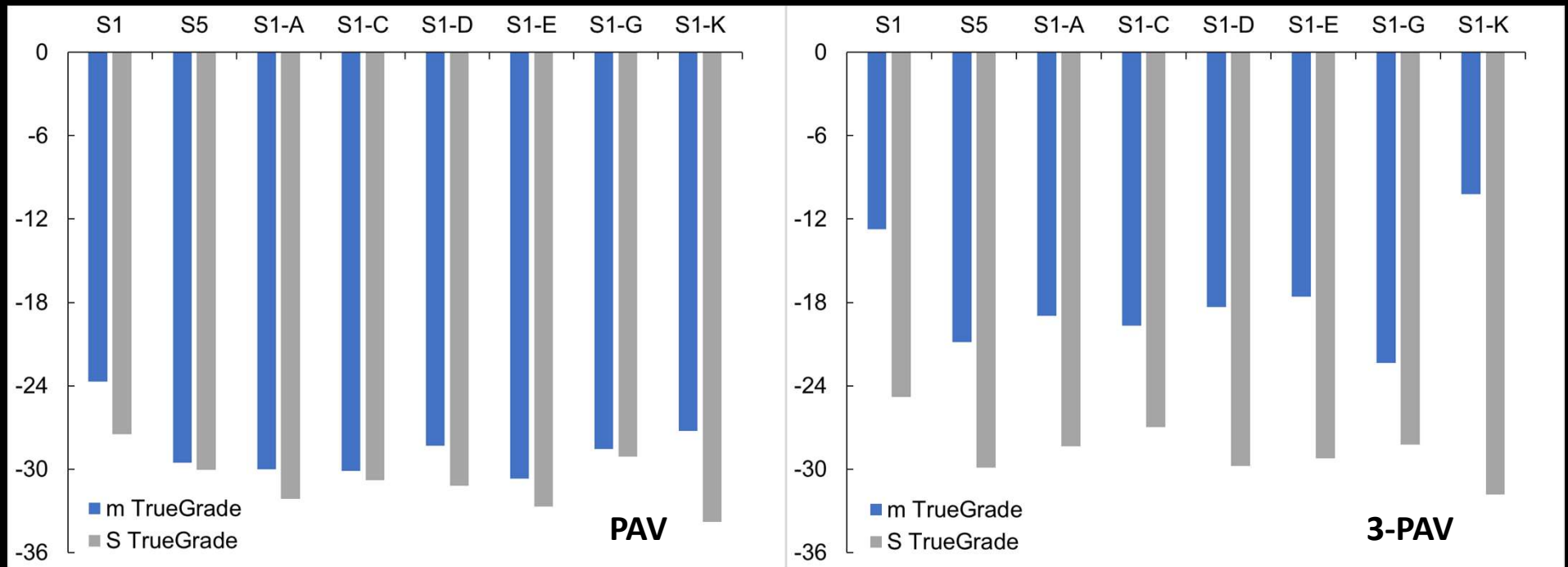
@ 0.005 rad/s

BBR ΔT_c



- ❖ ΔT_c improved with modification except K
- ❖ Glycol amine and Fatty acid derivatives perform better using the ΔT_c criteria than oil-based modifiers
- ❖ K is the worst performer
- ❖ Trends were more comparable for 2 & 3-PAV

m-value & Stiffness

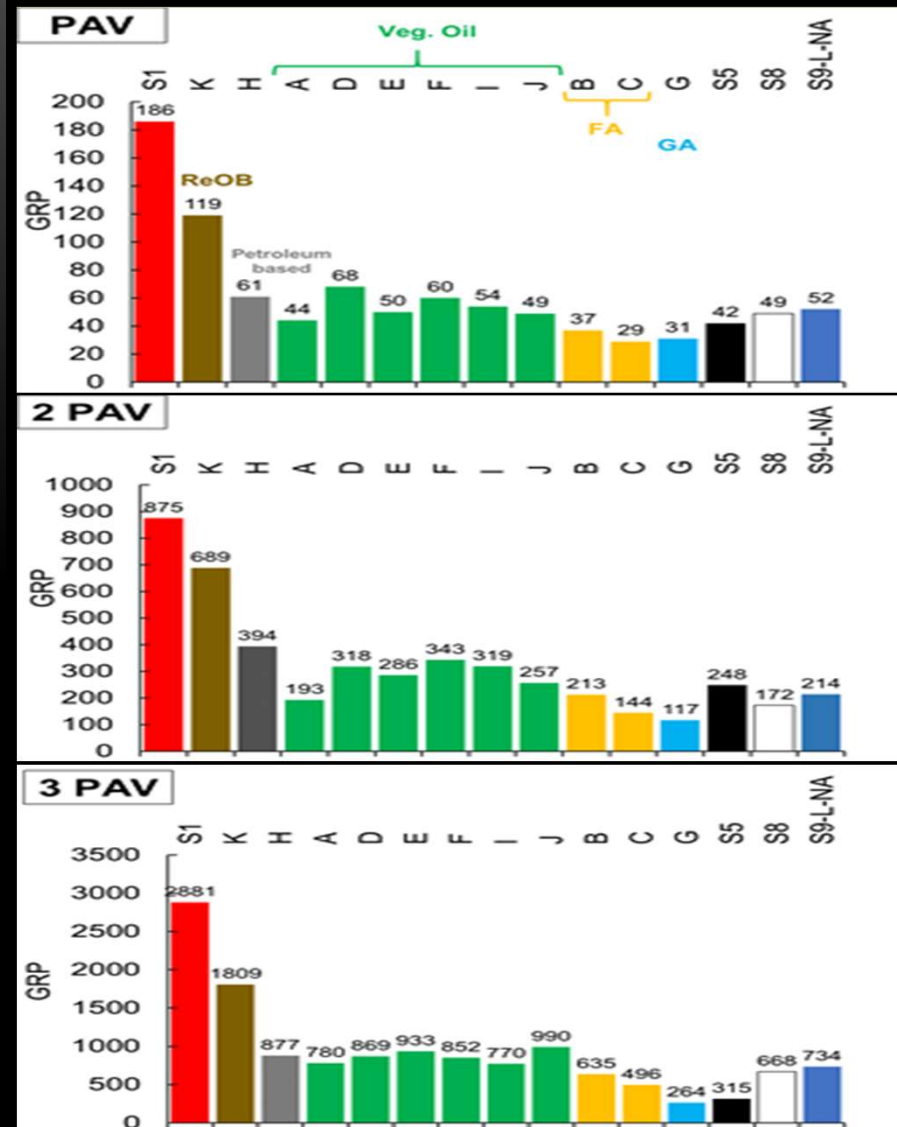


- ❖ Change in grade governed by m-value was most affected with aging
- ❖ Stiffness effect on grade with aging is insignificant

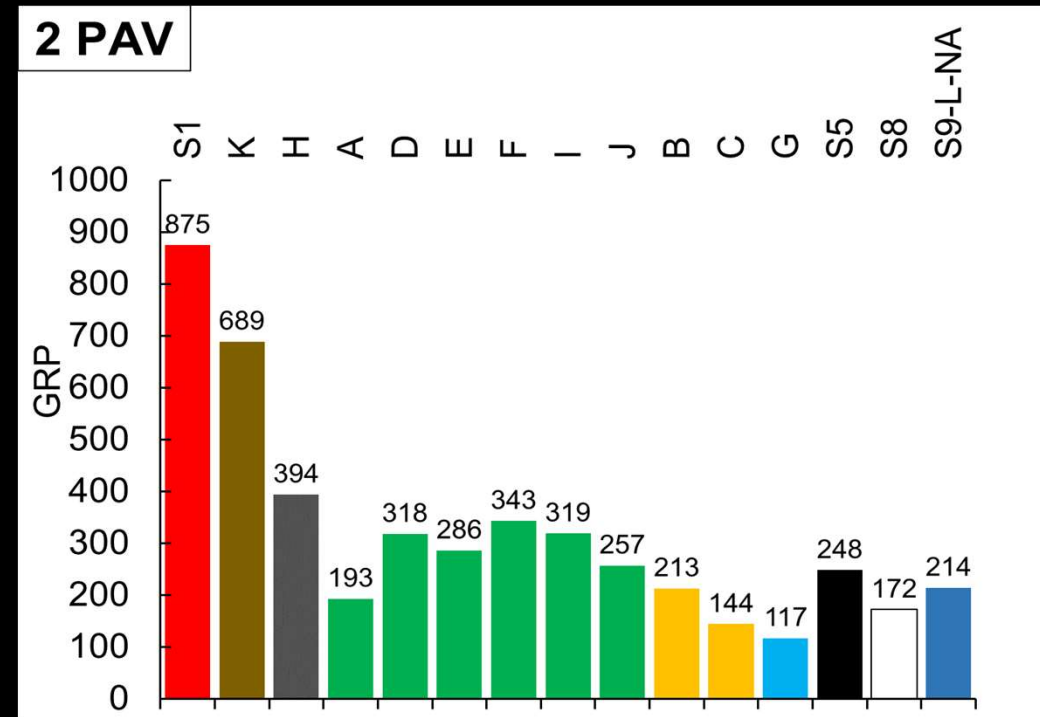
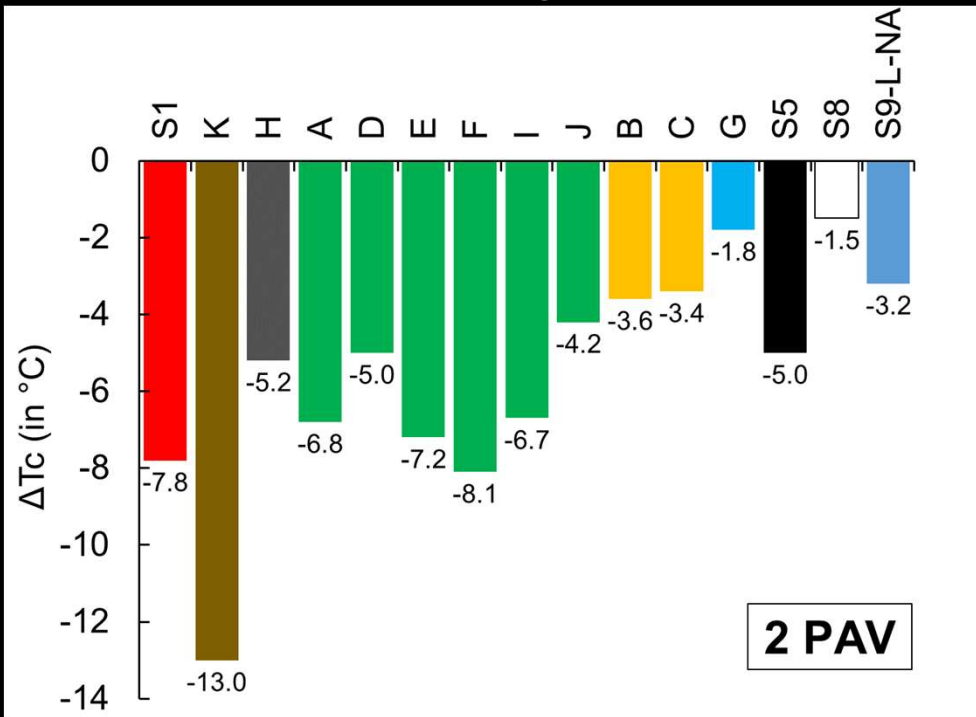
Glover Rowe Parameter

$$GR = G^* (\cos\delta)^2 / \sin\delta$$

- Glycol amine and fatty acid derivatives shows lower GRs over vegetable oil-based modifiers
- Veg. oil clusters together
- ReOB shows higher GR in all aging conditions
- All PAV conditions yield comparable trends



BBR ΔT_c vs. Glover Rowe Parameter



Two criteria characterize the performance of the modified binders similarly and provide the same general trends.

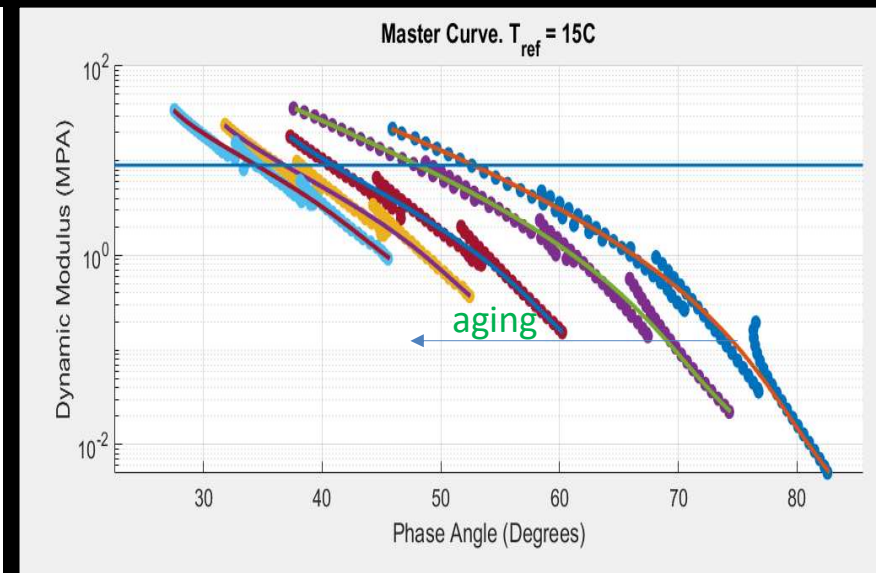
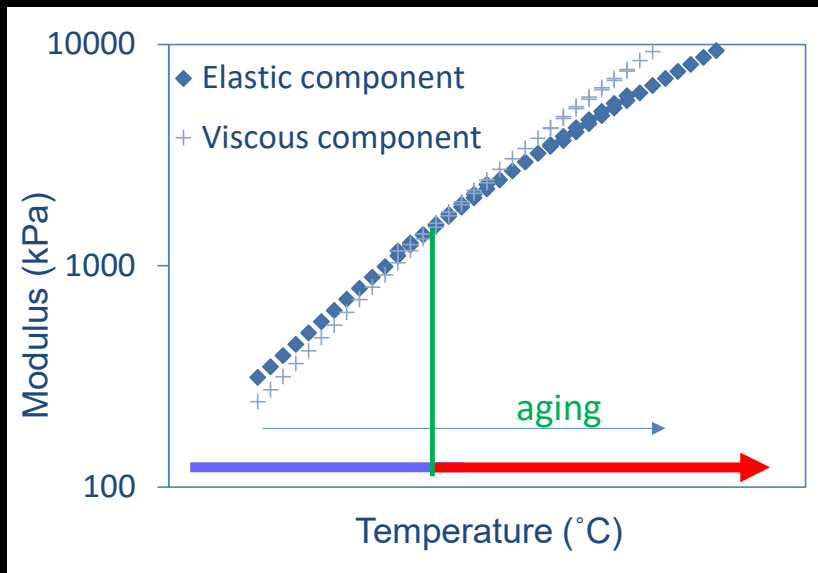
Small-strain parameters – Vehicle loading

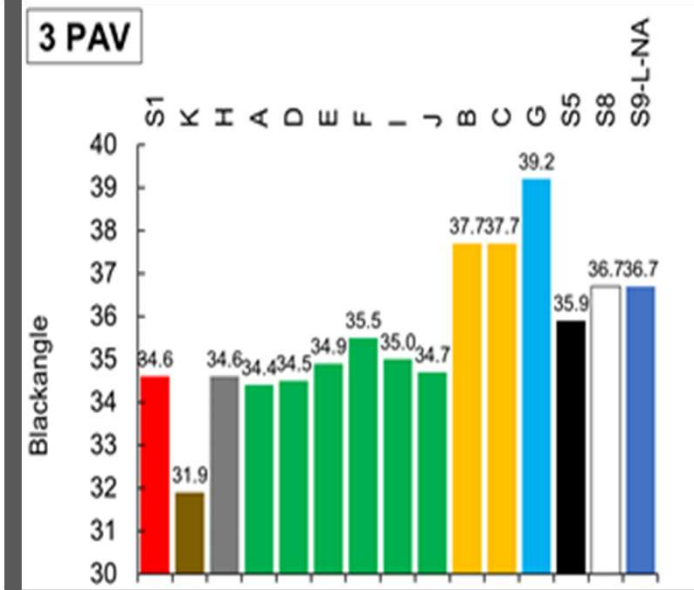
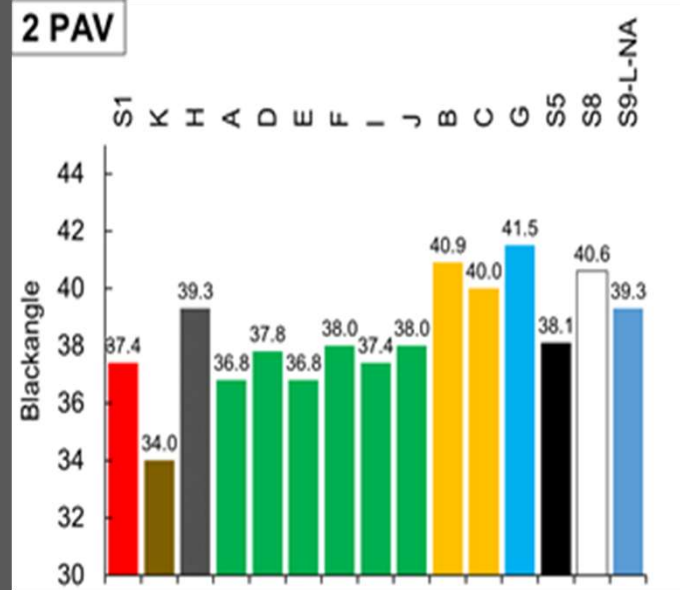
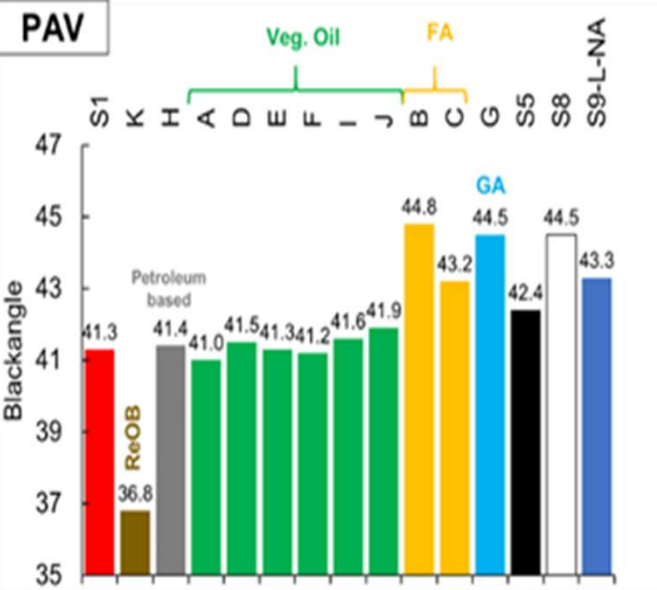
Not extreme temperatures – intermediate

DSR: Frequency Sweeps

- Crossover parameters
- Viscoelastic Transition Temperature

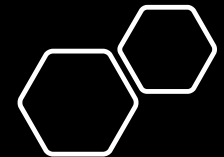
- Black angle
- Phase angle at $G^* = 8.96\text{MPa}$





Black Angle:
Phase Angle @ 8.9 MPa

- ❖ Glycol Amine & fatty acid derivatives retains more viscous part than elastic compared to vegetable oil-based modifiers
- ❖ ReOB performs worst
- ❖ Phase angle for vegetable oils are in similar range
- ❖ Results of all PAV conditions are comparable, except H (2-PAV)



Linear Amplitude Sweep (LAS) Test

Testing parameters:

- **Sample size:**
 - 8 mm dia. 2-mm gap
- **Temperature: @ Intermediate PG**
 - For 58-28 – 19°C, 64-22 – 25°C
- **Frequency:**
 - 10Hz (62.8 rad/s)
- **Strain level:**
 - 0.1 to 30% in 300 seconds



LAS Failure Investigation

Failure planes for PAV and 3 PAV significantly different

S1-D-3.1



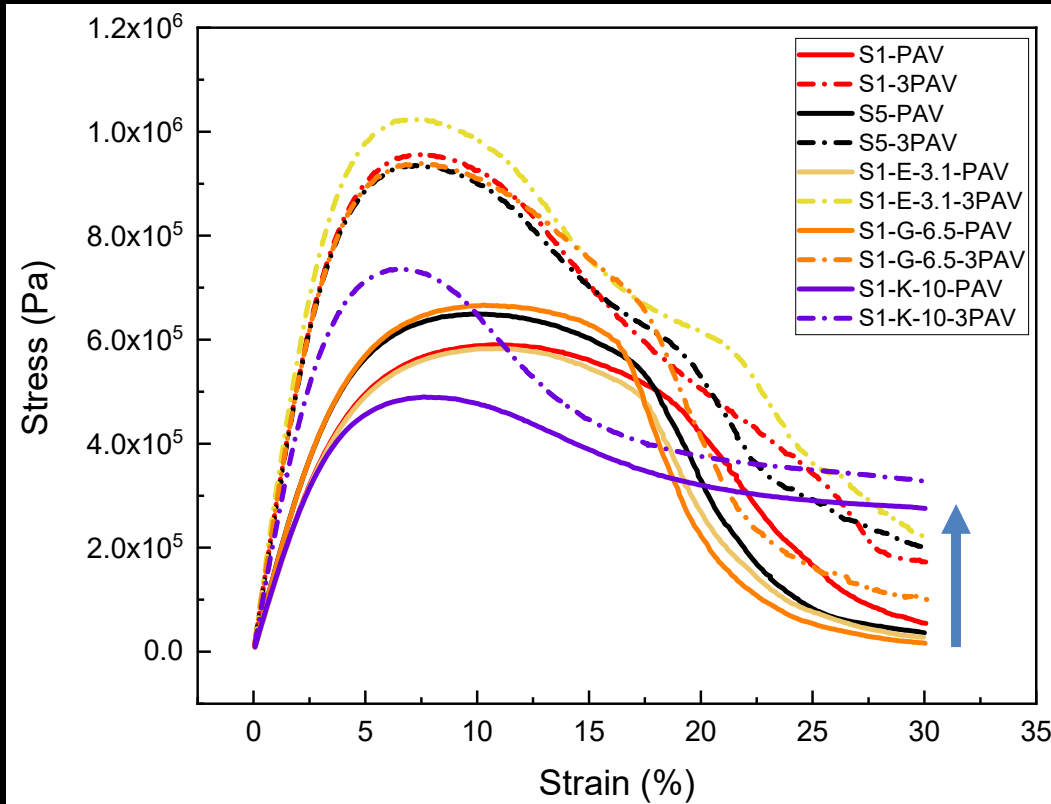
S1-C-3.1



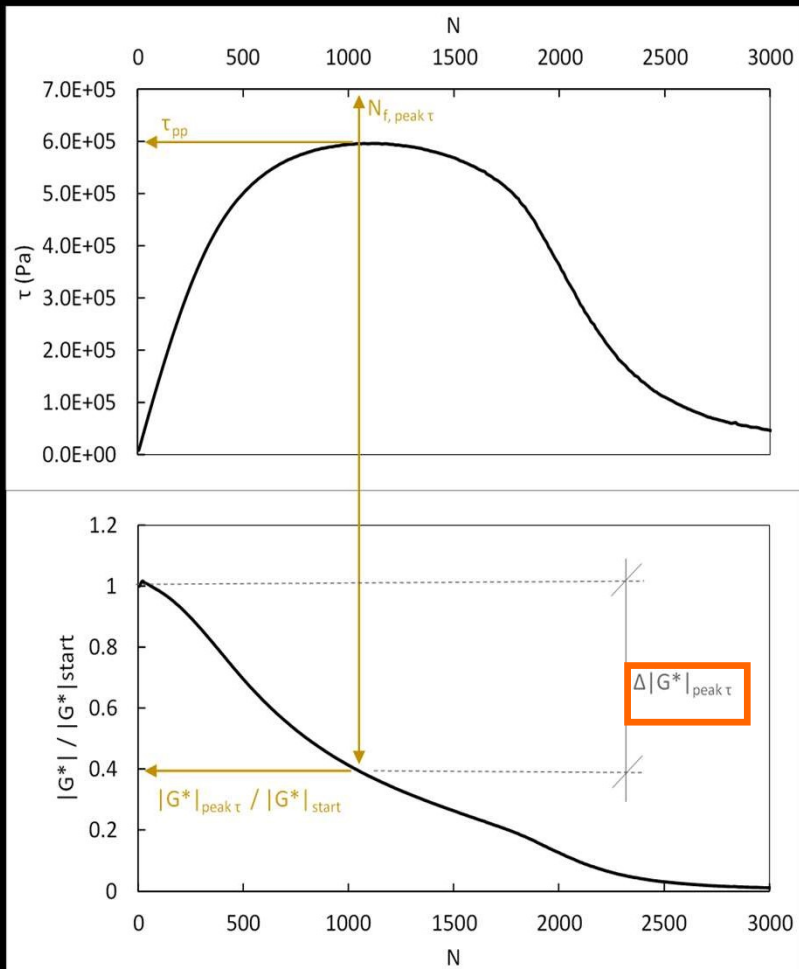
PAV

2-PAV

3-PAV



New parameter $\Delta |G^*|_{\text{peak } \tau}$



$\Delta |G^*|_{\text{peak } \tau}$ (delta G for short)

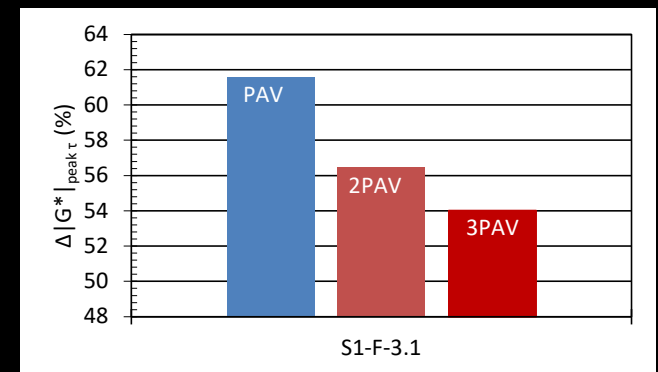
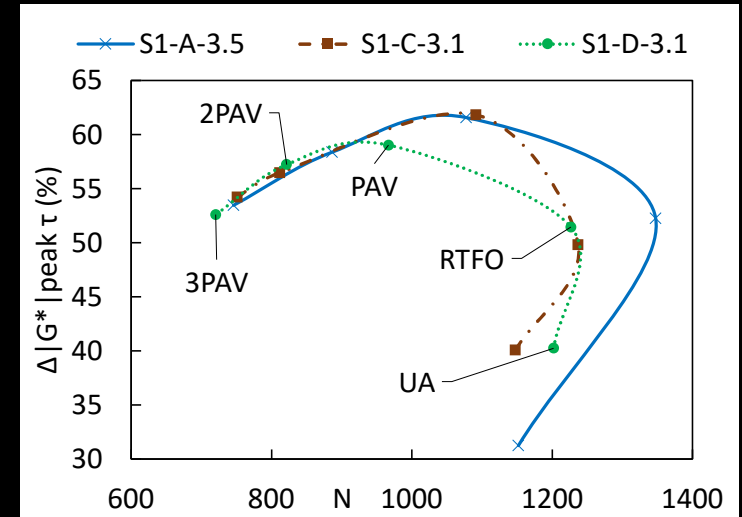
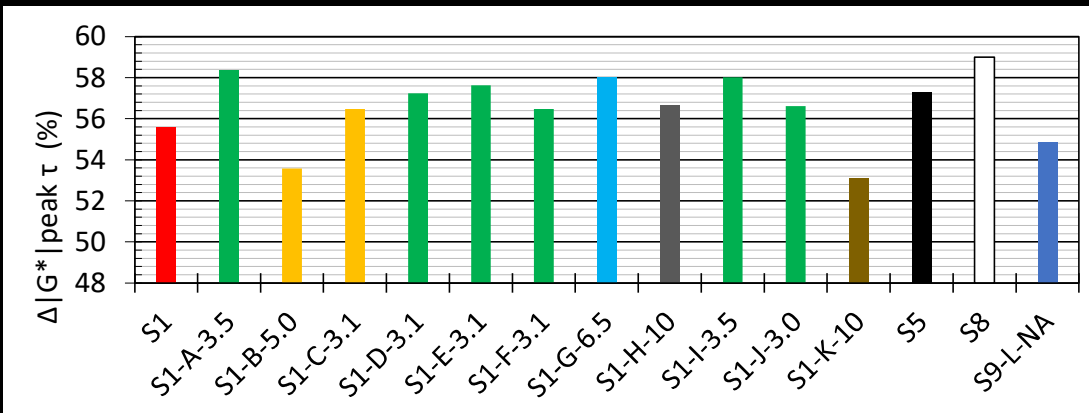
- ✓ Data until peak stress
- ✓ Avoid 3-D stresses
- ✓ Peak stress is an evident response phenomenon
- ✓ State of the sample as indicator
- ✓ Not endurance
- ✓ Not highly influenced by stiffness
- ✓ No convoluted post-processing
- ✓ Higher $\Delta |G^*|_{\text{peak } \tau}$ = **Better** performance

Findings enabled by $\Delta |G^*|_{\text{peak } \tau}$

- Optimum properties at almost-PAV-aging condition
- Consistent results that distinguish modified binders and aging

Effect of aging →

Effect of modification (2PAV)



Summary of Rheology Work

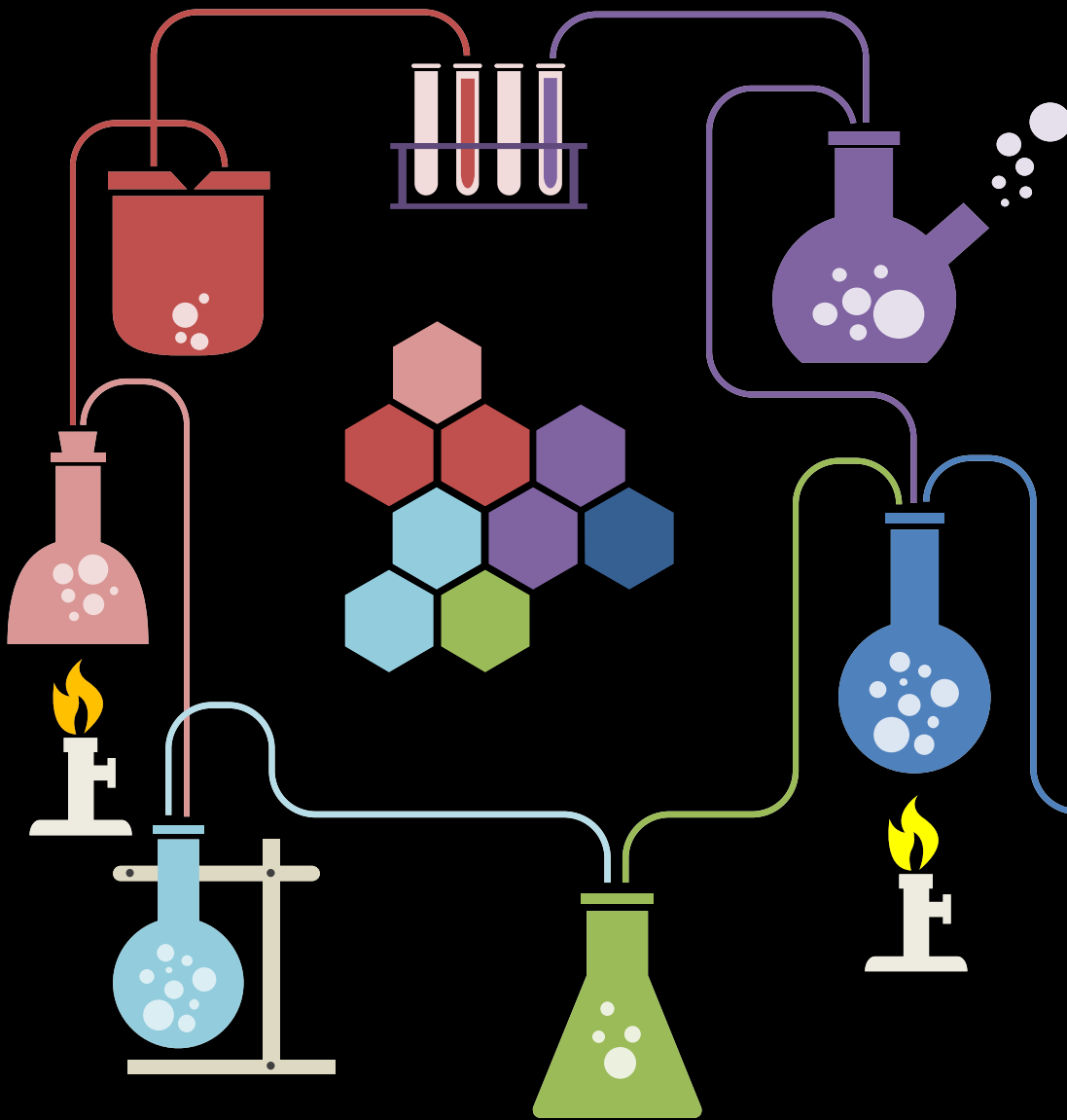


- ❖ Modifier K (ReOB) could not be modified to 58-28 with S1
- ❖ ReOB modifier consistently worst rheological performer
- ❖ Modification of S1 improved ΔT_c for all modifiers except K
- ❖ Glycol amine and fatty acid-based modifiers demonstrate better cracking resistance characteristics compared to vegetable oil-based modifiers.
- ❖ Small strain parameters: FS and ΔT_c are promising indicators for rheological performance and correlate well.
- ❖ ΔT_c trends for the modified binders are mostly consistent with aging, especially 2-PAV & 3-PAV
- ❖ m-value is the governing factor determining grade with long-term aging after 1PAV

Summary of Rheology Work



- ❖ Large strain parameters are indicators of different characteristics than small strain parameters.
- ❖ LAS and proposed $\Delta |G^*|_{\text{peak } \tau}$ shows excellent promise. It provides consistent trends with aging and known binder data from small strain tests. This parameter was able to distinguish some performance differences that the small strain parameters did not.

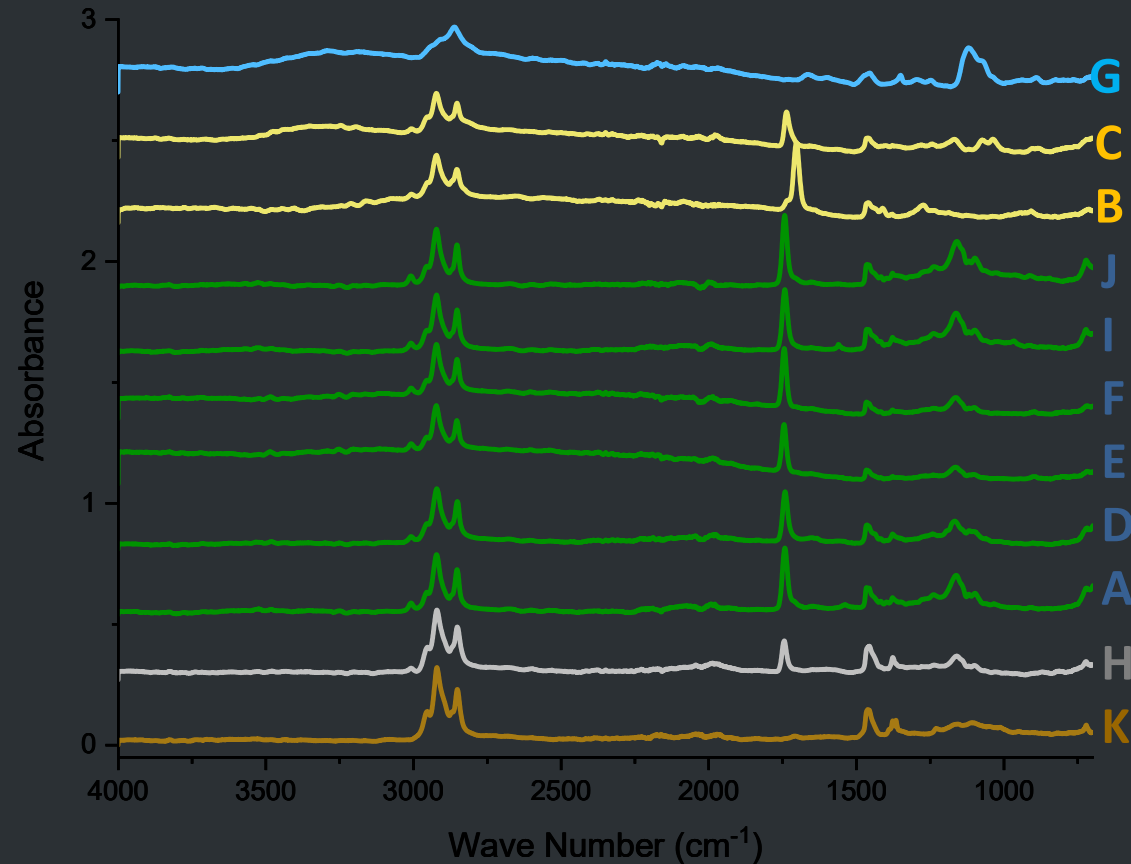


Modifier Chemistry Results

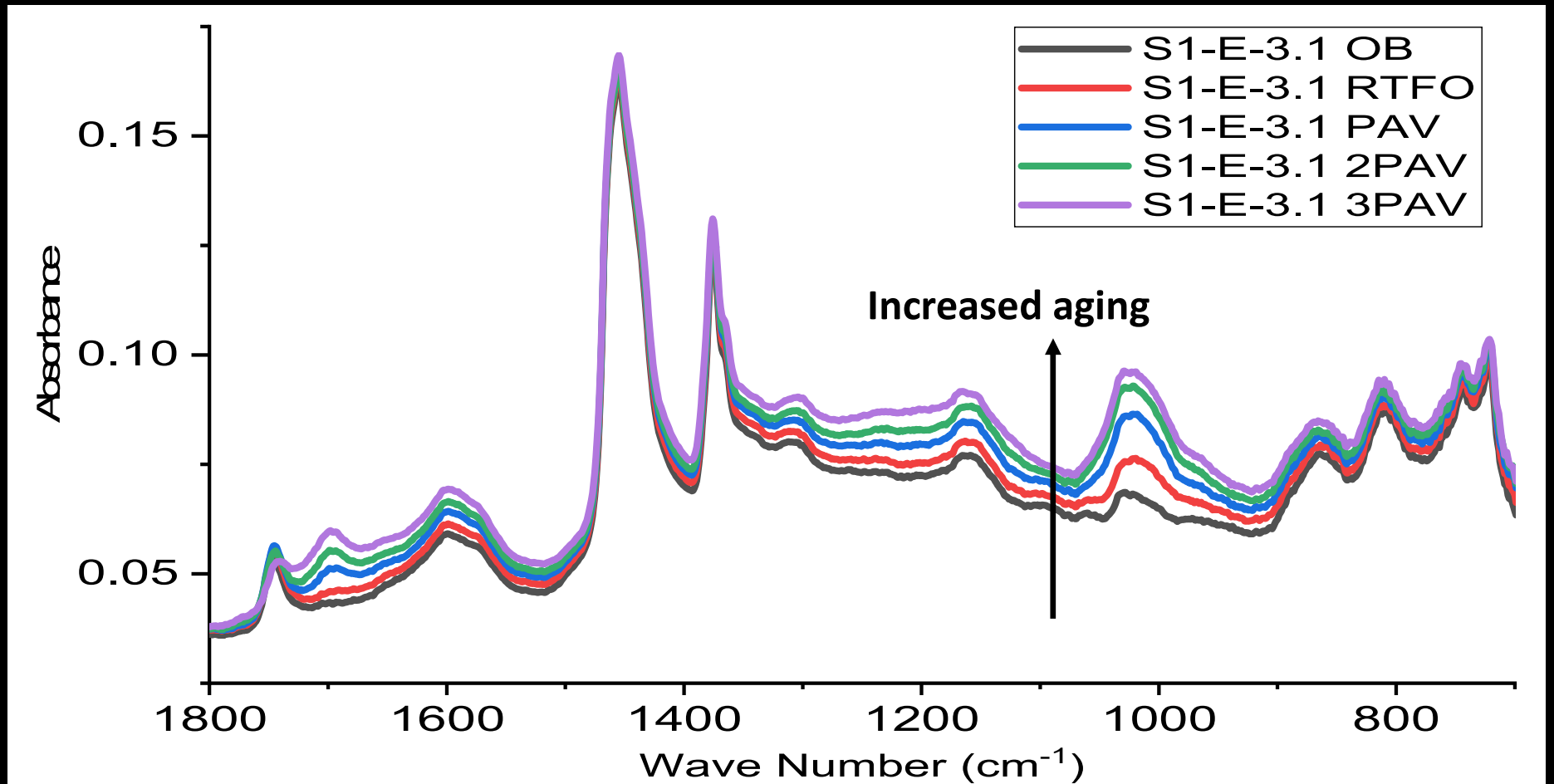
- ❖ Six Modifiers Tested
- ❖ Chemical Characterization
 - ❖ CHNS
 - ❖ FTIR
 - ❖ TGA
 - ❖ TLC-FID
 - ❖ GPC
- ❖ Develop a Fingerprint

Modifier Chemistry - FTIR

- Spectra of Veg. oil-based modifiers shows similar chemistry
- Fatty acid derivatives lacks $-C-O-$ group, confirmed by spectra
- ReOB lacks carbonyl peak, indicating absence of bio-based source
- Modifier H, presumably petroleum derivative shows signs of bio-oil presence



Impact of Aging on Binder Chemistry



Oxidation Indices

❖ Carbonyl Index (ICO)

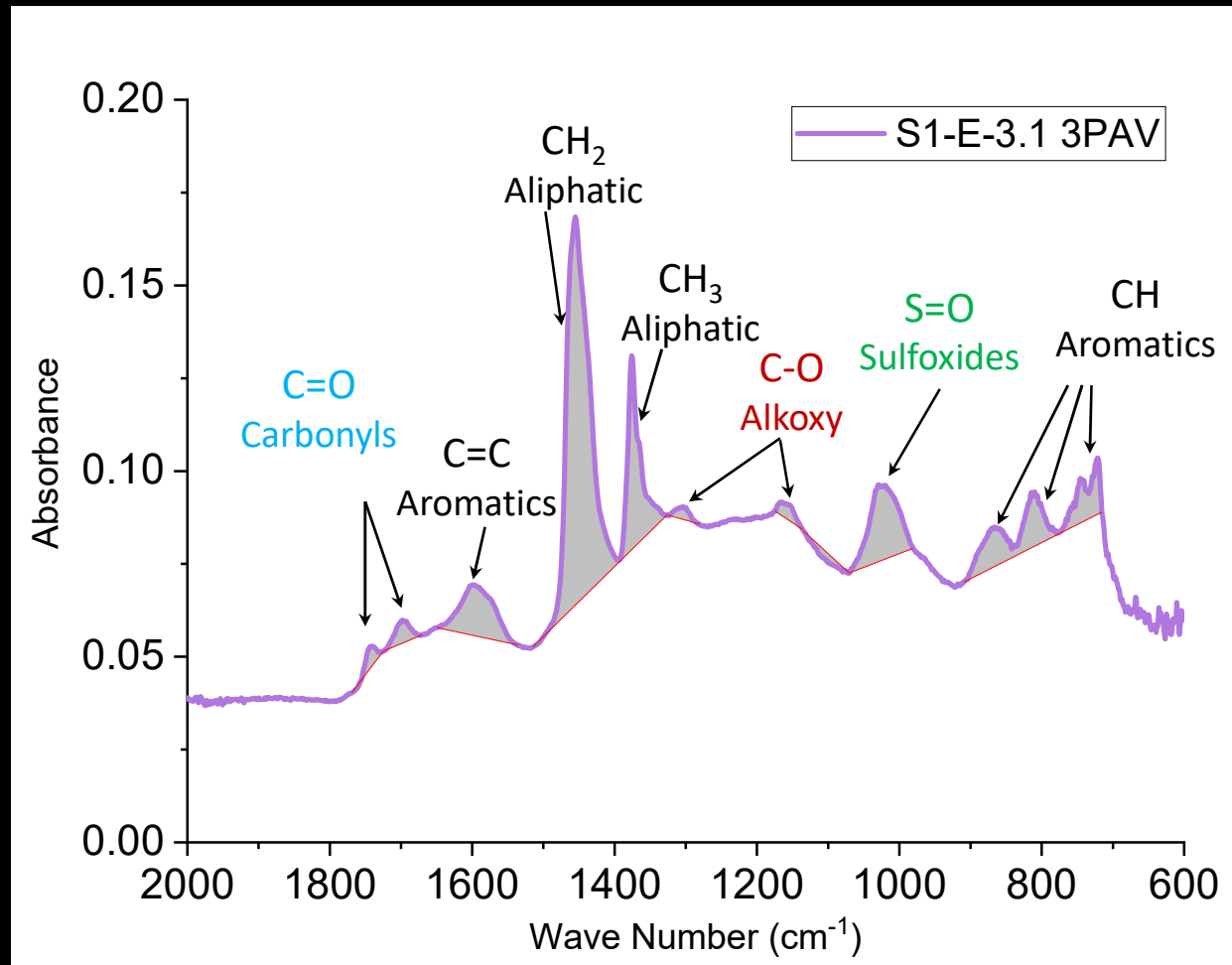
$$❖ ICO = \frac{\sum A_{1770-1650}}{\sum A}$$

❖ Sulfoxide Index (ISO)

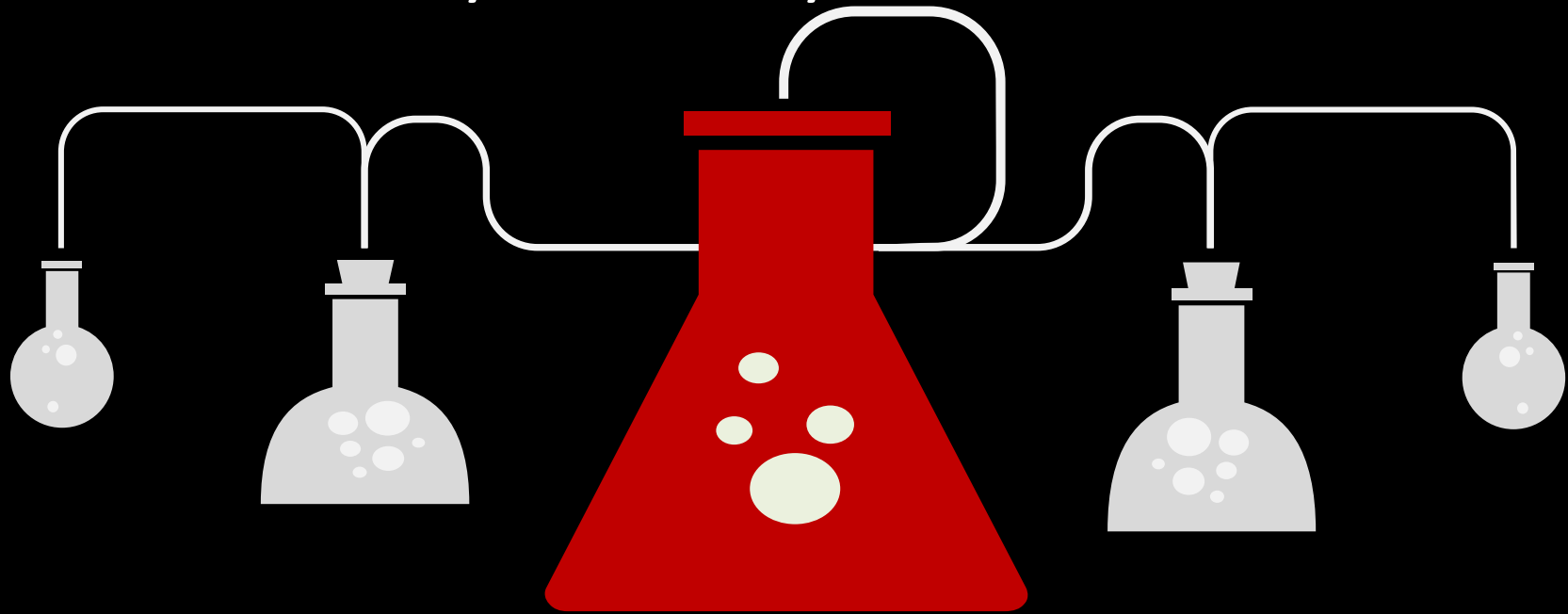
$$❖ ISO = \frac{\sum A_{1070-990}}{\sum A}$$

❖ ICO + ISO

❖ ICO + ISO + Alkoxy

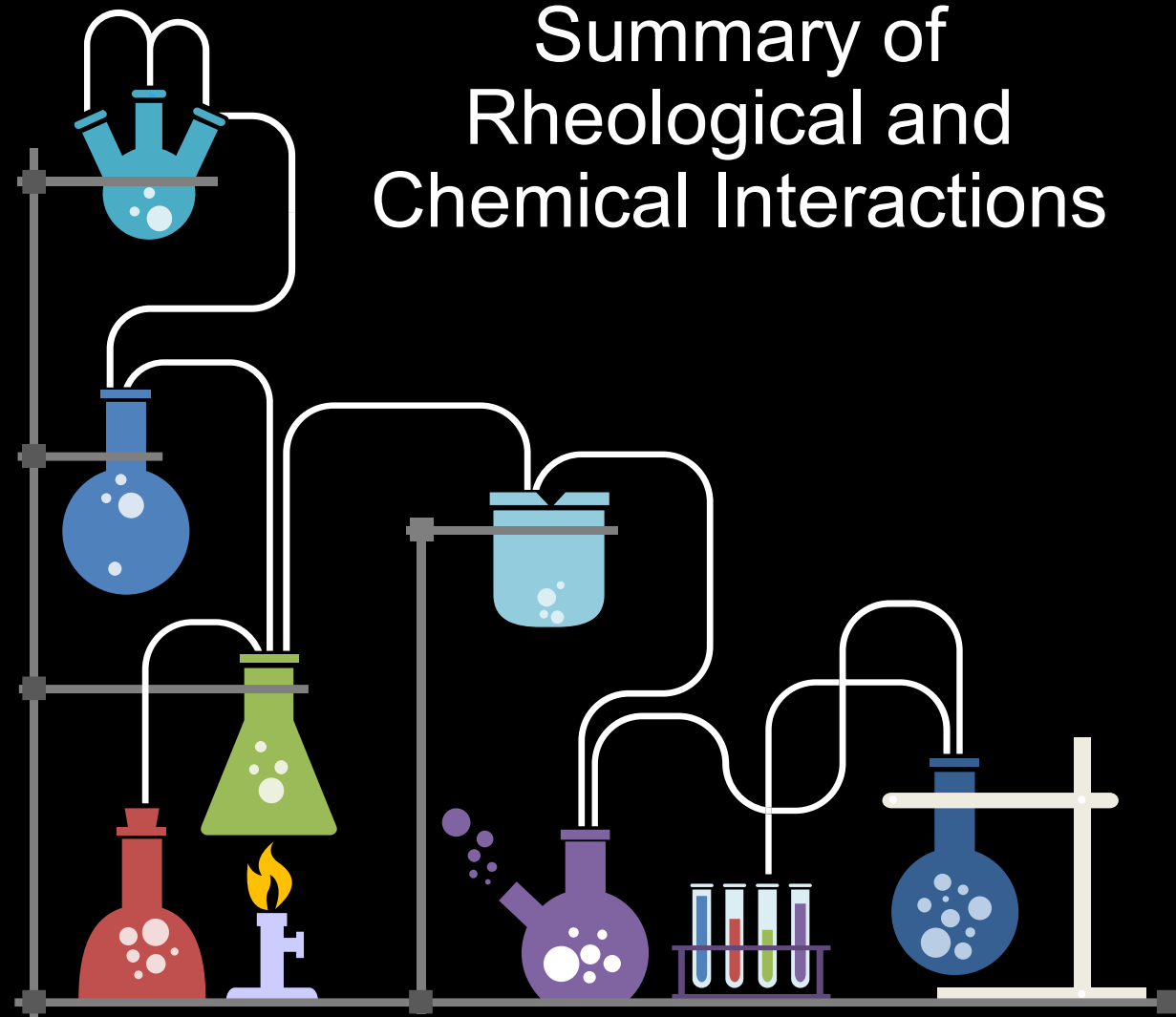


Modifier Chemistry Summary



- ❖ Oxidation products increase with aging, shown with increase in carbonyls, sulfoxides, and alkoxy groups
- ❖ Petroleum-based (asphalt like) modifier had significantly high MW, however, its FTIR spectra shows the presence of bio-based oil
- ❖ Glycol amine (GA) modifier had the most distinct chemical functional groups compared to other modifiers, and it is high in nitrogen (retards aging).
- ❖ Vegetable oil-based modifiers have similar FTIR spectra and MW distribution
- ❖ Fatty acid based modifiers had similar FTIR spectra, however, with different MW distribution, suggesting different molecular species.

Summary of Rheological and Chemical Interactions



Aging results in increased oxidation products which increase brittleness. It also results in forming larger molecules.

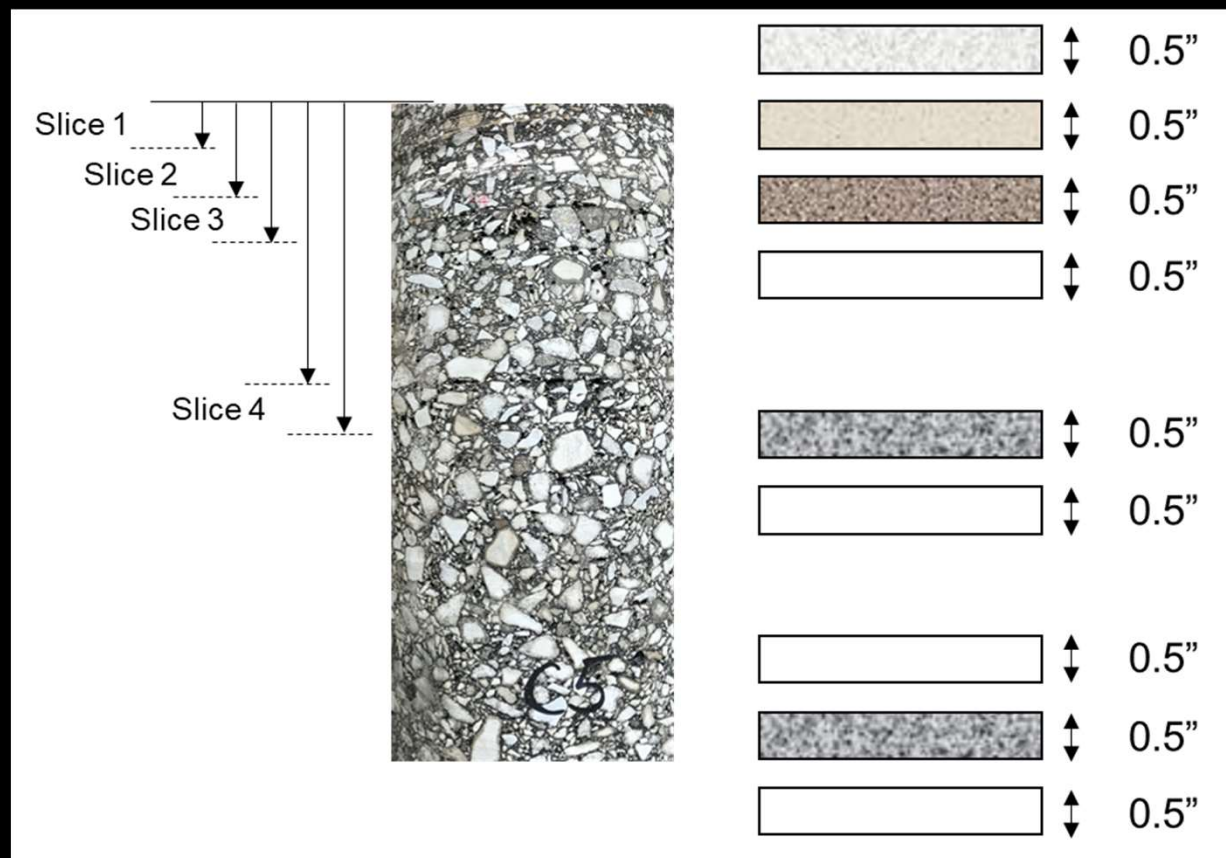
Field Core Inventory



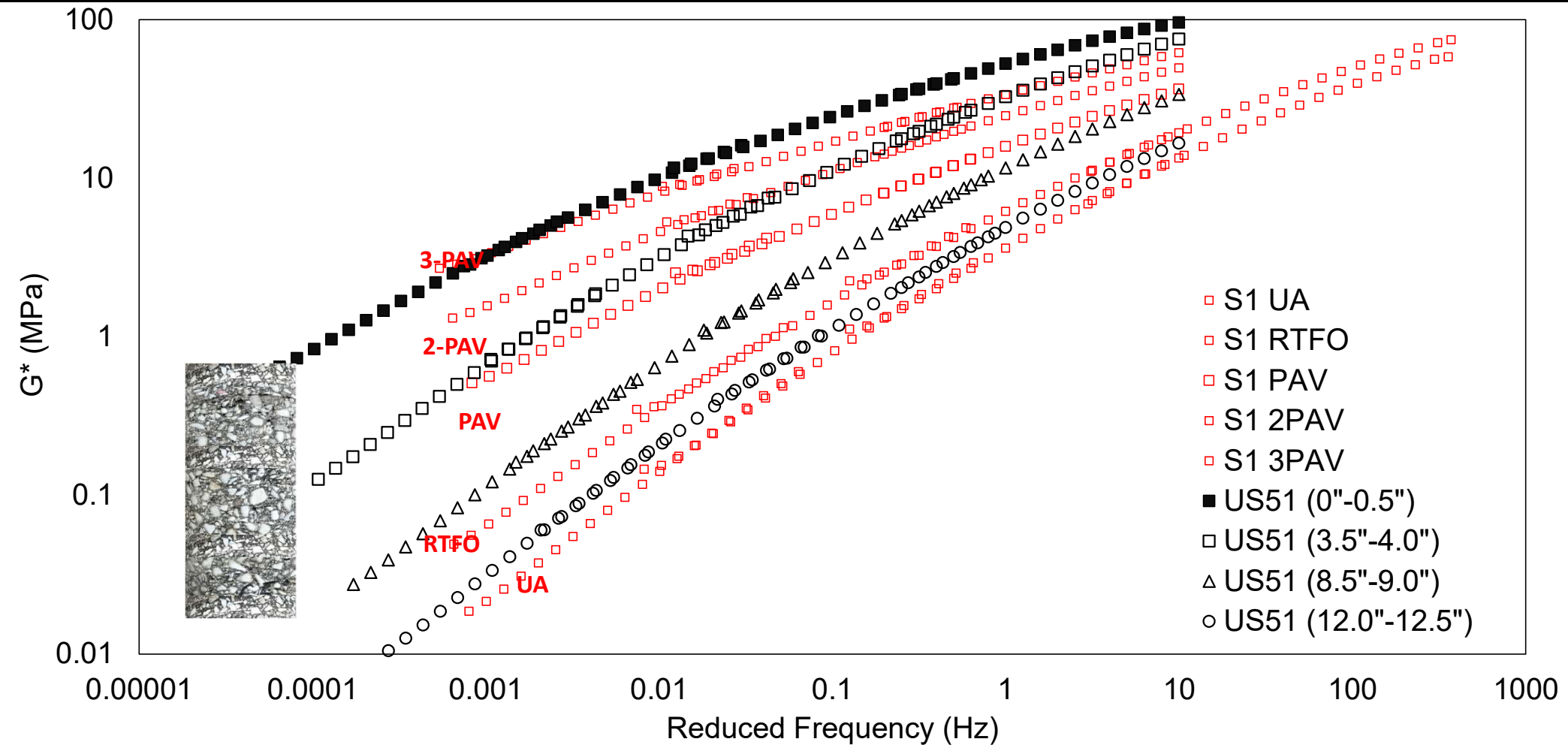
Field Core ID	District	Binder PG	Year of Construction	Year of Coring	Age
I-355	D2	64-22	2007	2018	11 yrs
I-90	D1	64-22	2006	2018	12 yrs
22STR2	D2	58-22	2004	2014	10 yrs
2RT26	D2	76-28	2004	2014	10 yrs
ICT L1	D5	64-22	2008	2019	11 yrs
ICT L2	D5	64-22	2009	2019	10 yrs
IL-125	D6	64-22	2009	2018	9 yrs
I-72 1E	D6	64-22	2003	2013	10 yrs
US-51	D8	64-22	2001	2018	17 yrs

Long-Term Field Aging

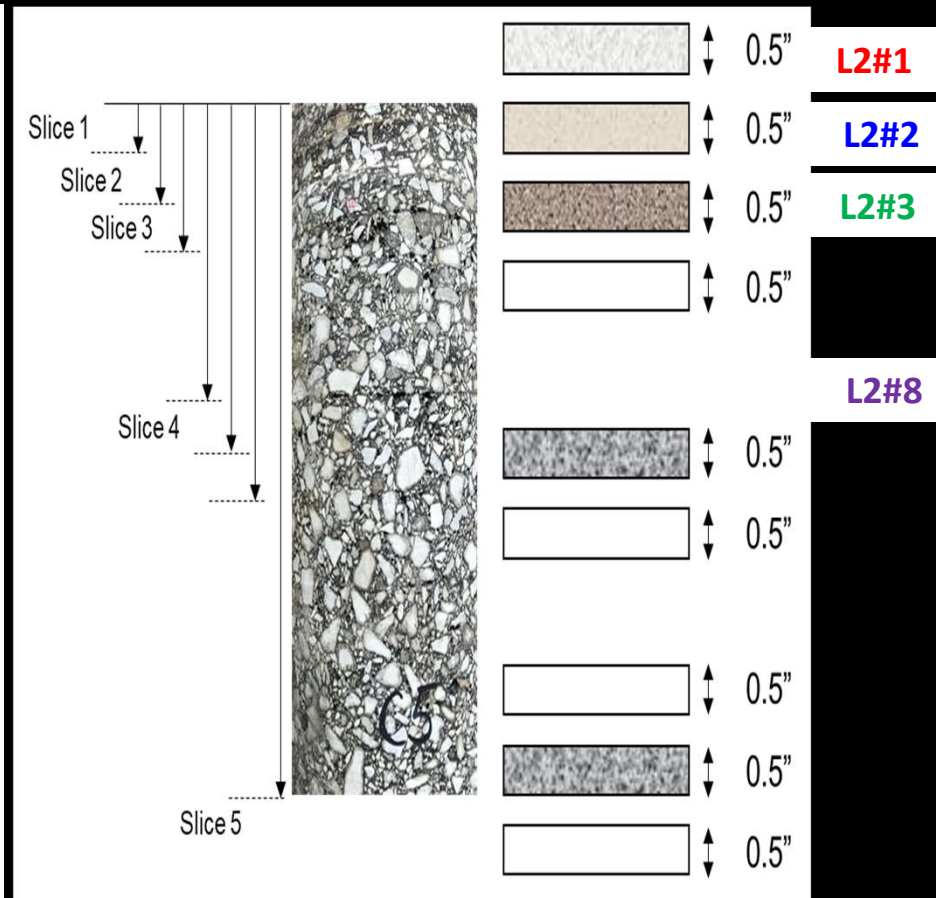
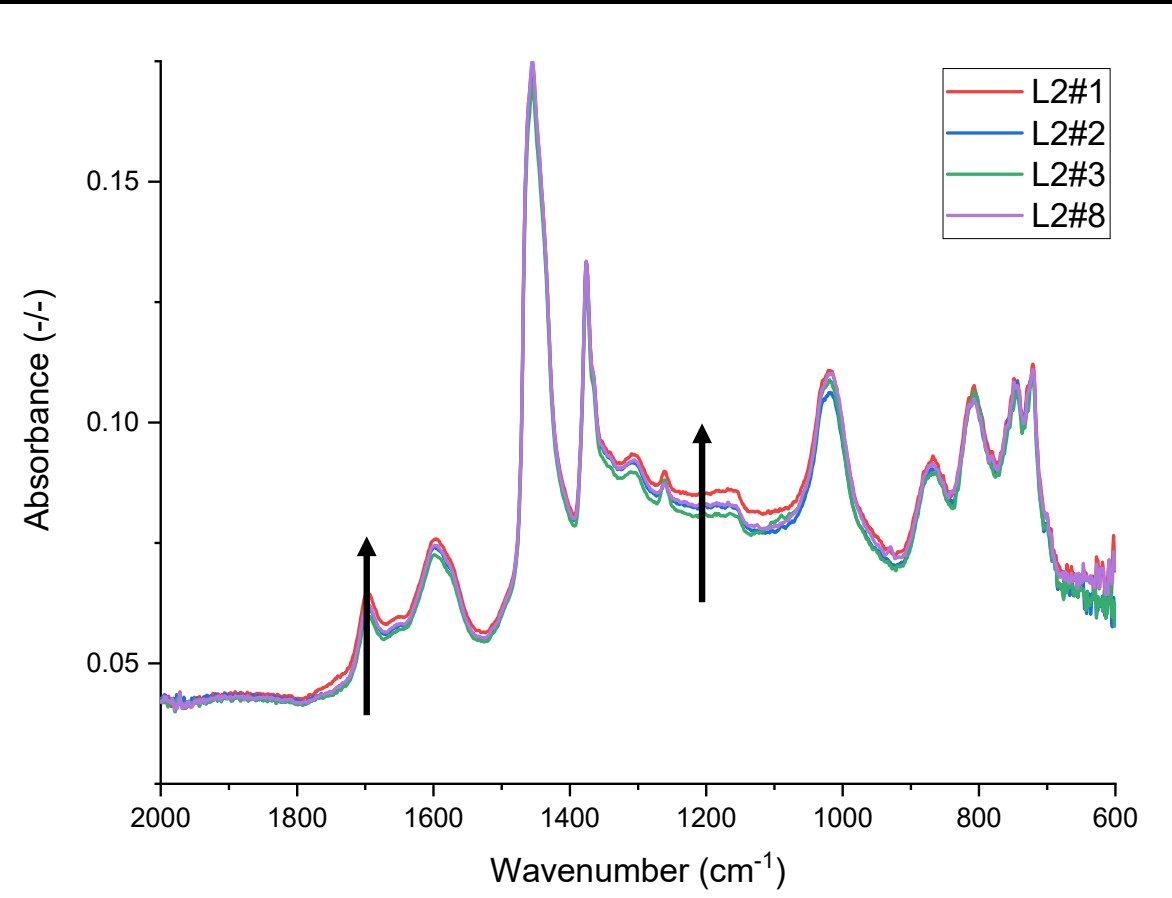
- ❖ Aging extent varies with AC layer depth
- ❖ Core sliced @ 0.5-in-depth to extract binder
- ❖ Top 0.5-in slices were considered for long-term aging characterization



Aging Gradient with Depth



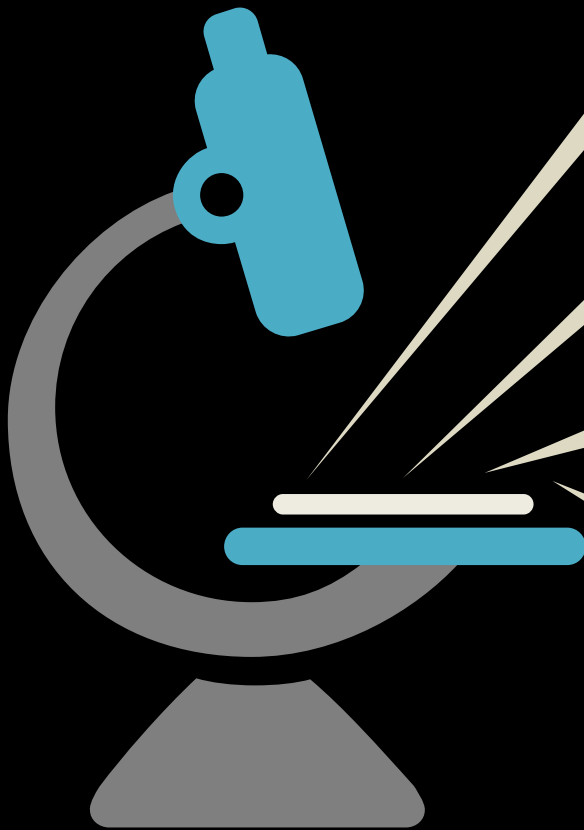
Field Core Chemistry



Field Aging of AC Surface

- ❖ **Field-aged binder is different than laboratory-aged binder**
- ❖ **Field aging varies with depth**
 - ❖ **Almost equivalent to 3 PAV at top 0.5 inch**
 - ❖ **Minimal aging at bottom of the 12-inch core, less than RTFO but more than unaged binder**
- ❖ **Results suggest that single PAV may not represent realistic field aging.**

Overall Summary



Rheology and chemistry tests presented distinct performance of the modifiers examined



All of the rheological parameters were significantly affected by aging, 2-3 PAV to represent field aging.

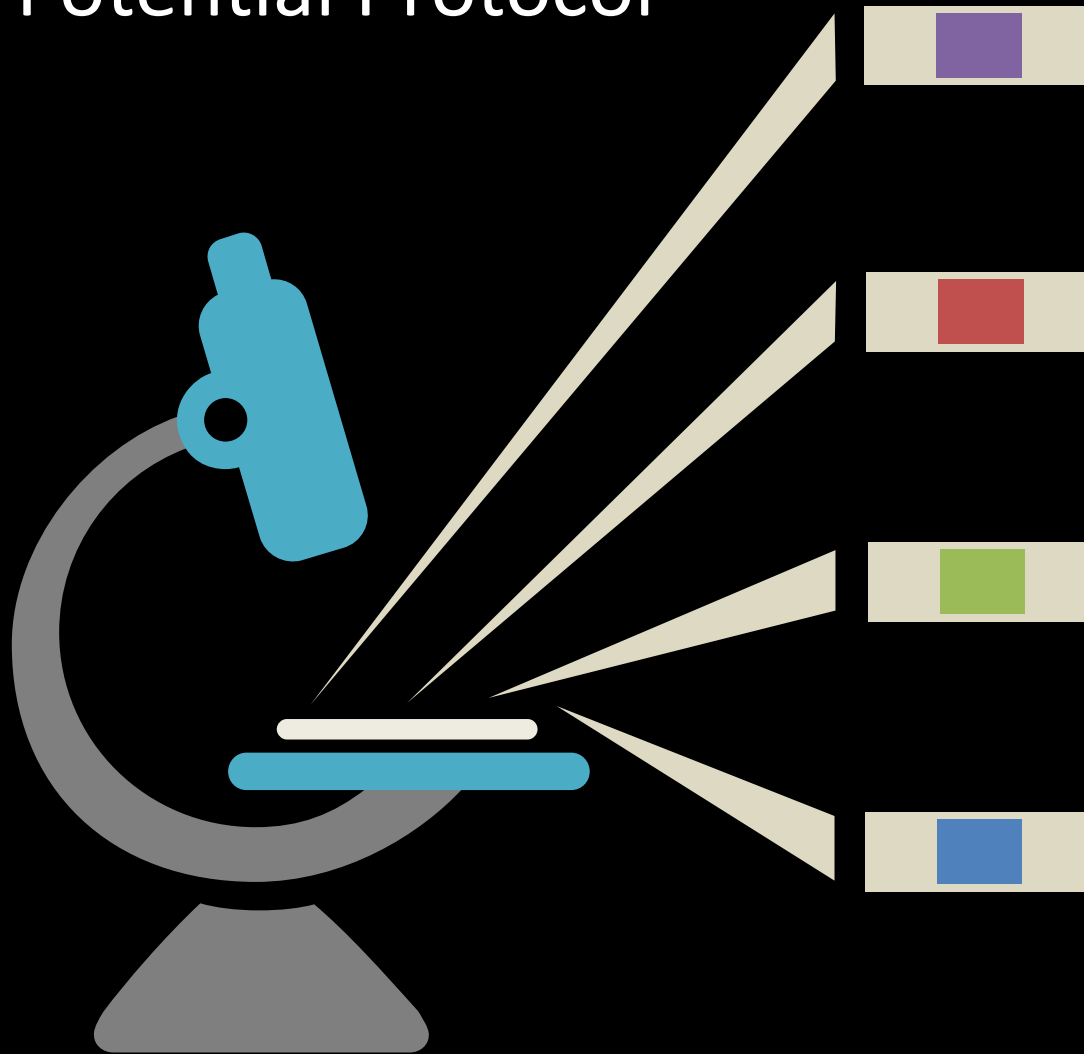


Three groups of modifiers emerged: Poor performing (ReOB), average performers (vegetable oils), and good performing (glycol amine & fatty acid derivatives)



Parameters like GR & ΔT_c are consistent with each other and show similar trends for modified binders with aging

Potential Protocol



Asphalt Binder Fact Sheet

Superpave™ PG

58-28 (60.3-30.4)

Rheology

Cracking Parameters

<i>Fatigue Cracking (Load Related)</i>	> 50%
<i>ΔG^*, LAS @ Int. temp. 2-PAV</i>	56%
<i>Thermal Cracking (Non-Load Related)</i>	12,000 kPa
<i>GR, @ Int. temp, 10 rad/s, PAV/2-PAV</i>	9,700 kPa
<i>Low Temperature Cracking (Non-Load related)</i>	-2.5/-5.0°C
<i>ΔT_c, PAV/2-PAV</i>	-1.8/-3.1°C

Advanced Rheology

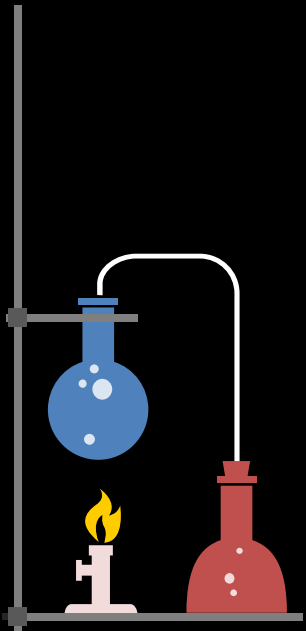
<i>Thermal Cracking (Non-Load Related)</i>	
<i>VETT</i>	
<i>Black Angle, @ $G^* = 8967$ kPa</i>	46° (min. 45°)
<i>GR, @ 15C, 0.005 rad/s, PAV/2-PAV</i>	589 kPa (max. 800 kPa)

Composition & Chemistry

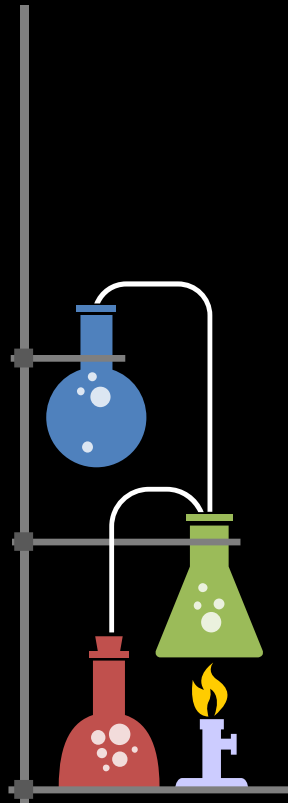
Oxidation Index

IDOT's Goal:

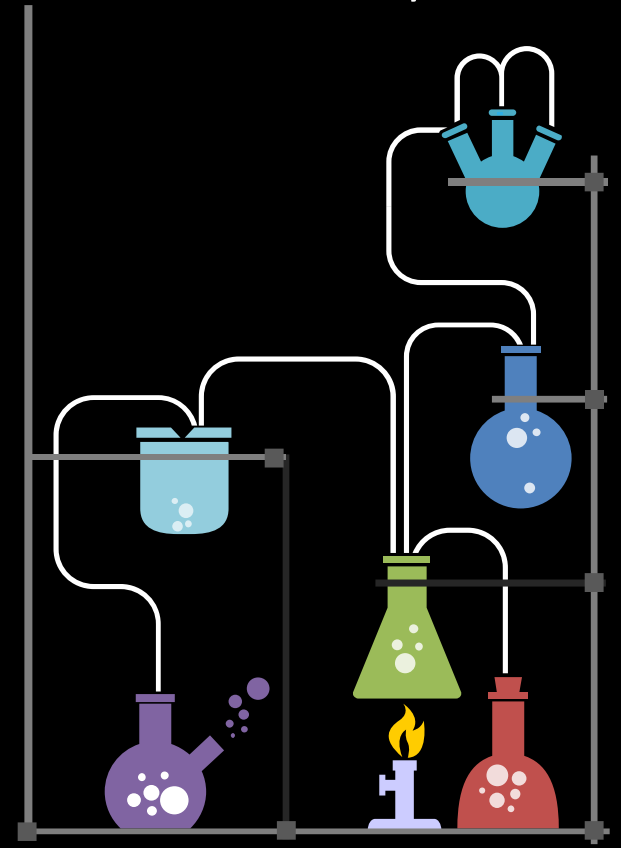
Implement a Protocol for testing and approving binder modifiers



Test approved modified binders in HMA and perform the long-term aging protocol and test for I-FIT



Provide Contractors binders with a known performance that can be used in mixed designs successfully





Illinois Department of Transportation

Kelly L. Morse
Chief Chemist

Bureau of Materials and Physical Research
126 East Ash St.
Springfield, IL 62704-4766
Tel: 217-782-1916 Fax: 217-782-2572
Cell: 217-725-5837
Kelly.Morse@illinois.gov

Questions?

