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Effects of Cross-Linking Agents on Stability & Rheological Properties of Polymer Modified Bitumen

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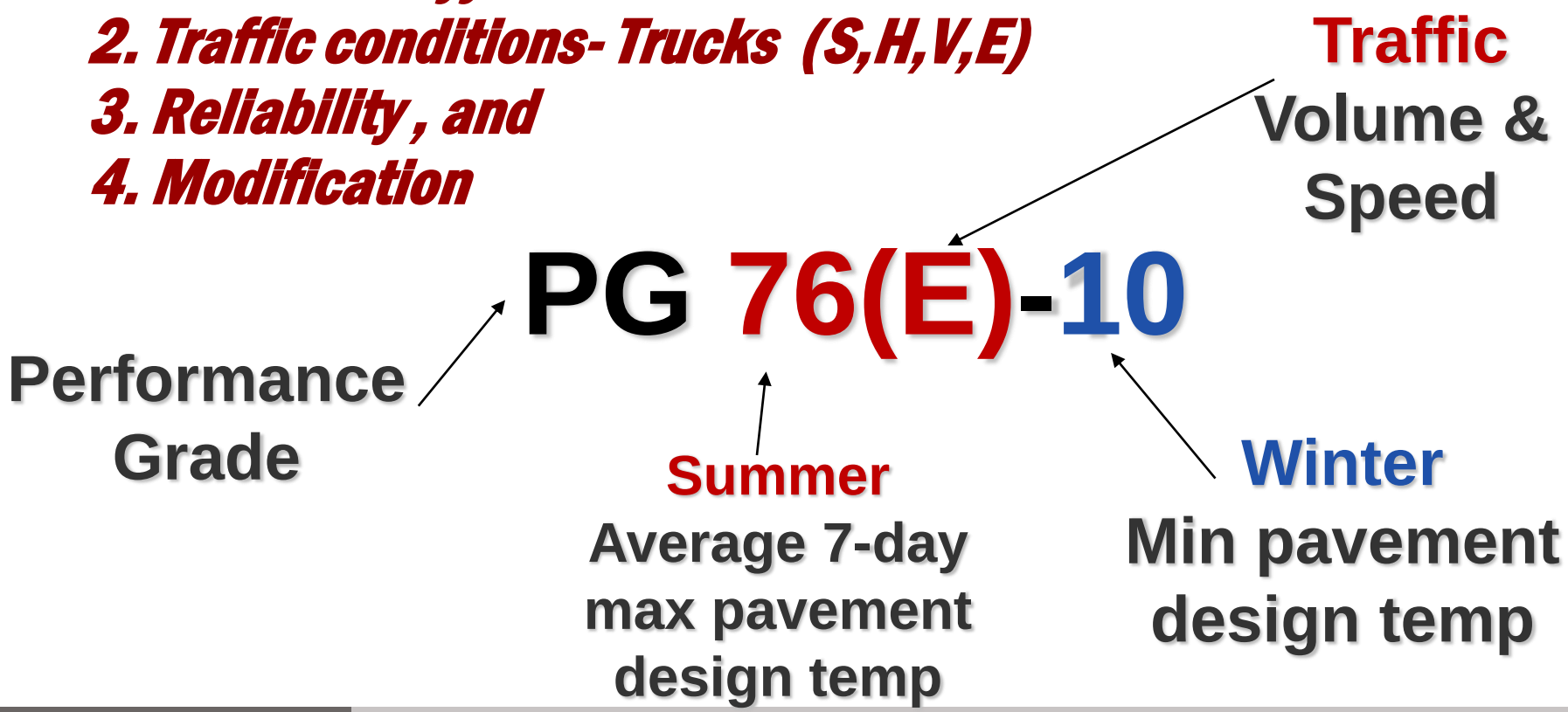
Hypothesis and Objective

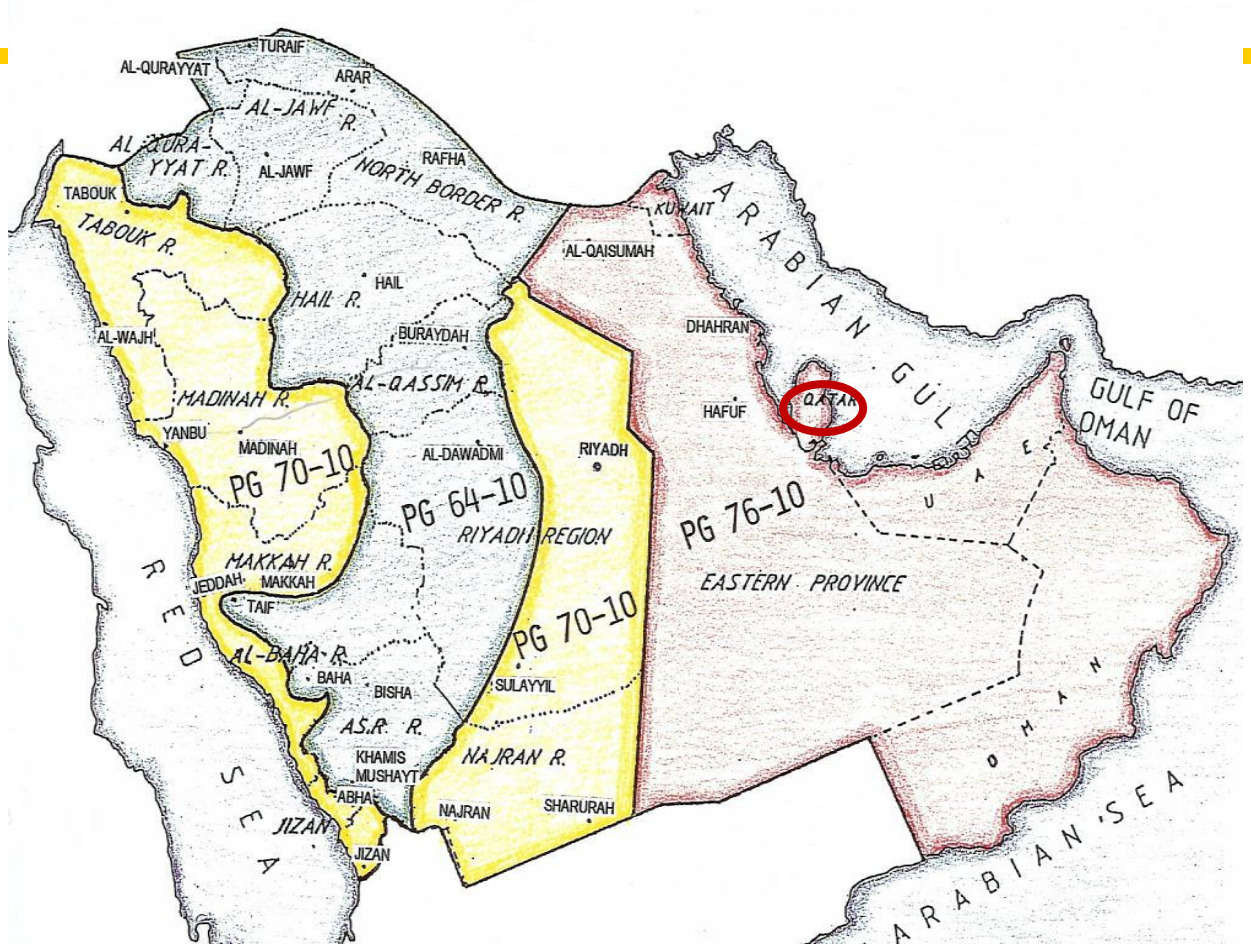
- **Hypothesis:**
  - Cross-linking of elastomeric polymers used for bitumen modification can significantly increase value of such polymers.
- **Objective:**
  - Evaluation of effectiveness of various cross-linking agents in improving stability & rheological properties of modified binders.

The New Grading System- M332–PG xx(z)-yy

1. Climate: xx-yy
2. Traffic conditions- Trucks (S,H,V,E)
3. Reliability , and
4. Modification



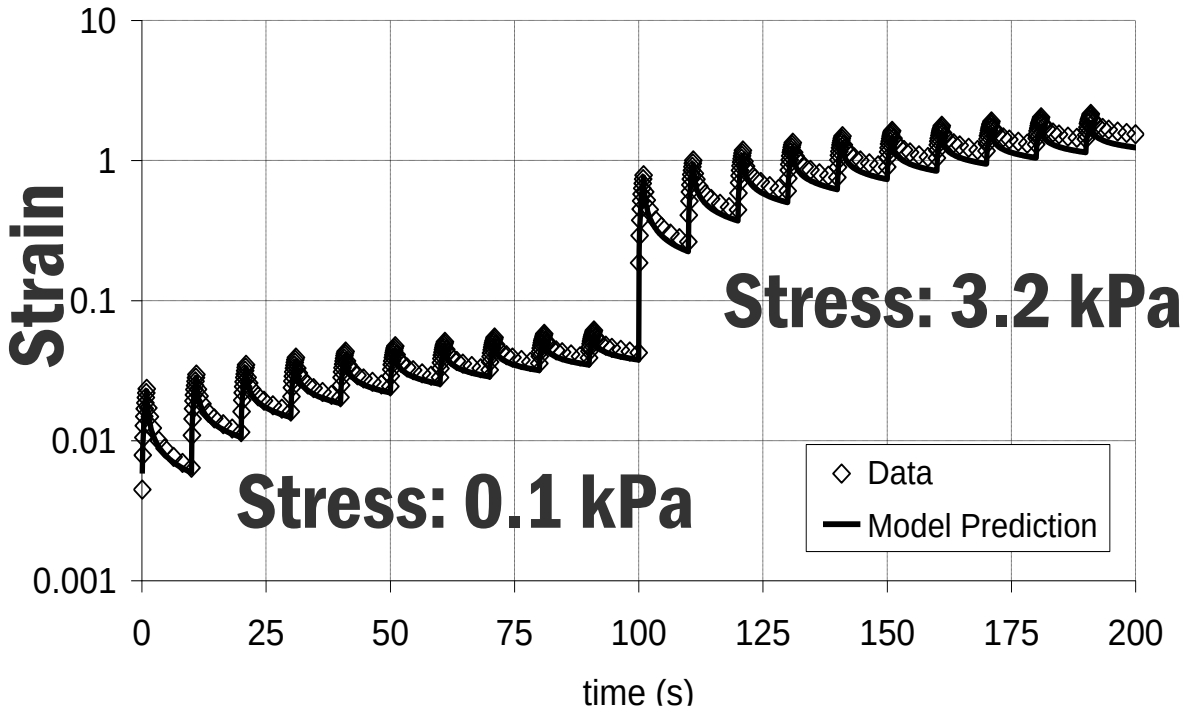
Middle East Region PG grading Requirements



Source: Eng. M. S. Aazam, MOT- KSA , 2006

Multiple Stress Creep and Recovery (MSCR) - ASTM 7045-10, AASHTO T350

- Creep stress:0.1 kPa, 3.2 kPa
- 10 cycles
  - 1 sec constant creep stress
  - 9 sec zero stress
- Output: **Creep compliance (Jnr) and Percent Recovery (%R)** at 0.1 kPa, and 3.2 kPa



1. AASHTO MP19 Specifications Based on NCHRP 9-10 Project – Report 459

	Rolling Thin-Film Oven Residue (T 240)	
Mass change, max, percent [f]	1.00	
MSCR, T350: Traffic Grades	Test Temperature	
Standard Traffic "S" Grade $J_{nr3.2}$, **max 4.0 kPa^{-1}** , J_{nrdiff}, max 75%	70	76
Heavy Traffic "H" Grade $J_{nr3.2}$, **max 2.0 kPa^{-1}**, , J_{nrdiff}, max 75%\	70	76
Very Heavy Traffic "V" Grade $J_{nr3.2}$, **max 1.0 kPa^{-1}** , J_{nrdiff}, max 75%	70	76
Extremely Heavy Traffic "E" Grade $J_{nr3.2}$, **max 0.5 kPa^{-1}** , J_{nrdiff}, max 75%	**70**	**76**

G* ~ 6-8 times Higher

Advanced Performance Grading System for Qatar – AASHTO MP19

- **Direct and effective consideration of Traffic**

Traffic Volume Design ESALs[a] (Million)	Adjusting the Jnr limits Measured at Environmental Grade		
	Traffic Speed - Load Rate		
	Standing[b]	Slow[c]	Standard[d]
0.3 to < 3	H	Standard	S
3 to < 10	V	High	H
10 to < 30	E	Very high	V
≥ 30	E	Extremely high	E

b-Standing Traffic—Average traffic speed is < 20 km/h. [C] *Slow Traffic*—Average traffic speed >20 to <70 km/h, [d] *Standard Traffic*—average traffic speed is > 70 km/h.

Materials to Produce PG 76 E-10

- One bitumen: 60/70 Pen Grade from Middle East Source – PG 64
- One Target Modified Grade: PG 76 E - 10
  - 2 Polymers:
    - Elastomer- Linear and Radial SBS
    - Functionalized(Oxidize)PE
  - 7 Cross-Linking Agents
    - Sulfur-based
    - Non-sulfur based

Cross-Linking Agents Used

Cross-linking Agent	CL1 (Sulfur)	CL2	CL3	CL4	CL5	CL6	CL7
Physical State	FP	FP	FP	Gel	FP	FP	FP
Color	Yellow	Yellow	Yellow	Yellow	Yellow	Yello-brown	Yello-brown
Specific Gravity*	2.07	1.59	1.54	NA	NA	1.1	1.1
Melting Point (°C)*	113	82	63	NA	NA	107	107
H_2O Solubility*	IS	IS	Not very soluble	IS	IS	Partially	Partially
Odor*	MO	C	C	C	MO	MO	MO

** Values obtained from manufacturer's specification; FP - Fine Powder, IS – Insoluble, C – Characteristic, MO – Mild to odorless*

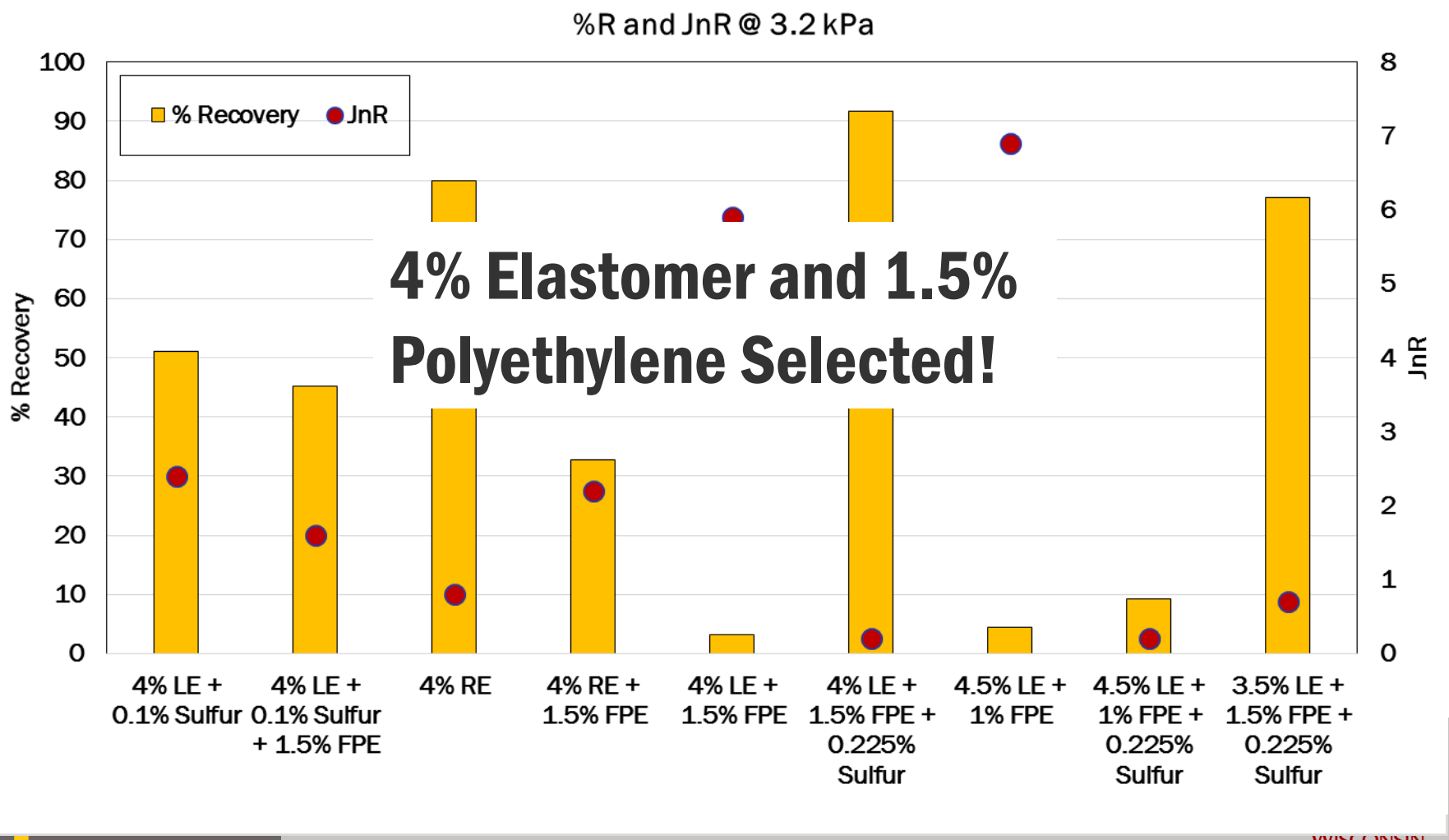
Trail Testing with Sulphur (CL1) – Convert 60/70 Pen to PG 76 E -10

- To select Elastomer and Functionalized Polyethylene to be used

PMB	Elastomer (%)	F Polyethylene (%)	Cross-linking Agent
1	4	0	0.1% CL1
2	4	1.5	0.1% CL1
3	4#	0	0
4	4#	1.5	0
5	4	1.5	0
6	4	1.5	0.225% CL1
7	4.5	1	0
8	4.5	1	0.225% CL1
9	3.5	1.5	0.225% CL1

**Neat Bitumen; # Radial Elastomer; Note: All % are by weight of neat bitumen*

Results of Initial Trial Testing



Experimental Plan (Second Phase) - None to 0.3% CL, Vary Curing Time

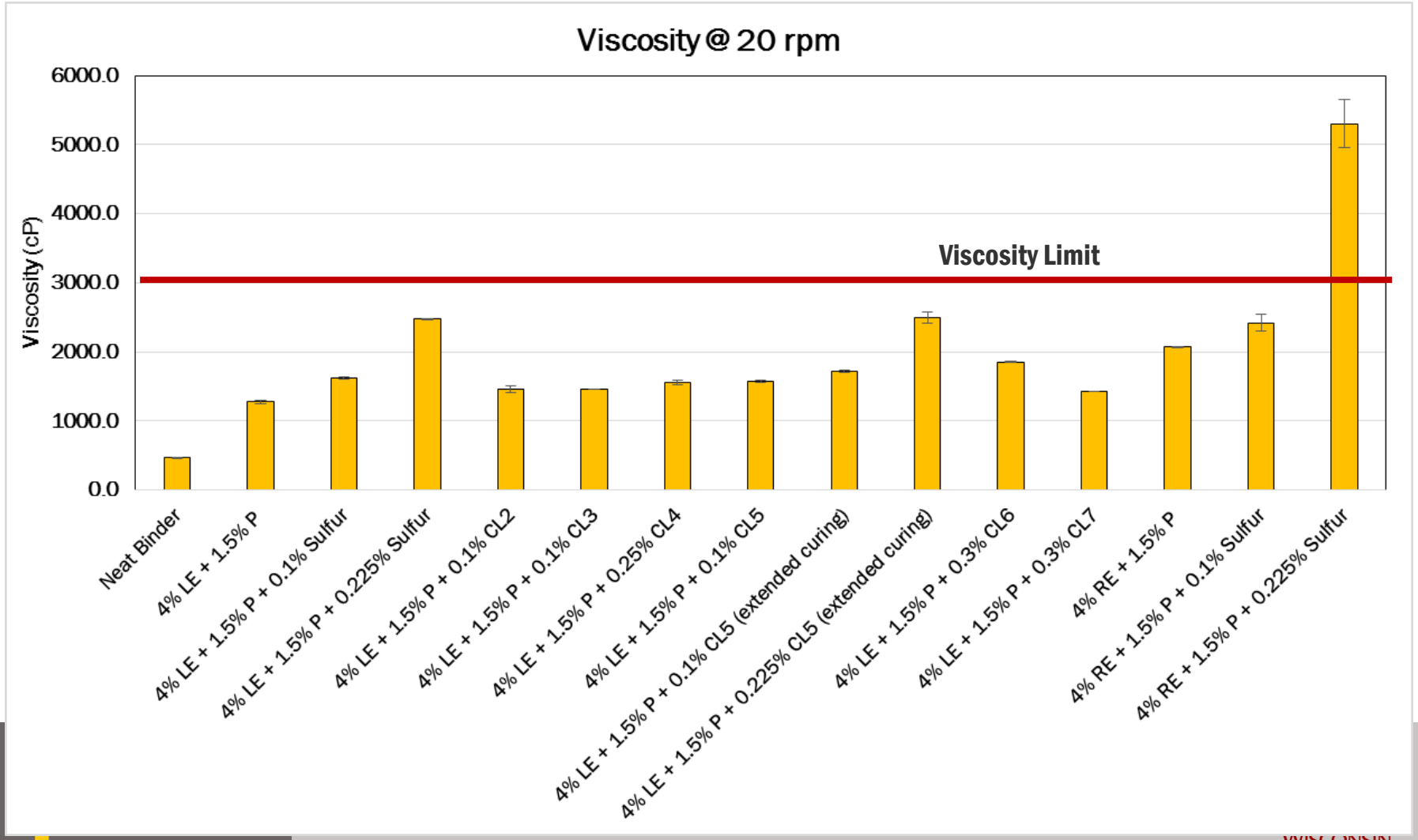
Binder	Elastomer (%)	Polyethylene (%)	Cross-linking Agent
1*	0	0	0
2	4	1.5	0
3	4	1.5	0.1% CL1
4	4	1.5	0.225% CL1
5	4	1.5	0.1% CL2
6	4	1.5	0.1% CL3
7	4	1.5	0.25% CL4
8	4	1.5	0.1% CL5
9	4	1.5	0.1% CL5 (with extended curing)
10	4	1.5	0.225% CL5 (with extended curing)
11	4	1.5	0.3% CL6
12	4	1.5	0.3% CL7

**Neat Bitumen; Note: All % are by weight of neat bitumen*

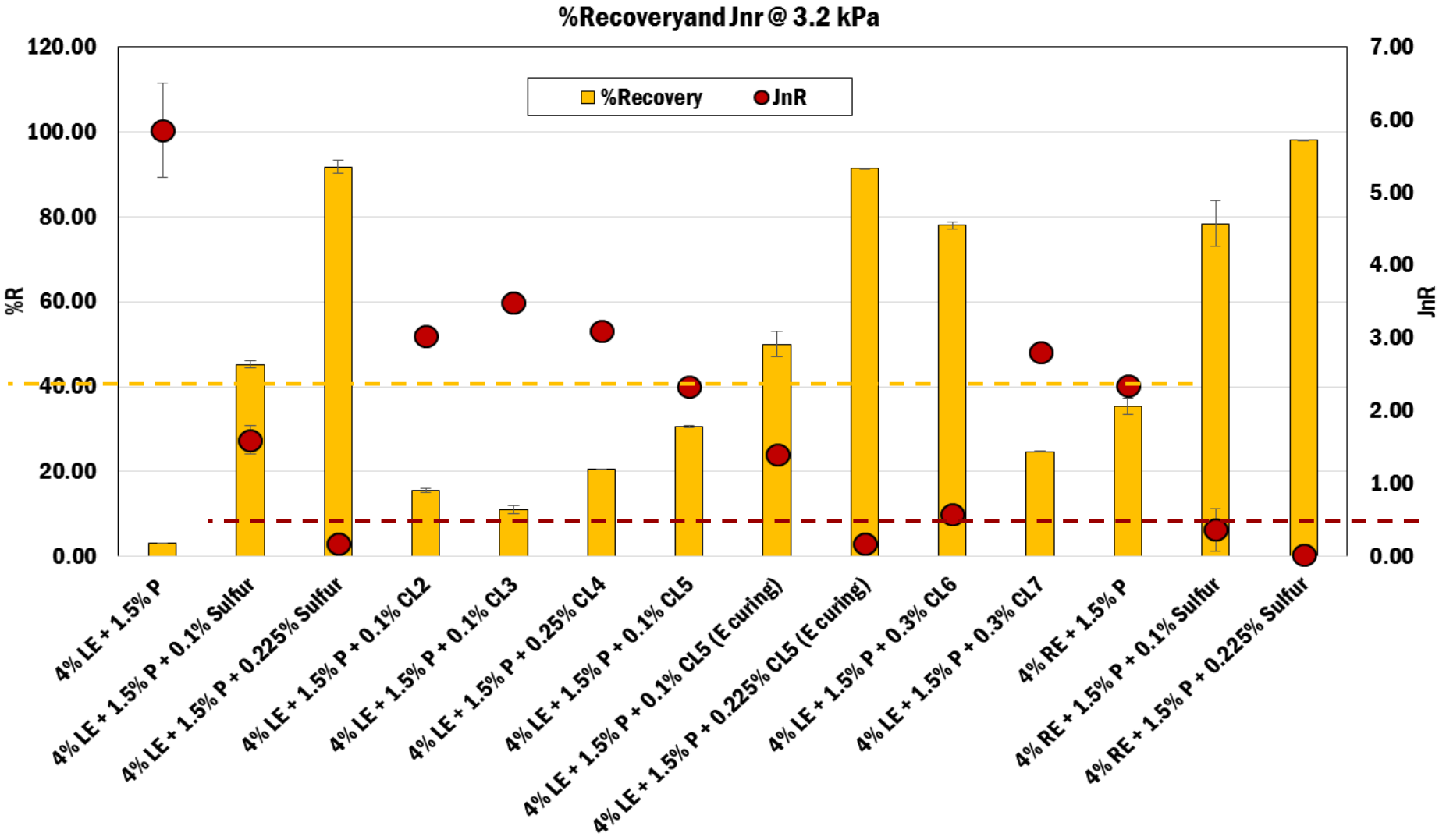
Testing Methods

Test Method	Standards	Evaluation Parameters/Response	Test Conditions
Rotational Viscometer (RV)	AASHTO T-316 or ASTM D 4402	Viscosity	Test Temperatures (°C): 135 Speed (rpm) 1, 20, 100
Multiple Stress Creep Recovery (MSCR) Test	AASHTO TP70 or ASTM D7405	J_{nr}, and Stress Sensitivity	Test Temperatures (°C): 76 Stress Levels (kPa) 0.1, 3.2
Storage Stability	ASTM D5892	J_{nr}, and Stress Sensitivity	Test Temperatures (°C): 76 Stress Levels (kPa) 0.1, 3.2

RV Results
- RE + Sulfur is the only failure



MSCR Results – 3.2 kPa



MSCR results- at 0.1, 3.2, and 10 kPa

PMB	%Recovery			J_{nr}		
	0.1 kPa	3.2 kPa	10 kPa	0.1 kPa	3.2 kPa	10 kPa
Neat Binder	12.81			30.61		
4% LE + 1.5% FPE	89.85			0.20		
4						
4% LE+1.5% FPE+0.225% CL5 (E C)	99.49			0.01		
4% LE + 1.5% FPE + 0.3% CL6	98.34			0.03		
4% LE + 1.5% FPE + 0.3% CL7	98.47			0.02		
4% RE + 1.5% FPE	92.11			0.09		
4% RE + 1.5% FPE + 0.1% Sulfur	101.91			-0.01		
4% RE + 1.5% FPE + 0.225% Sulfur	102.56			-0.02		

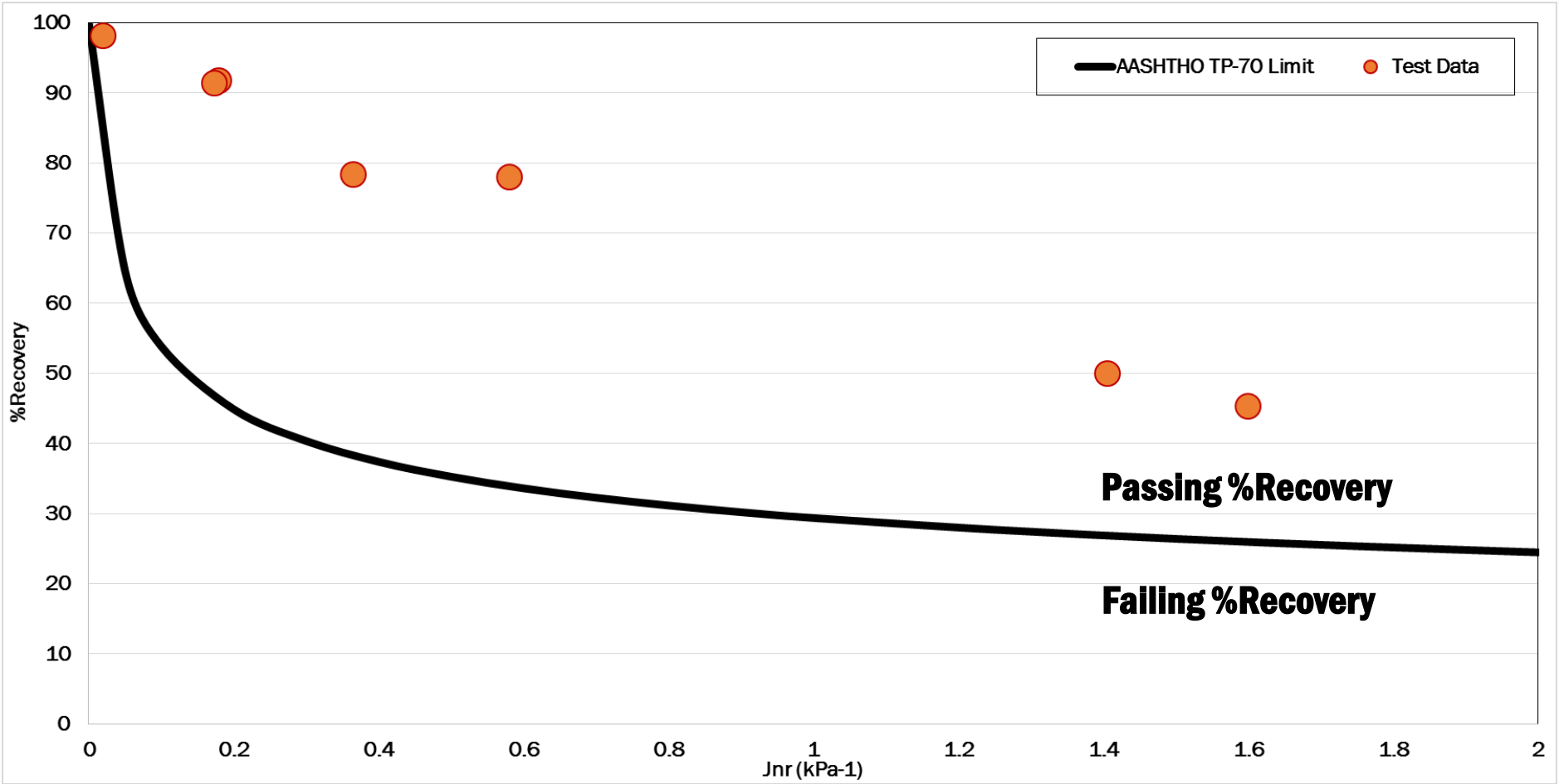
No Difference at 0.1 kPa

Therefore, this stress level is not useful; It is too low.

MSCR results- at 3.2kPa, and 10 kPa
Which PMBs can meet the E grade?

PMB	%Recovery @76 C		J_{nr} @ 76 C		
	3.2 kPa	10 kPa	1.0 kPa	3.2 kPa	10 kPa
Neat Binder	13.04			31.99	
4% LE + 1.5% FPE	3.17			5.85	
4% LE + 1.5% FPE + 0.1% Sulfur	45.21			1.60	
4% LE + 1.5% FPE + 0.225% Sulfur	91.72		0.02	0.18	
4% LE + 1.5% FPE + 0.1% CL2	15.60			3.02	
4% LE + 1.5% FPE + 0.1% CL3	10.99			3.48	
4% LE + 1.5% FPE + 0.25% CL4	20.58			3.10	
4% LE + 1.5% FPE + 0.1% CL5	30.56			2.34	
4% LE+1.5% FPE + 0.1% CL5 (E C)	49.94			1.41	
4% LE+1.5% FPE+0.225% CL5 (E C)	91.34		0.01	0.17	
4% LE + 1.5% FPE + 0.3% CL6	77.96		0.03	0.58	
4% LE + 1.5% FPE + 0.3% CL7	24.63			2.80	
4% RE + 1.5% FPE	35.30			2.35	
4% RE + 1.5% FPE + 0.1% Sulfur	78.31		-0.01	0.37	
4% RE + 1.5% FPE + 0.225% Sulfur	98.04		-0.02	0.02	

Jnr vs. %Recovery at 3.2 kPa stress level



MARC MODIFIED ASPHALT RESEARCH CENTER

All binders pass the criteria!

THE UNIVERSITY of WISCONSIN MADISON

Grade of the cross-linked binder from the Jnr values

Binder	@3.2 kPa		Grade
	%R	JnR	
4% LE + 1.5% FPE + 0.1% Sulfur	45.2	1.6	H
4% LE + 1.5% FPE + 0.225% Sulfur	91.7	0.2	E
4% LE + 1.5% FPE + 0.1% CL2	15.6	3.0	S
4% LE + 1.5% FPE + 0.1% CL3	10.9	3.5	S
4% LE + 1.5% FPE + 0.25% CL4	20.6	3.1	S
4% LE + 1.5% FPE + 0.1% CL5	30.6	2.3	S
4% LE + 1.5% FPE + 0.1% CL5 (E curing)	49.9	1.4	H
4% LE + 1.5% FPE + 0.225% CL5 (E curing)	91.3	0.2	E
4% LE + 1.5% FPE + 0.3% CL6	77.9	0.6	V
4% LE + 1.5% FPE + 0.3% CL7	24.6	2.8	S
4% RE + 1.5% FPE	35.3	2.4	S
4% RE + 1.5% FPE + 0.1% Sulfur	78.3	0.4	E
4% RE + 1.5% FPE + 0.225% Sulfur	87.7	0.02	E

S: Standard
Jnr: 4.0 (1/kPa)

H: Heavy
Jnr: 2.0 (1/kPa)

V: Very Heavy
Jnr: 1.0 (1/kPa)

E: Extremely Heavy
Jnr: 0.5 (1/kPa)

Ranking of Modified Binders

- **RV Test**
  - Poor performance: Viscosity > 3000 cP
  - Very good performance: Viscosity < 3000 cP
- **MSCR test**
  - Poor performance: J_{nr} > 4.0
  - Average performance: J_{nr} between 2.0-4.0
  - Good performance: J_{nr} between 0.5-2.0
  - Very good performance: J_{nr} below 0.5.
- **Storage stability test**
  - Poor performance: %Difference >20%,
  - Average performance: %Difference between 15%-20%
  - Good performance: %Difference between 10-15%
  - Very good performance: %Difference below 10%.

Ranking of Best 7 Modified Binders - Only 7 had no poor performance

Binder	RV Test	MSCR Test	Storage Stability Test	Ranking
4% LE + 1.5% FPE + 0.225% Sulfur				1
4% LE + 1.5% FPE + 0.3% CL6				2
4% LE + 1.5% FPE + 0.225% CL5 (extended curing)				3
4% LE + 1.5% FPE + 0.1% CL5 (extended curing)				4
4% LE + 1.5% FPE + 0.25% CL4				5
4% LE + 1.5% FPE + 0.1% Sulfur				6
4% LE + 1.5% FPE + 0.3% CL7				7
4% RE + 1.5% FPE + 0.1% Sulfur				-
4% LE + 1.5% FPE + 0.1% CL2				-
4% LE + 1.5% FPE + 0.1% CL3				-
4% LE + 1.5% FPE + 0.1% CL5				-
4% RE + 1.5% FPE				-
4% LE + 1.5% FPE				-
4% RE + 1.5% FPE + 0.225% Sulfur				-

	Very Good
	Good
	Average
	Poor

Conclusions

- Influential parameters:
  - Type of cross-linking agent
  - Concentration of Cross-linking agent
  - Polymer type, and
  - Curing time
- Cross-linking concentration was by far the most important
- Viscosity and MSCR are interrelated, while storage stability is completely independent of viscosity and MSCR
- Cross-linking is necessary for storage stability

Conclusions

- MSCR testing and analysis issues:
  - Testing at 0.1 kPa **should not be used**
  - Stress sensitivity is important, but stress levels should be selected in a **more realistic way (> 10 kPa)**
  - **Jnr Difference** criterion needs some modification and some justification.

Over Loading

Source: Prof. Kim Jenkins

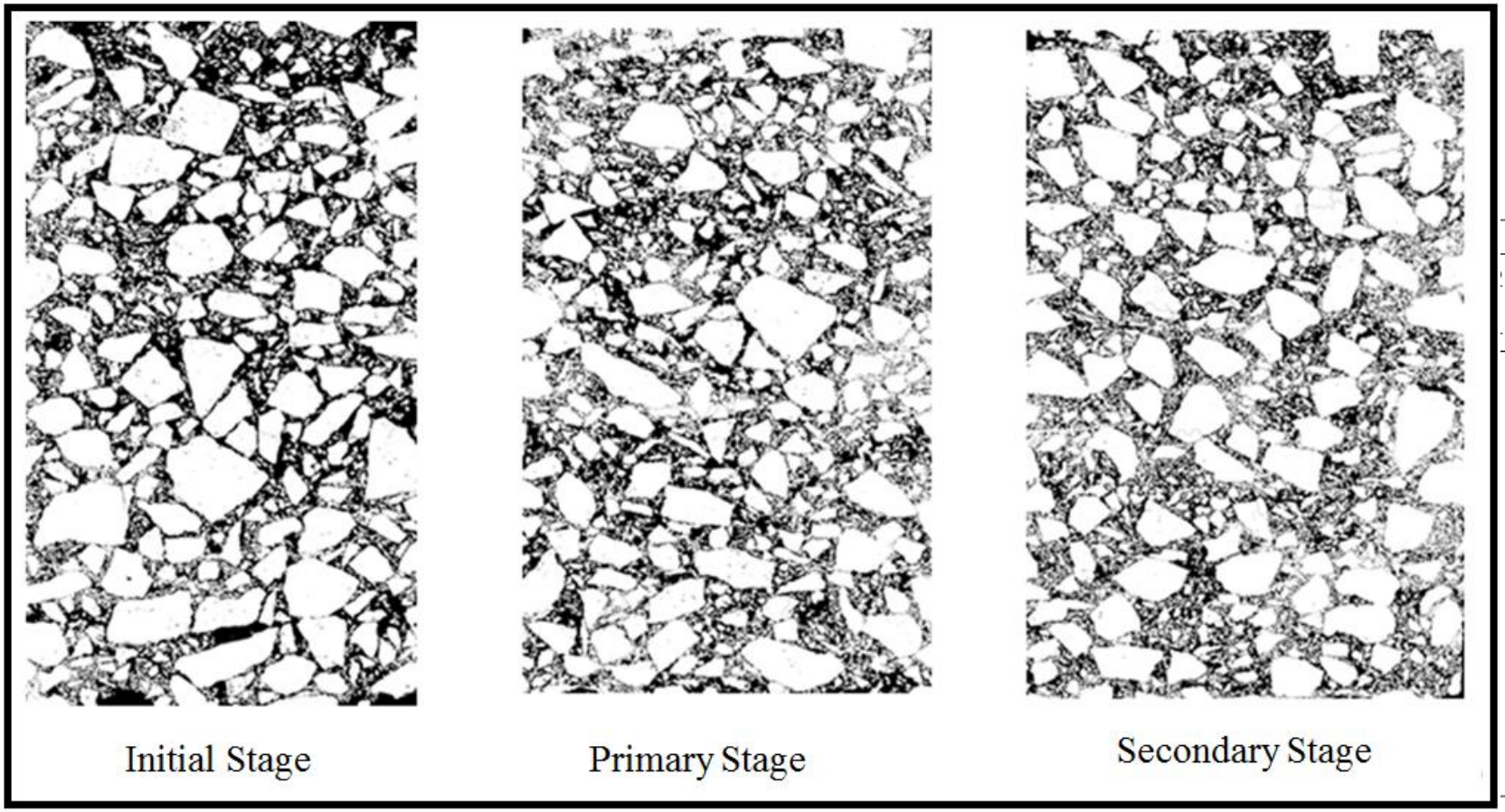

Axles of evil


Thank you!
Questions?

Tracking Micro-Structural Evolution of HMA in Rutting- Methodology

Imag
stag
prop

Bin
Air



FE Simulation of Asphalt Mixture Behavior - Macro Scale

- Extending the analysis results to the case of a standard 18 kip (80 kN) load, the average shear stress in the binder phase of all of the mixtures considered in this study were calculated

Binder \ Gradation	Fine	Intermediate	Coarse
HIHD	14	11	22
LIHD	16	12	23
HILD	16	12	23
LILD	18	13	24

Average shear stress level (KPa) in binder phase of mixtures