

Developing a Fundamental Understanding of the Chemistry of Warm Mix Additives

TxDOT Project 6591

Education Material
Handouts summarizing the project goals,
methods, and findings

Please use presentation mode to review the
slides and contents

Project Objectives and Research Approach



Evaluate influence of WMA additives on:
1. Chemical properties of the binder
2. Rheological properties of the binder

Synthesize information
to assess expected
mixture properties

Synthesize
information to
provide final
recommendations



Limited validation based on:
1. Engineering properties of the mixture
2. Mixture performance

Tasks

Task 1. Review on state of the art and literature search

Task 2. Selection of materials, WMA additives, and processes

Task 3. Chemical and physio-chemical properties

Task 4. Rheology of binders and performance

Task 5. Performance of mixtures

Task 6. Recommendations for the use of WMA mixtures

Task 7. Final report

Task 1: Review on state of the art and literature search

- Summary of literature review
- "Quick reference" table of findings

Refer to interim report for a full summary from the review

DRAFT SUMMARY FROM LITERATURE REVIEW FOR PROJECT 0001

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REFERENCES

Type of Technology	Reference Mixture / Binder	Concentration	Notes	Findings	Reference
Foaming	HMA	N/A	Rotary Compactor (RSC) Indirect Tensile Strength (ITS)	Mixing temperature and compaction effort does not affect the compactability of a mix (RSC). Mixing temperature affects the strength of a mix (ITS).	Jenkins et al, 1999
Foaming	HMA	N/A	Rotary Compactor/ Rolling Wheel Compactor Dynamic Creep Test/ Flow Number Test Three Point Beam Fatigue Test California Abrasion Test Thermal Stress Restraint Cooling Test	No significant difference in performance between WMA and HMA was observed. The properties of the final binder should be analyzed after the combination has been made. The use of emulsions in asphalt plants may cause a problem because of the water evaporation that occurs during production. No major problems were encountered during the placement and compaction operations. The air voids of the WMA were comparable to the HMA. The WMA sections were exposed to traffic very soon after construction with no problems.	Koenders et al, 2002
Foaming	HMA	N/A	AASHTO M 320 Asphalt Penetration Analyzer (APA) AASHTO T 261 AASHTO T 269 T 5-S-365	The WMA mixture had a better fatigue life than HMA mixture. WMA mixtures were more susceptible to moisture damage.	Johnston et al, 2006
Foaming	HMA	N/A	Uniaxial Tests Shear Test Flexural Stiffness Test	Half Warm Foamed Mixtures had comparable results to HMA at high temperature in terms of compression strength but it had lower values at low temperature. Half and HMA mixtures had comparable flexural stiffness values at high frequency. Binder properties were significantly affected by the addition of sandbl and montan was. The force density testing results showed that sandbl and montan was caused the greatest increase in stiffness. The BBR testing results showed that the addition of the wax used in this study stiffen the binder, which indicates that these may make the binder more susceptible to low temperature cracking. The addition of PMA decreased the creep stiffness, implying that the it may decrease the low temperature cracking when compared to the control. The authors concluded that the effects on the binders and mixtures from adding the waxes were minimal, and the changes that were seen were	Van de Ven et al, 2007
Sandbl Asphalt 8 Lowvis A SealWax 4442 Innovat	Base Binder HMA	2% and 4% by weight of binder	Conventional Binder Test (CT) Force Density Test BBR Test Tensile Stress Restraint Specimen Test (TSRST) Creep Test Dynamic Creep Test Complex Modulus Test		Edwards et al, 2006

Task 1: Review on state of the art and literature search

Summary

	Mixing and compaction	Rutting resistance	Moisture damage resistance	Fatigue cracking resistance
Chemical (Evotherm)	Similar	Similar to lower	Mostly lower	Not reported
Wax based (Sasobit)	Similar	Similar to better	Mixed results	Better
Particle foaming (Aspha-min)	Similar	Mixed results	Mixed results	Not reported
Direct foaming	Similar	Similar to lower	Similar to lower	Not reported

Note 1: In some cases WMA did not perform as well as HMA but still met the specification criteria

Note 2: Most results are based on mixture performance

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Task 2: Selection of materials and additives



Binder



Select binders with diverse chemical makeup



Aggregate



Select absorptive aggregate



Additive



Select additives representing each of the prominent technologies

Task 2: Selection of materials and additives

Selection of Binders

Objective:

Select binders to have diversity in terms of chemical makeup and potential chemical interactions

Diversity in chemical makeup:

- (i) Based on wax content
- (ii) Based on natural acid content

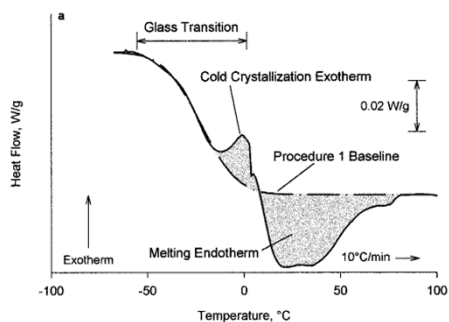
Total of 32 different asphalt binders from Texas were included in the screening process

Task 2: Selection of materials and additives

Selection of Binders: 1 of 2 Based on wax content



Differential Scanning Calorimeter



Thermograph

Task 2: Selection of materials and additives

Selection of Binders: 1 of 2 Based on wax content

Sample Name	Crystallization Onset °C	Crystallization Exotherm, J/g	Melt Midpoint °C	Melt Endotherm J/g	PG Grade	Remarks
1001-38 G	47.44	1.71	26.15	6.19		
1001-41 F	46.16	2.69	27.66	5.93	PG76-28 Valero	High wax
1001-41 B	46.65	4.47	27.41	5.33	PG76-22 Valero	High wax
1001-40 K	46.16	3.27	27.63	5.27		
1001-41 D	46.23	4.01	27.34	4.99		
.		
.		
1001-38 H	33.17	0.59	30.53	2.48		
1001-39 G	39.17	1.42	30.33	2.46		
1001-38 J	33.38	0.59	30.82	2.42		
1001-40 F	34.11	0.79	30.66	2.36		
1001-39 D	41.41	1.76	30.58	2.25	PG64-22 Jebro	Low Wax
1001-40 G	30.51	0.3	31.22	2.14		
1001-41 A	33.67	1.4	33.47	1.62	PG64-22 Pelican	Low wax

Task 2: Selection of materials and additives

Selection of Binders: 2 of 2 Based on acid content

- 0.1M TBAH was used as the titrant
- Titrant was standardized with benzoic acid every day before titration experiments
- Samples were dissolved in an organic solvent (a mixture of ethyl alcohol and chlorobenzene)
- A pH electrode was used to measure the potential change of the system during a titration experiment
- A titration curve was curve-fitted with five-parameter sigmoid functions and then took first derivative to determine inflection points
- Acid numbers were calculated by the amounts of titrant consumed at the inflection points

Task 2: Selection of materials and additives

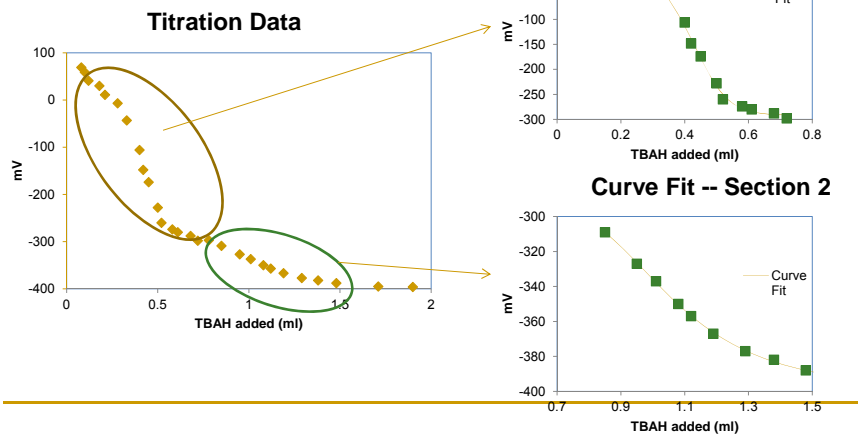
Selection of Binders: 2 of 2 Based on acid content



Task 2: Selection of materials and additives

Selection of Binders: 2 of 2 Based on acid content

Total Acid Numbers



Task 2: Selection of materials and additives

Selection of Binders: 2 of 2 Based on acid content

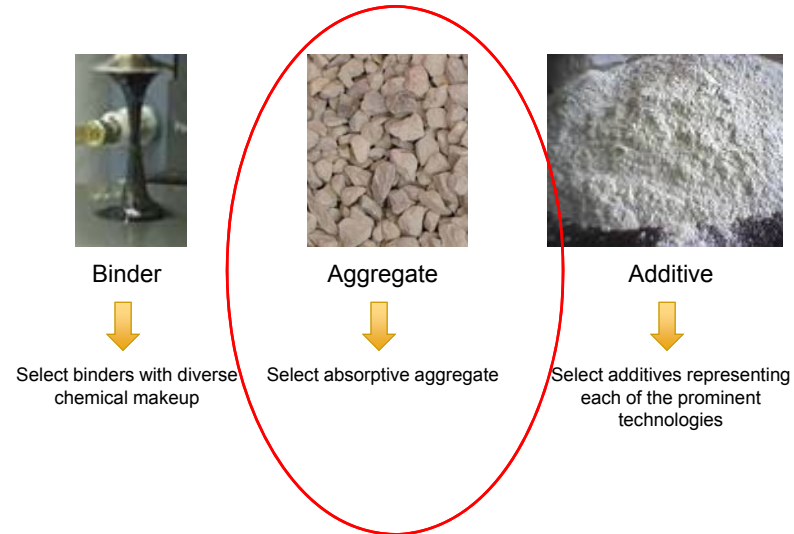
Asphalt binders with high acid content:

PG 76-28 from Valero
PG 64-22 from Calumet

Asphalt binders with low acid content:

PG 64-22 from Valero
PG 70-22s from Valero

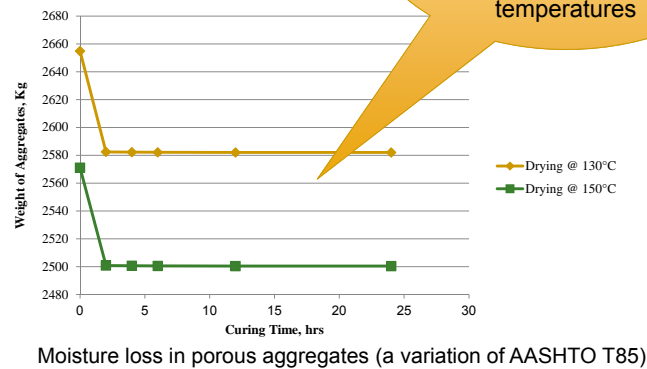
Task 2: Selection of materials and additives



Task 2: Selection of materials and additives

Selection of Aggregate

Previous studies had shown that siliceous aggregates lose moisture at the same rate at different temperatures, BUT Do porous aggregates retain absorbed moisture?



Task 2: Selection of materials and additives



Binder



Use DSC & Titration tests to screen binders for wax and acid content



Aggregate



Select absorptive aggregate



Additive



Select additives representing each of the prominent technologies

Task 2: Selection of materials and additives

Selection of Additives

Additives for binders with different wax contents

- Controls A & B – Neat Binders
- Sasobit®
- Cecabase RT 945
- Evothrm DAT
- Evothrm 3G
- Rediset® WMX

Additives for binders with different acid contents

- Controls A & B- Neat binders
- Advera WMA
- Cecabase RT 945
- Dehydrated Advera WMA

Note: Additives mixed with acid based binders were selected based on their alkalinity.

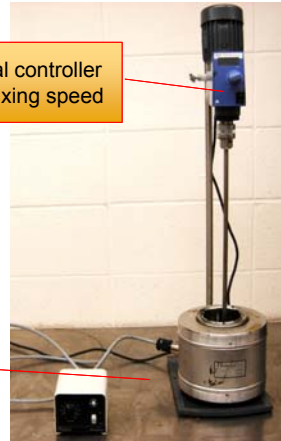
Task 2: Selection of materials and additives

Mixing of additives to the asphalt binder

- RW 20 Digital Overhead Mixer.
- Manufacturers recommendation
 - Dosage of additives
 - Mixing temp
 - Mixing time

Digital controller
for mixing speed

Temperature jacket that fits around
quart can with temperature controller



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Task 3: Chemical properties

Main Objectives

- Select asphalt binders based on their chemical make up
- Identify chemical interactions between asphalt binders and WMA additives
- Investigate reasons behind observed performance

Test Methods

- DSC (wax content)
- Acid titration (acid content)
- FTIR (carbonyl area as a measure of oxidative aging)

Tasks

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Task 3. Chemical and physio-chemical properties

Task 4. Rheology of binders and performance

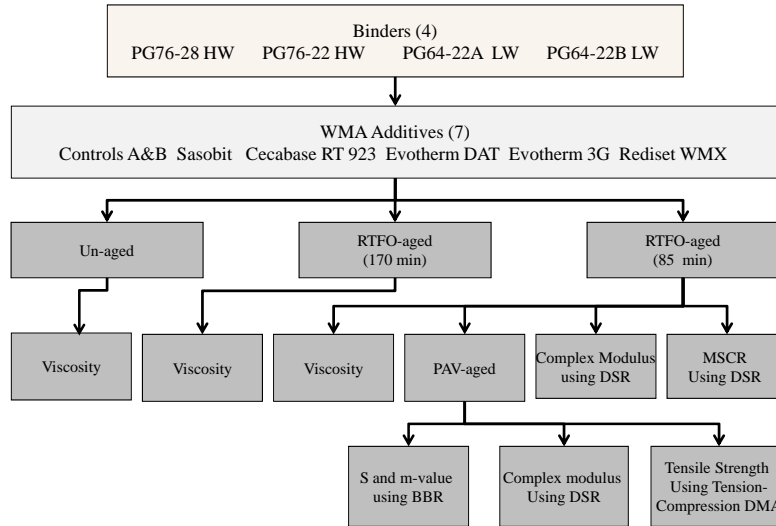
Task 5. Performance of mixtures

Task 6. Recommendations for the use of WMA mixtures

Task 7. Final report

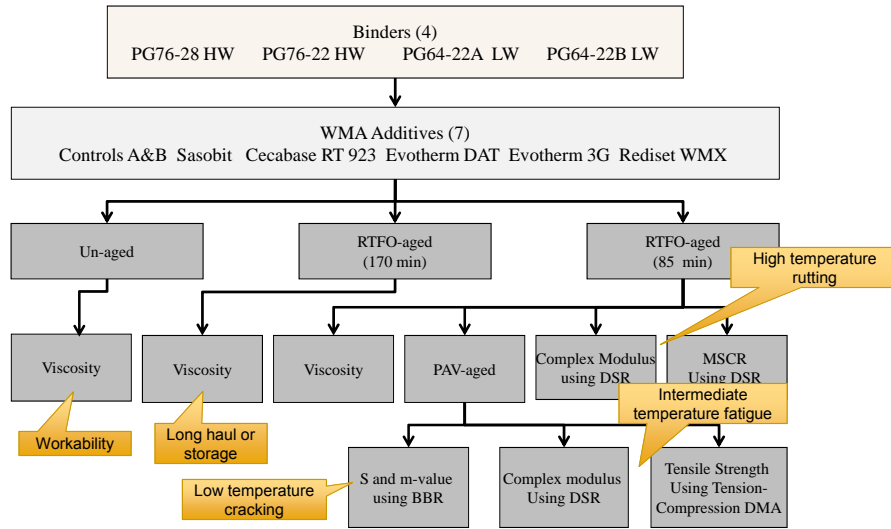
Task 4: Rheological properties of binder

Two test plans: (i) Binders with varying wax content
(ii) Binders with varying acid content



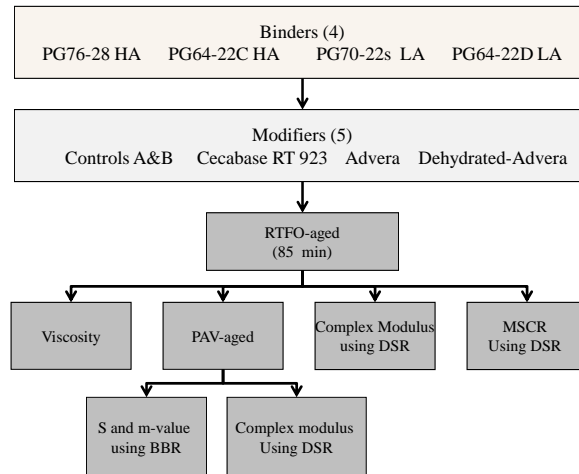
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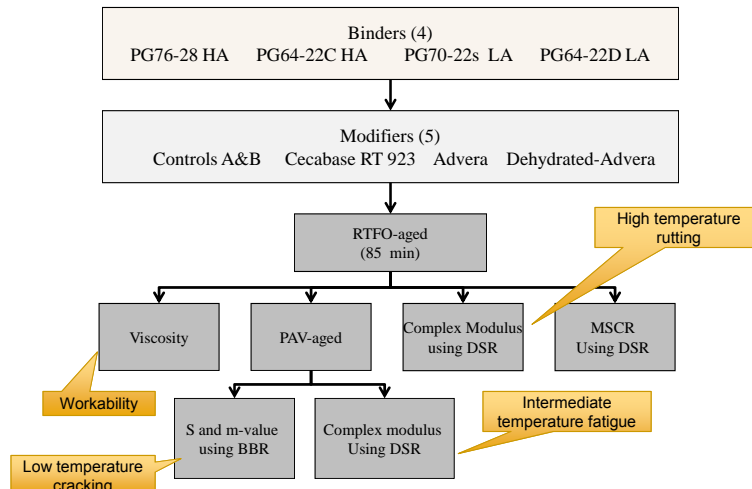
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Task 4: Rheological properties of binder

Two test plans: (i) Binders with varying wax content
(ii) Binders with varying acid content



Task 4: Rheological properties of binder

Controls and terminology

- Control A = Binder RTFO aged at 163C (current standard)
- Control B = Binder RTFO aged at 143C
- WMA binder** = Binder + Additive RTFO aged at 143C

Control A vs. Modified binders → Influence of additives + reduced mixing temperatures

Control B vs. Modified binders → Influence of additives


Task 4: Rheological properties of binder

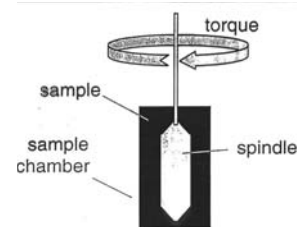
Viscosity

Rutting

Fatigue Cracking

Low Temp Cracking

1. Viscosity of unaged binder (mixing workability) - some or no reduction in viscosity
2. Viscosity of RTFO aged binder (compaction workability) – some or no reduction in viscosity
-  3. Viscosity of extended RTFO aged binder (long hauls or silo storage) – WMA additives were very beneficial especially for the two PG 76 binders that had very high viscosities if stored at HMA temperatures for long durations of time



Task 4: Rheological properties of binder

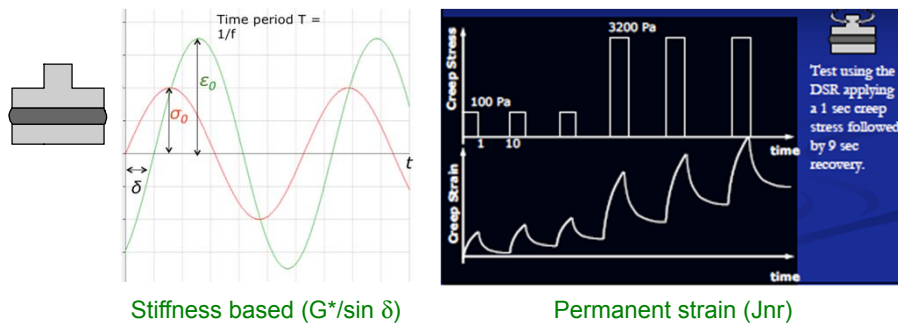
Viscosity

Rutting

Fatigue Cracking

Low Temp Cracking

1. Results are based on $G^*/\sin\delta$ and MSCR non-recoverable compliance



Task 4: Rheological properties of binder

Viscosity

Rutting

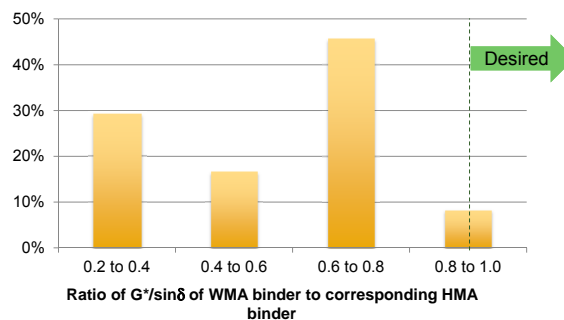
Fatigue Cracking

Low Temp Cracking

1. Results are based on $G^*/\sin\delta$ and MSCR non-recoverable compliance

2. Sasobit typically compensated for the reduced stiffness associated with reduced aging (3 out of 4 cases); this was consistent for both parameters

3. WMA additives other than Sasobit typically had a $G^*/\sin\delta$ that was 80% or less than that for a corresponding HMA binder (distribution based on 24 binder-additive pairs shows in Figure)



Task 4: Rheological properties of binder

Viscosity

Rutting

Fatigue Cracking

Low Temp Cracking

4. WMA additives (other than Sasobit) further aggravated the reduction in stiffness due to reduced aging (in other words for about half the additive-binder combinations the stiffness loss was due to the additive itself and not due to reduced aging)

5. Results based on MSCR were similar to results based on $G^*/\sin\delta$ but more sensitive

i 6. PG 76 binders (high wax) were very sensitive to reduced aging and additives (other than Sasobit); Jnr increased by 2 to 8 times due to reduced aging and 5 to 50 times due to addition of additives and reduced aging!!

Task 4: Rheological properties of binder

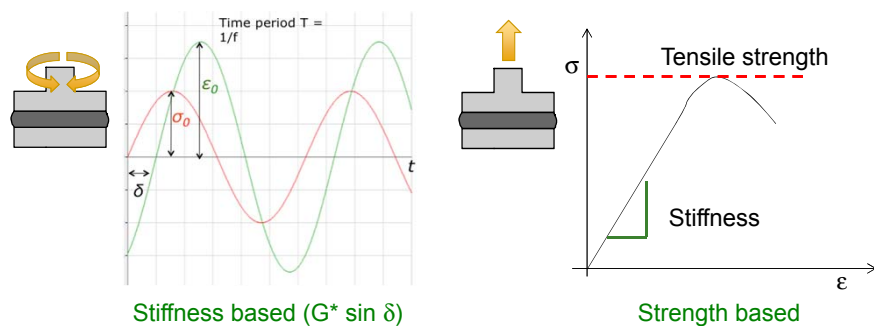
Viscosity

Rutting

Fatigue Cracking

Low Temp Cracking

1. All combinations were evaluated using $G^*\sin\delta$ at intermediate temperatures and a subset were also evaluated using direct tensile fracture test



Task 4: Rheological properties of binder

Viscosity

Rutting

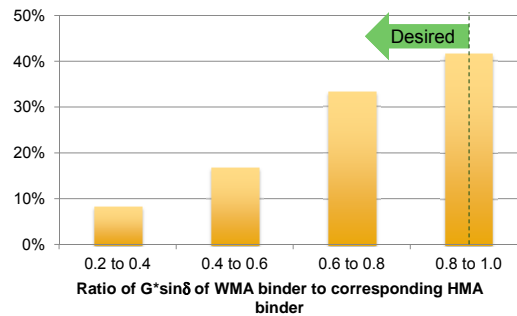
Fatigue Cracking

Low Temp Cracking

1. All combinations were evaluated using $G^*\sin\delta$ at intermediate temperatures and a subset were also evaluated using direct tensile fracture test

i 2. Sasobit modified WMA binders had similar stiffness as HMA (3 of 4 cases) at intermediate temperatures; therefore a WMA with Sasobit and RAP may be at risk for cracking

3. WMA additives other than Sasobit typically had a $G^*\sin\delta$ that less than that for a corresponding HMA binder (distribution based on 24 binder-additive pairs show in Figure)



Task 4: Rheological properties of binder

Viscosity

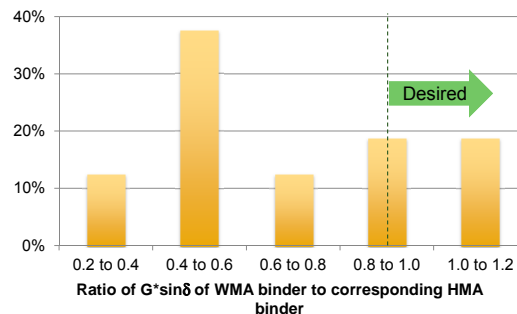
Rutting

Fatigue Cracking

Low Temp Cracking

4. Results based on fracture / strength testing of binder were very different

i 5. In most cases the WMA binders had a reduced strength (energy until failure) compared to the corresponding HMA (distribution based on 16 binder-additive pairs show in Figure)



Task 4: Rheological properties of binder

Viscosity

Rutting

Fatigue Cracking

Low Temp Cracking

1. All combinations were evaluated using stiffness and m-value at low temperatures
2. WMA binders were very similar in terms of stiffness and m-value to HMA binders
3. WMA binders with Sasobit showed a slight increase in susceptibility to low temperature cracking based on these parameters

Why is there no influence of reduced short-term aging temperature after long-term?

Will addition of RAP to WMA increase susceptibility to low temperature cracking?

Task 4: Rheological properties of binder

Viscosity

Rutting

Fatigue Cracking

Low Temp Cracking

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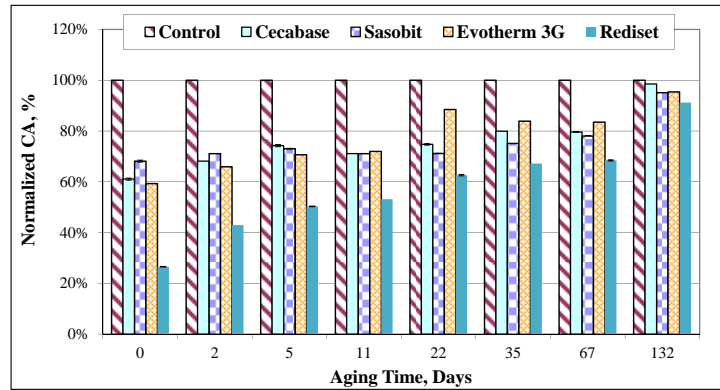
Task 4: Rheological properties of binder

Viscosity

Rutting

Fatigue Cracking

Low Temp Cracking



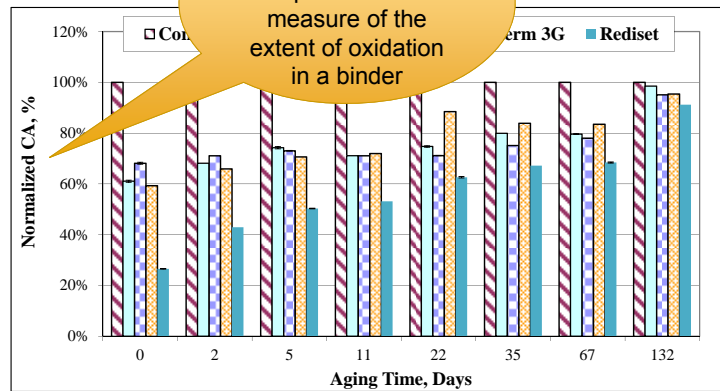
Task 4: Rheological properties of binder

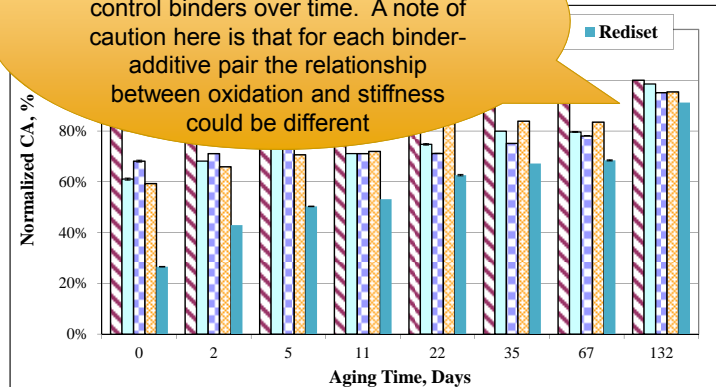
Viscosity

Rutting

Cracking

Low Temp Cracking

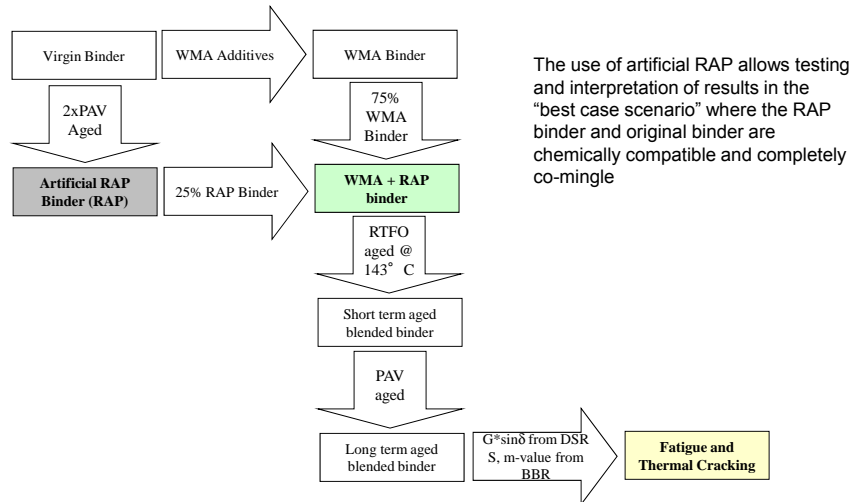




Will addition of RAP to WMA increase susceptibility to low temperature cracking?

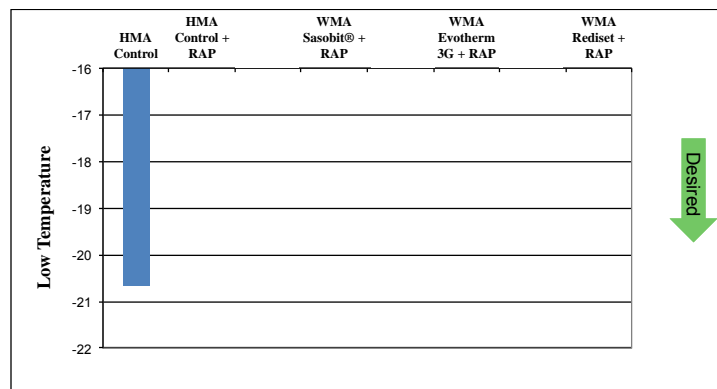
Task 4: Rheological properties of binder

Influence of RAP on WMA binder rheology



Task 4: Rheological properties of binder

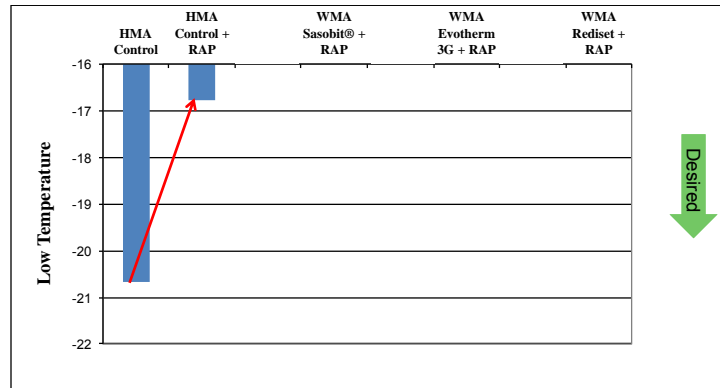
Influence of RAP on WMA binder rheology – LOW TEMPERATURE



- PG 64-22
- Low temperature grade based on m-value and estimated temperature sensitivity
- Best case scenario (25% RAP binder fully blended and same base binder)

Task 4: Rheological properties of binder

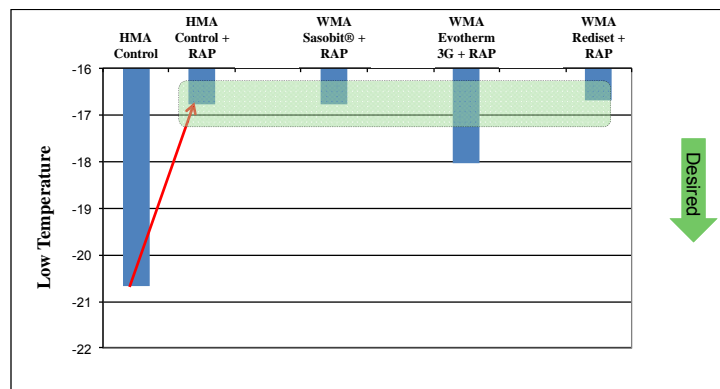
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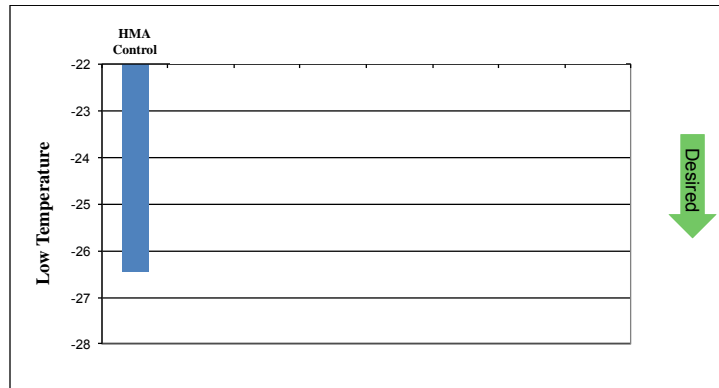
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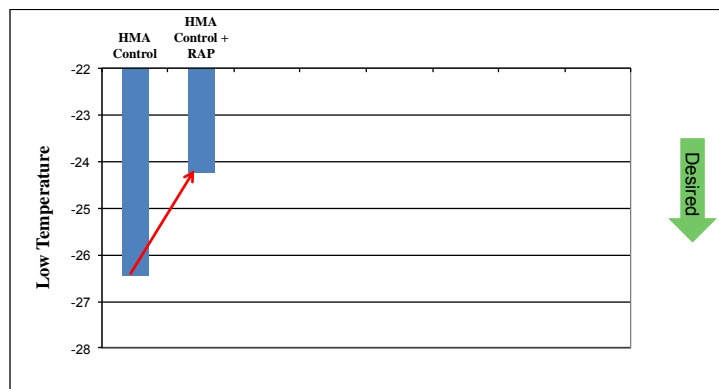
Influence of RAP on WMA binder rheology – LOW TEMPERATURE



- PG 76-28
- Low temperature grade based on m-value and estimated temperature sensitivity
- Best case scenario (25% RAP binder fully blended and same base binder)

Task 4: Rheological properties of binder

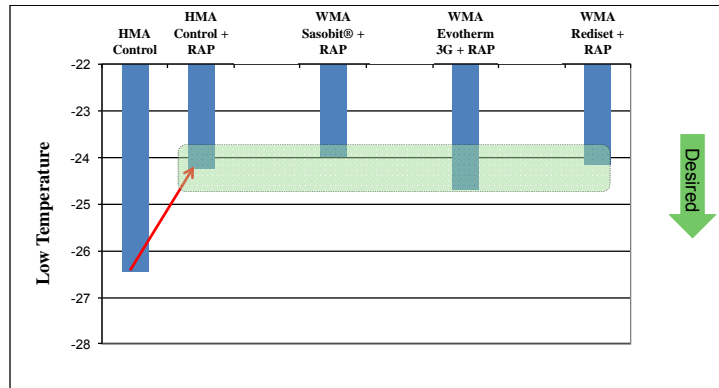
Influence of RAP on WMA binder rheology – LOW TEMPERATURE



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Task 4: Rheological properties of binder

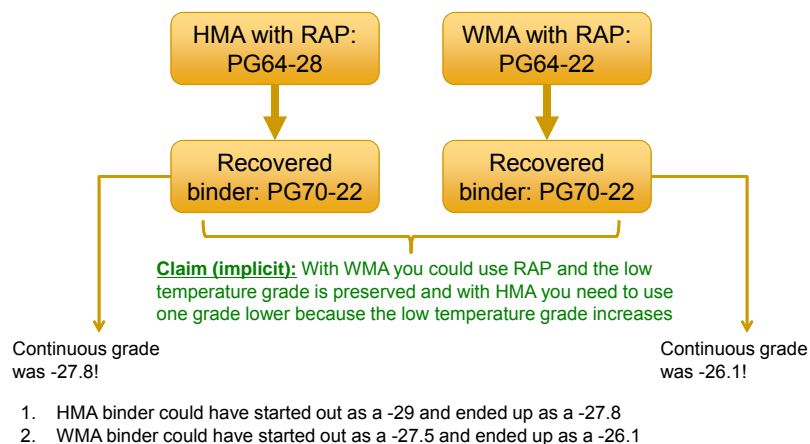
Influence of RAP on WMA binder rheology – LOW TEMPERATURE



- PG 76-28
- Low temperature grade based on m-value and estimated temperature sensitivity
- Best case scenario (25% RAP binder fully blended and same base binder)

Task 4: Rheological properties of binder

Side note on MWV data (Evotherm) ...



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Task 5: Performance of mortars / mixtures

How we plan to test the mortar?



Compaction in a
Superpave gyratory
compactor



Ends of the compacted
sample are removed
using a saw



About 15 to 20 test
specimens are cored
from a single SGC
compacted sample

Task 5: Performance of mortars / mixtures

How we plan to test the mortar?



Task 5: Performance of mortars / mixtures

Why test the mortar?

1. There is no binder test for moisture damage
2. Validate the observations and expected performance for fatigue cracking based on binder tests
3. Allows for larger number of test replicates

Task 5: Performance of mortars / mixtures

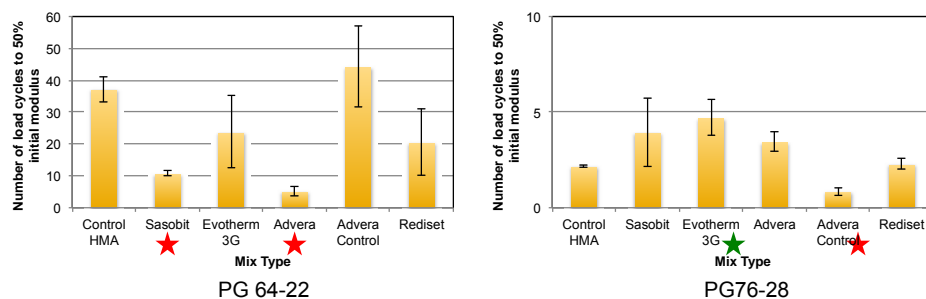
Mix design for mortar or FAM



Task 5: Performance of mortars / mixtures

Fine Aggregate Mixtures

1. How the do WMA additives affect fatigue cracking?



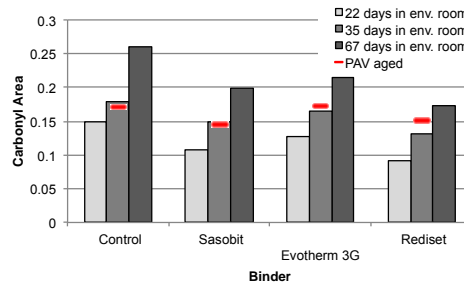
- Controls were cured at mixing temperature and others at (mixing temperature – 20C)
- Four hour curing time was used for all mixes
- ★ indicates significantly different at $\alpha=0.05$ compared to HMA using Fisher's LSD
- All tests are stress controlled

Task 5: Performance of mortars / mixtures

Fine Aggregate Mixtures

2. What happens to fatigue cracking resistance after long-term aging?

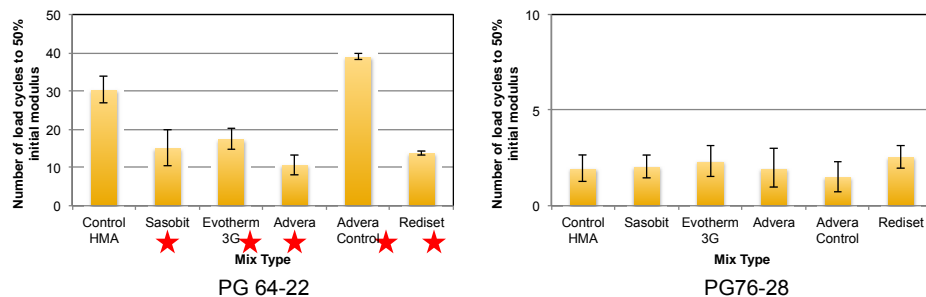
- Long-term aging of mixtures or mortars is not straightforward
- We used PAV level of aging as a benchmark
- For thin films of binder, about 30 days at 60C reaches the same level of oxidative aging as the PAV
- Loose mix was aged for 30 days



Task 5: Performance of mortars / mixtures

Fine Aggregate Mixtures

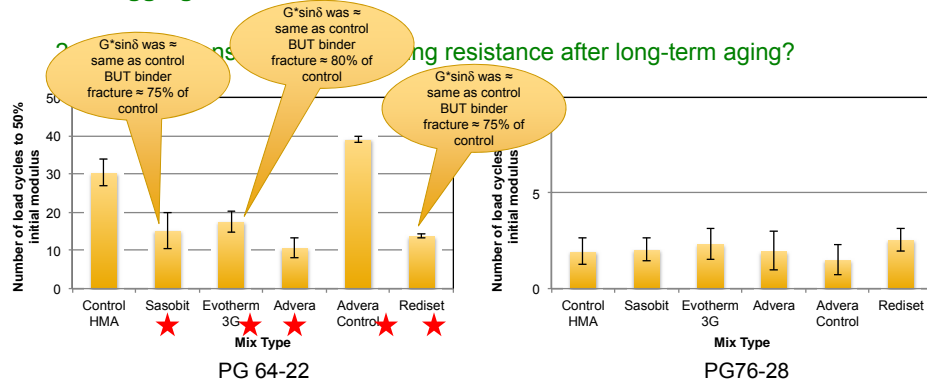
2. What happens to fatigue cracking resistance after long-term aging?



- Controls were cured at mixing temperature and other at mixing temperature – 20C; all mixes were then aged as loose mixes at 60C for 30 days
- ★ indicates significantly different at $\alpha=0.05$ compared to HMA using Fisher's LSD
- All tests are stress controlled

Task 5: Performance of mortars / mixtures

Fine Aggregate Mixtures

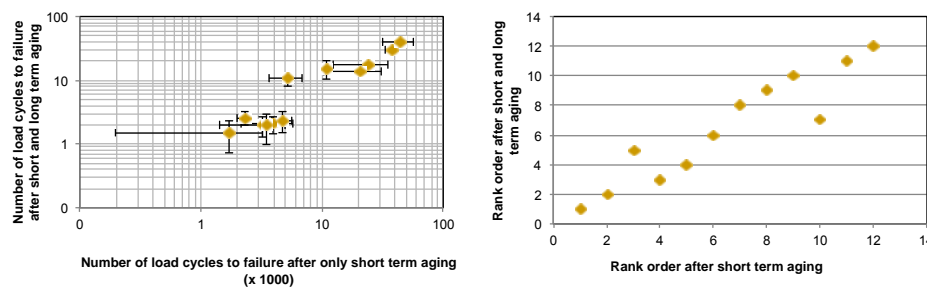


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Task 5: Performance of mortars / mixtures

Fine Aggregate Mixtures

3. Does the rank order change after long-term aging?

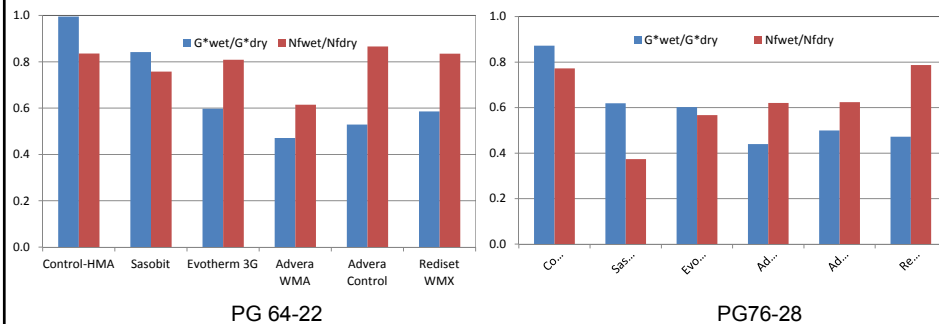


- Based on mortars with one type of aggregate only
- Other studies on mixtures indicate that for a given aggregate different binders aged at consistent rates in mixtures (Morian et al. 2011)

Task 5: Performance of mortars / mixtures

Fine Aggregate Mixtures

4. What about moisture sensitivity?



Task 5: Performance of mortars / mixtures

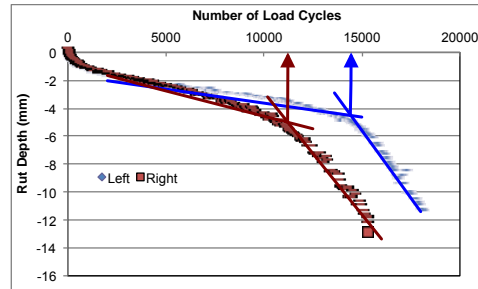
Full Asphalt Mixtures

1. What is the influence of WMA on rutting and moisture damage at high temperatures?
2. What is the influence of WMA on stiffness at intermediate temperatures?
3. What is the influence of WMA on fracture at low temperatures?

Task 5: Performance of mortars / mixtures

Full Asphalt Mixtures

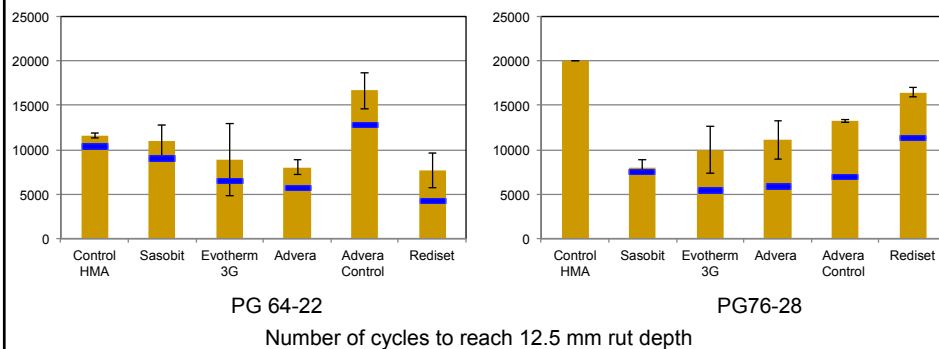
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Task 5: Performance of mortars / mixtures

Full Asphalt Mixtures

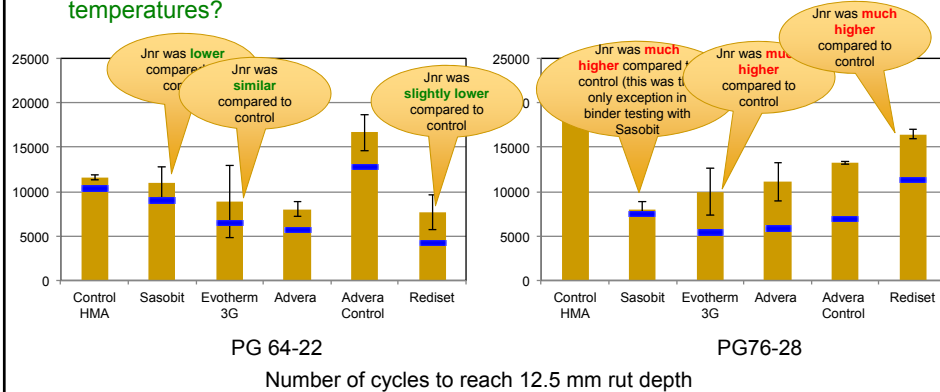
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Task 5: Performance of mortars / mixtures

Full Asphalt Mixtures

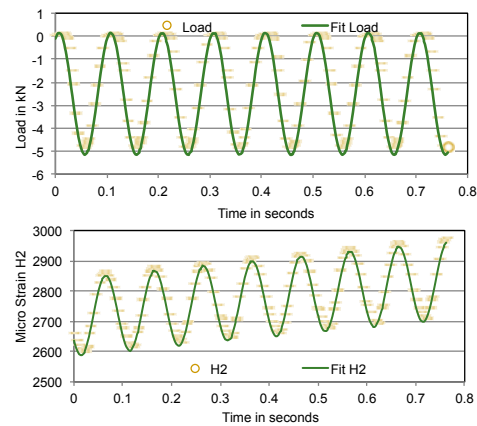
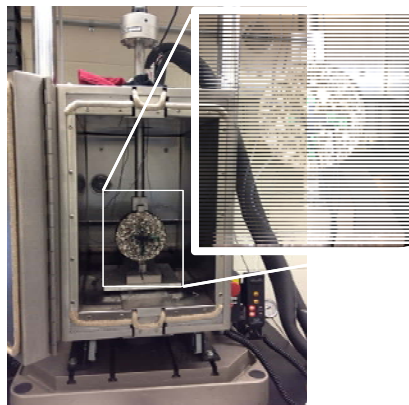
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Task 5: Performance of mortars / mixtures

Full Asphalt Mixtures

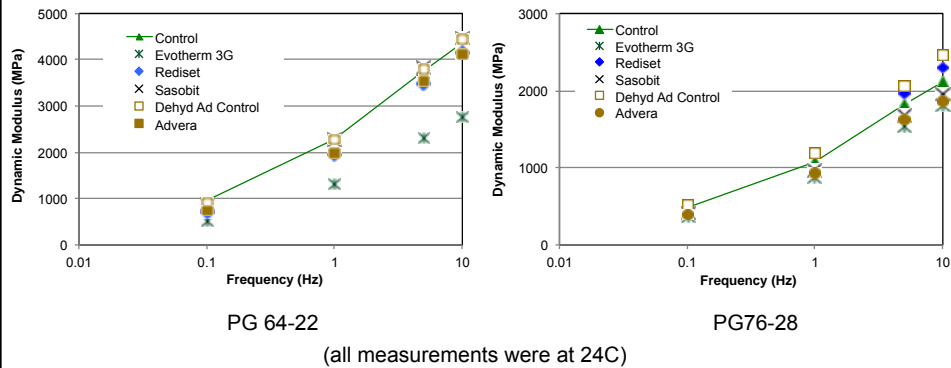
2. What is the influence of WMA on stiffness?



Task 5: Performance of mortars / mixtures

Full Asphalt Mixtures

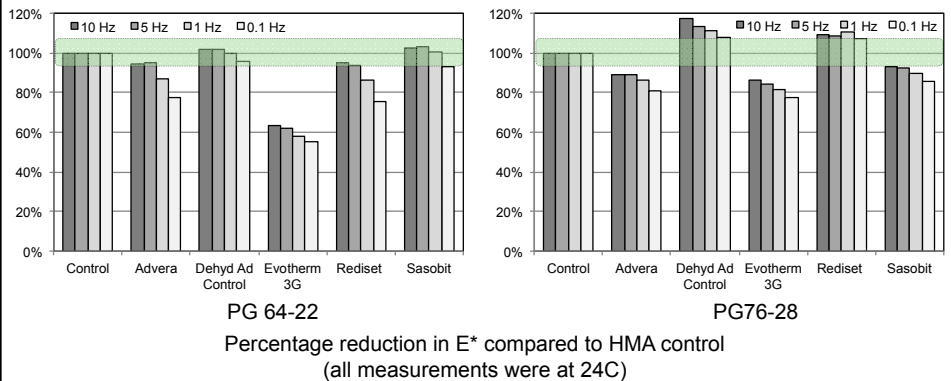
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Task 5: Performance of mortars / mixtures

Full Asphalt Mixtures

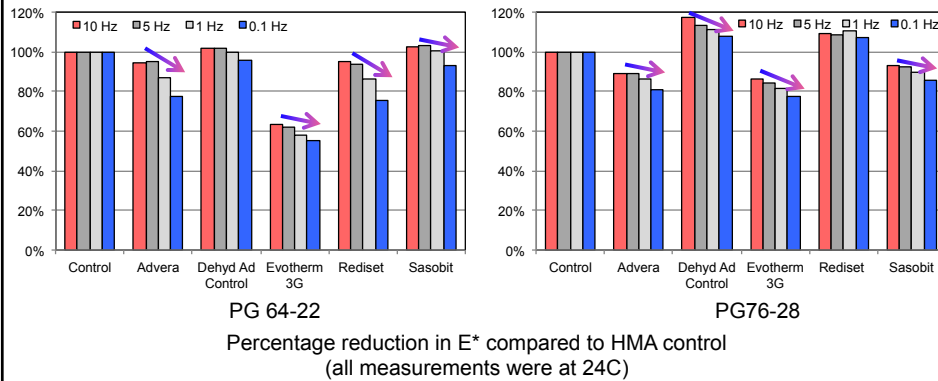
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Task 5: Performance of mortars / mixtures

Full Asphalt Mixtures

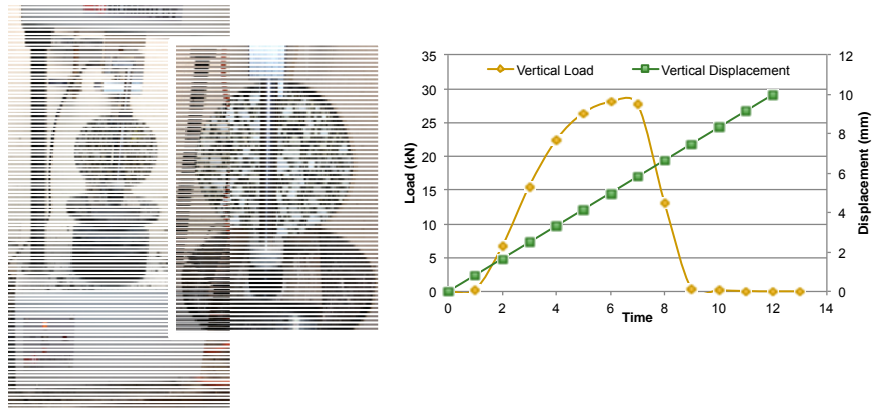
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Task 5: Performance of mortars / mixtures

Full Asphalt Mixtures

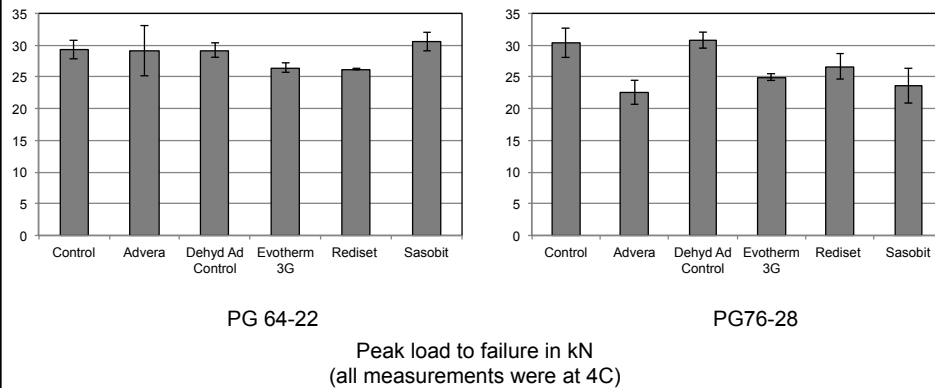
3. What is the influence of WMA on fracture at low temperatures?



Task 5: Performance of mortars / mixtures

Full Asphalt Mixtures

3. What is the influence of WMA on fracture at low temperatures?



Broader conclusions – Binder testing

Viscosity / Workability

- WMA additives seem to be very helpful, especially for longer storage/haul of mixes with PG 70 or 76 grade

Early age rutting resistance:

- Except for Sasobit (in most cases), WMA mixtures may be susceptible to rutting unless specifically designed
- Reduced rutting resistance was not just due to reduced aging but also due to the additives themselves

Broader conclusions – Binder testing

Long-term aged stiffness and cracking resistance

- After long-term aging, stiffness and relaxation of WMA modified binders tend to be similar to conventional binders

Implications of using RAP

- Use of WMA + RAP with WMA can help mitigate initial risk for rutting but may not provide any significant benefits over HMA + RAP.

Broader conclusions – Mortar and mixture testing

Fatigue Cracking

- WMA additives reacted differently with different binders in terms of their fatigue cracking resistance after long-term aging
 - PG64 showed reduced fatigue cracking resistance
 - PG76 showed no significant change
 - Consistent with binder fracture for PG64 measured at similar temperature
- Indirect tensile strength of short-term aged mixtures either did not change or reduced slightly depending on the binder – WMA additive pair
- General trends reported in the literature for different additives and binder combinations
 - WMA improved cracking resistance (Johnston et al. 2006)
 - WMA resulted in similar cracking resistance (Kristjansdottir 2007, Gandhi 2008, Johns 2009, D'Jones 2010)
 - WMA reduced cracking resistance (Akisetty 2008, Su et al. 2009)
 - WMA has mixed influence on cracking resistance (Haggag 2011)

Broader conclusions – Mortar and mixture testing

Modulus / Stiffness

- Stiffness of WMA mixtures was similar or lower compared to HMA at different frequencies
- WMA additives were more sensitive to stiffness reduction at lower rates of loading (equivalent to higher temperatures)
- Binder absorption in aggregate had a significant effect on mixture stiffness

Rutting

- WMA mixtures were generally more susceptible to rutting
- Rutting results from Hamburg were qualitatively consistent with binder testing with WMA additives

Broader conclusions – Mortar and mixture testing

Moisture induced damage

- Based on mixture and mortar testing WMA mixtures had similar or less resistance to moisture induced damage compared to the control; this does not necessarily imply that the WMA mixtures will fail requirements
- The above findings are generally consistent with the literature