North East Asphalt User/Producer Group
Portsmouth 20 - 21 October 2004

“ Asphalt chemically modified with polyphosphoric acid “

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PhD Chemistry

Innophos Formerly Rhodia

INNOVALT™

Context-Litterature review

• For the last few years, the use of product based on **Polyphosphoric Acid (PPA)** as a performance chemical asphalt modifier has strongly increased, especially in North America. *Field trials have expanded to Europe and Latino America with additives based on polyphosphoric acid chemistry*

•Publications :

- •2004 Journal of Pavement and Road Design (To be published Nov2004))
- •2004 TRB Hussain Bahia et. al.
- •2002 TRB Ho, et. al.
- •1992 FHWA Report Chollar, et. al.…

•Patents :

- •Air blown : 3 (Lion Oil, Exxon, Shell)
- •Chemical modification : 1 (Tosco Lion)
- •Polymer modified asphalt : 6 (MTE, Ergon (Innophos), Elf, Exxon, Marathon, Innophos)

• Recent presentations on **PPA** as asphalt modifier :

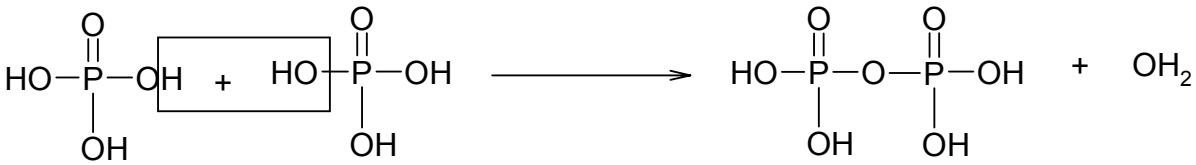
- • RMAUPG 2004 (Sante Fe) -2004 (Phoenix (AZ))
- • Eurobitume 2004 (Vienna (Austria))
- • Petersen Asphalt Conference 2004 (Cheyenne (WY))
- • 4th International Asphalt Congress 2004 (Cartagena (Colombia))
- • NEAUPG (2004 Portsmouth)…

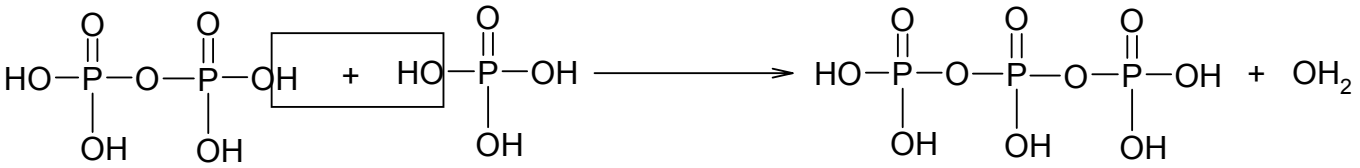
summary

- What is polyphosphoric acid (PPA) ?
- How PPA influence the asphalt rheology ?
- How PPA is working (investigation study) ?
- Does PPA work with all asphalt ?
- Is a PPA modified asphalt compatible with aggregates ?
- Could PPA be combined with Polymer ?
- Is a PPA+Polymer modified asphalt compatible with aggregates ?
- Is it a tried and tested technology ?

What is Polyphosphoric acid ?

Polyphosphoric acid is an Inorganic polymer,
obtained by thermocondensation of Orthophosphoric acid





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Main physical chemical characteristics

- 0%wt of Free water
- Viscous liquid (25°C) from 840 cP on up
- Freezing point = below 0 to 15°C
- Medium strong acid : Acidity function (Hammet) = 6 (ref H2SO4 = 12)
- Highly soluble in organics
- Non oxidizing molecules

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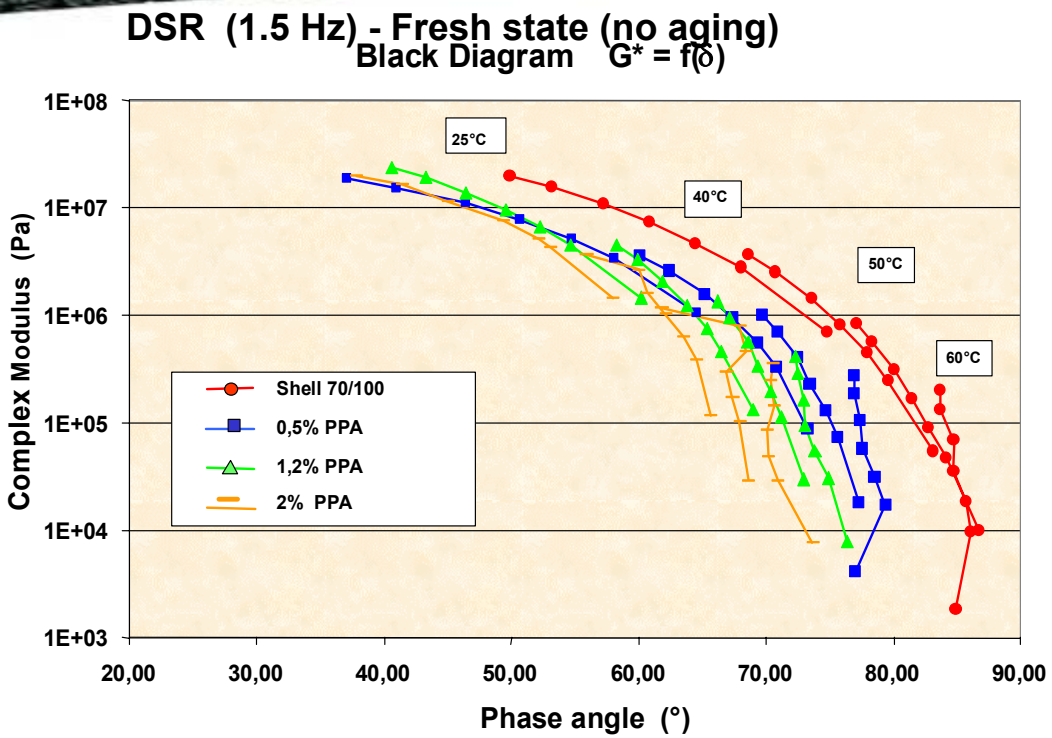
Asphalt Characteristics

Asphalt : Two different asphalt are used

General description	Saturated (%wt)	Aromatics (%wt)	Resins (%wt)	Asphaltene (n-heptane) (%wt)	PG grade
Paraffinic	4	48%	30%	9,3%	64-22
Naphtenic	4	38%	32%	17%	67-22

Asphalt Rheological Behavior : Effect of Polyphosphoric Acid



	neat	1.2% PPA
G* 60° (kPa)	1.95	5.82
d 60°	85.5	81
G* 25° (MPa)	0.79	1.27
G*/sinδ : Tc(°C)	64	71.5

Paraffinic asphalt (PG 64-22)

- **Polyphosphoric acid** improves the rheological behavior at high temperature compared to the neat binder :
  complex modulus G* is increased and phase angle δ is reduced.

  - large effect from 0 to 1.2% PPA
  - no more effect at content > 1.2%

Typically : + 1 PG grade, with 1% PPA

PPA contributes to more interactions within the asphaltenes network, leading to increased elastic bahavior.

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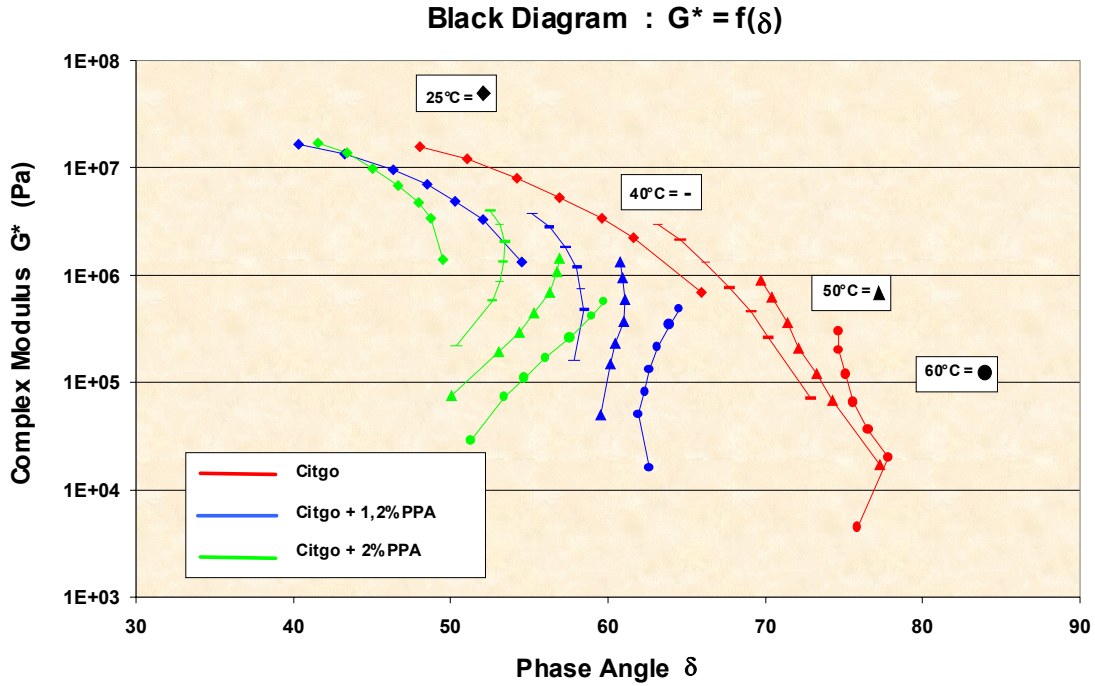
Asphalt Rheological bahavior : Effect of Polyphosphoric Acid

DSR (1.5 Hz) - Fresh state (no aging)

Naphthenic asphalt (PG 67-22)



	neat	1.2% PPA
G* 60° (kPa)	4.58	16.32
δ 60°	75.9	62.6
G* 25° (MPa)	0.68	1.31
G*/sinδ : Tc(°C)	69.5	82

- Similar effect as with paraffinic asphalt, but naphthenic asphalt is <u>much more</u> reactive with PPA.

- **Polyphosphoric acid** improves the rheological behavior at high temperature :
  complex modulus G* increases and phase angle δ is reduced.

  - large effect from 0 to 2% PPA

Typically : + 2 PG grade, with 1% PPA

Large range of interactions between asphaltenes -> consolidated network.

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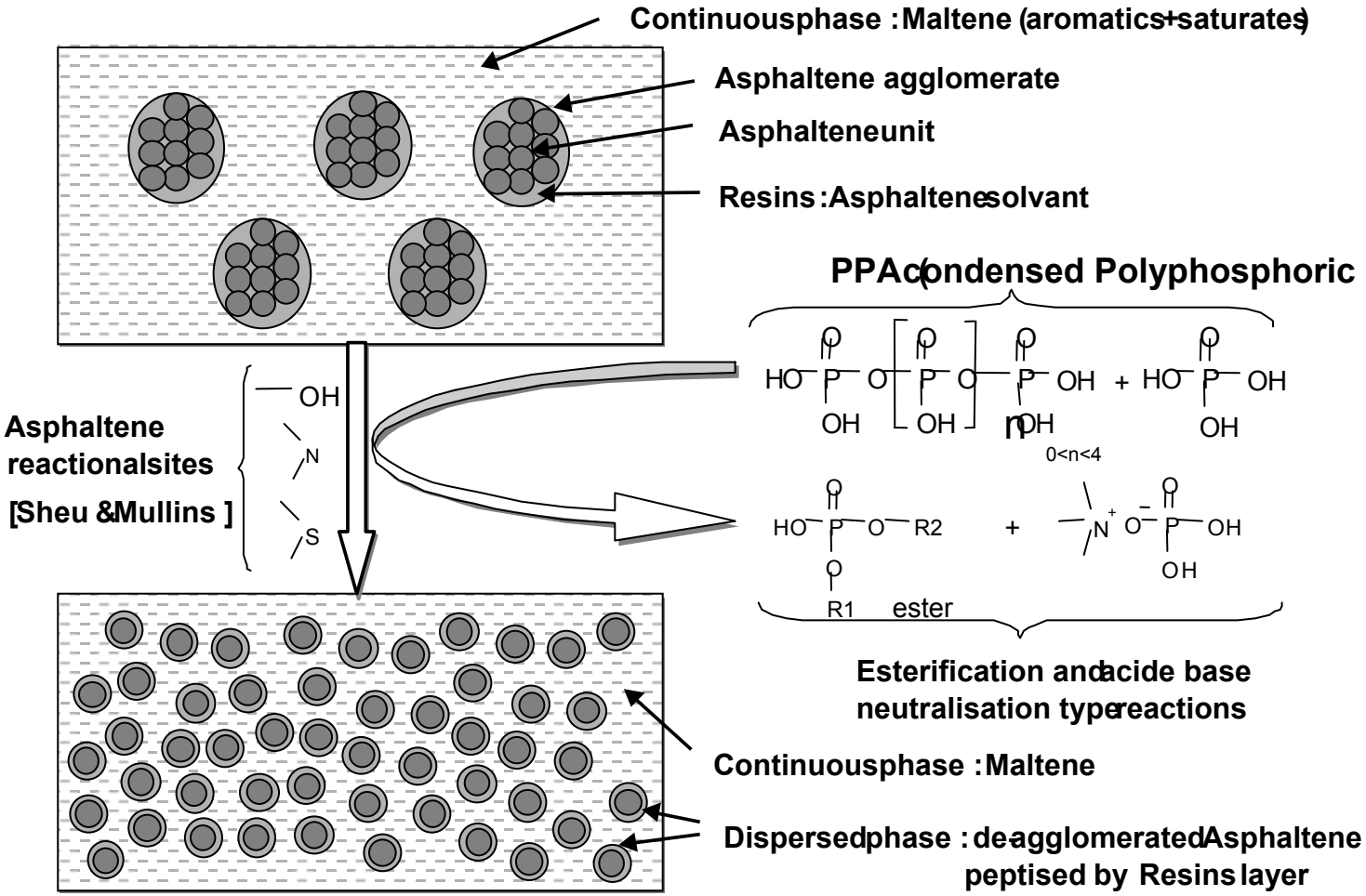
Polyphoshoric acid - asphalt interaction : Model

Asphaltenes Dispersion : *Polyphosphoric acid acts as a 'defloculant'*



R1, R2 : H or C linked to asphaltene resines molecules

Published at Eurobitume 2004, Study done in partnership with LCPC (French Central Laboratory of Road and Bridges)

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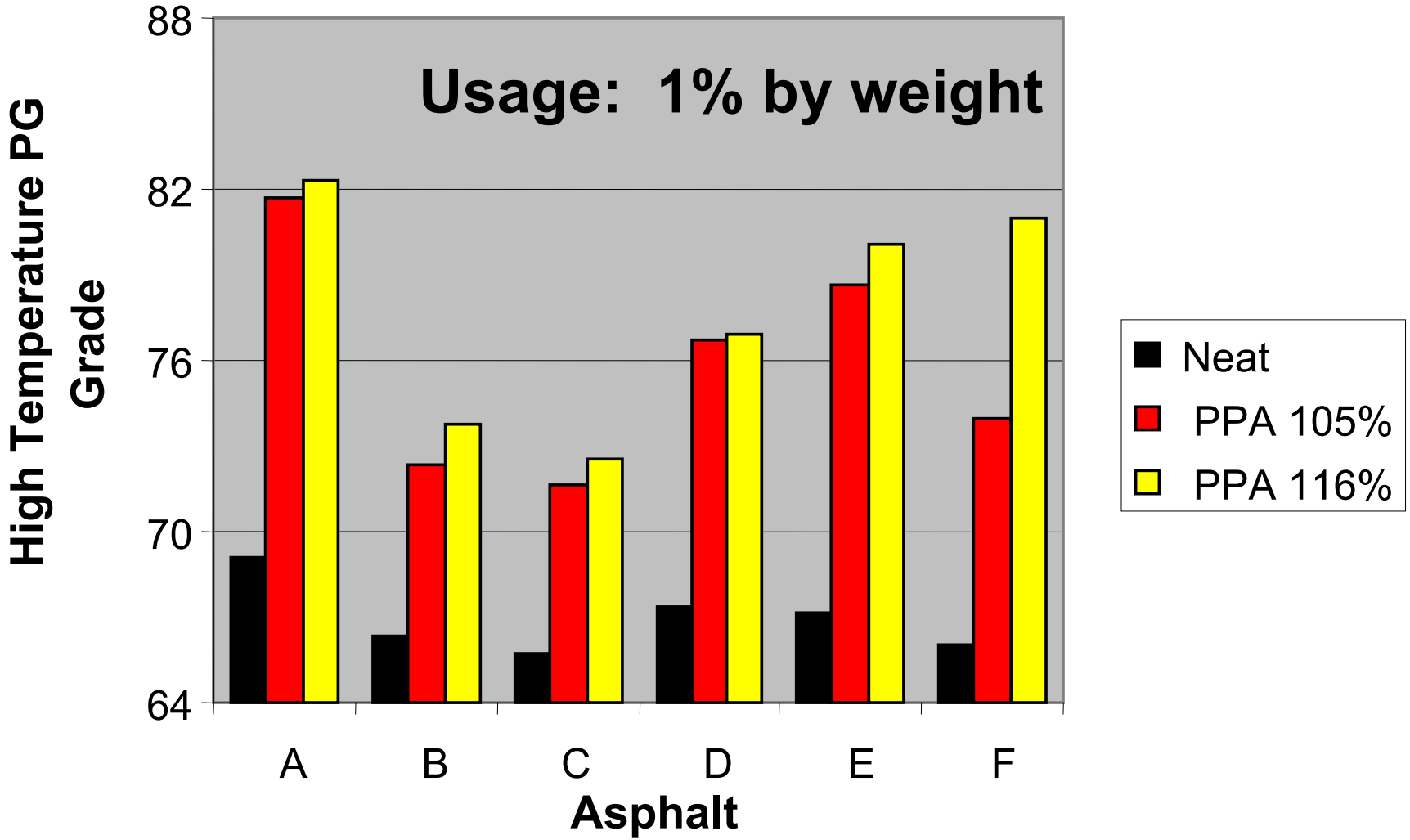
HIGH TEMPERATURE PERFORMANCE

A = CITGO
B = BP Canada

C = TOSCO
D = Marathon

E = CHEVRON
F = Mayan (AC-20)

DSR (RTFO)



PPA improves the High Critical Temperature Tc

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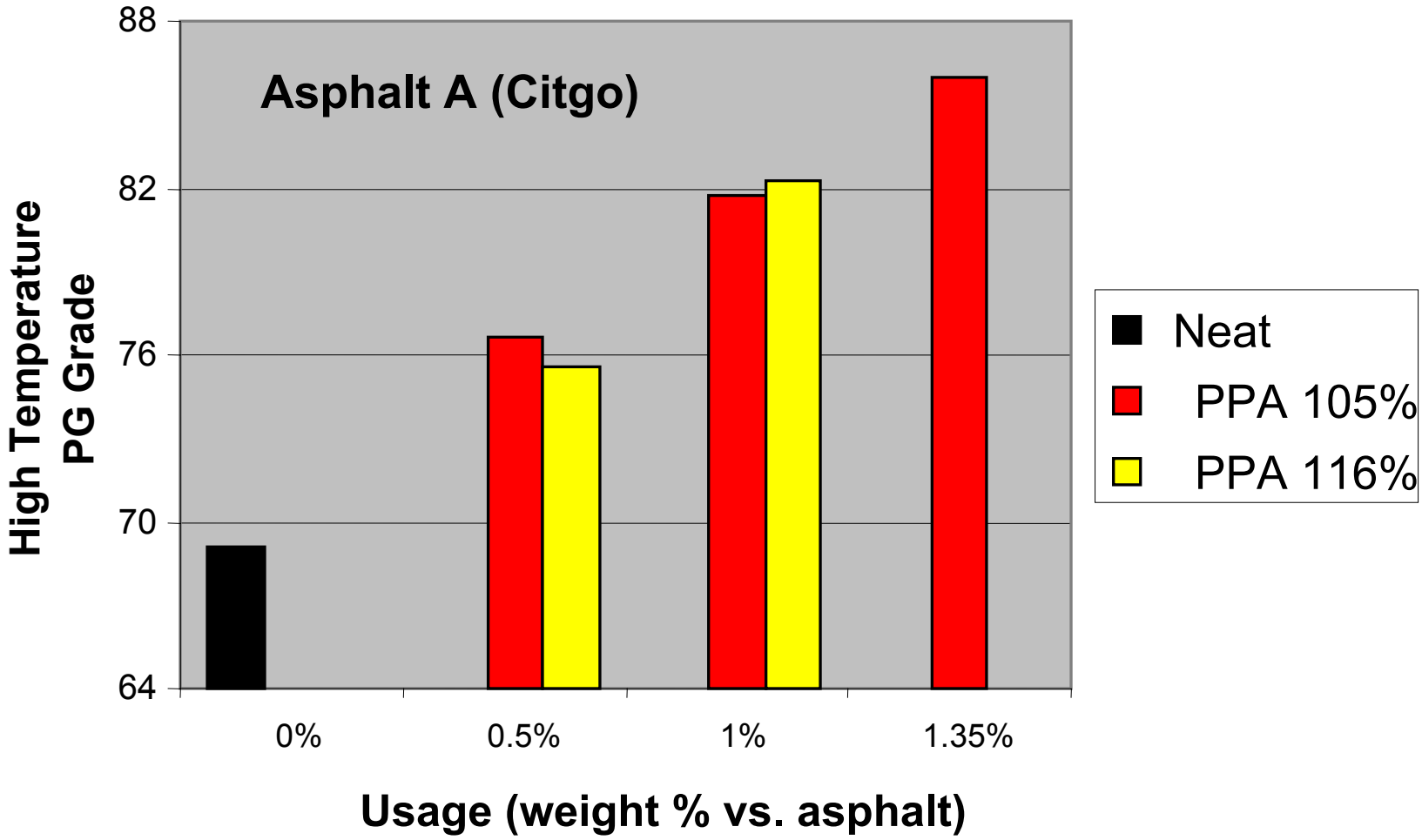
PPA : HIGH TEMPERATURE PERFORMANCE

DSR (RTFO)



One to two grade jump with PPA (cf asphalt spec)

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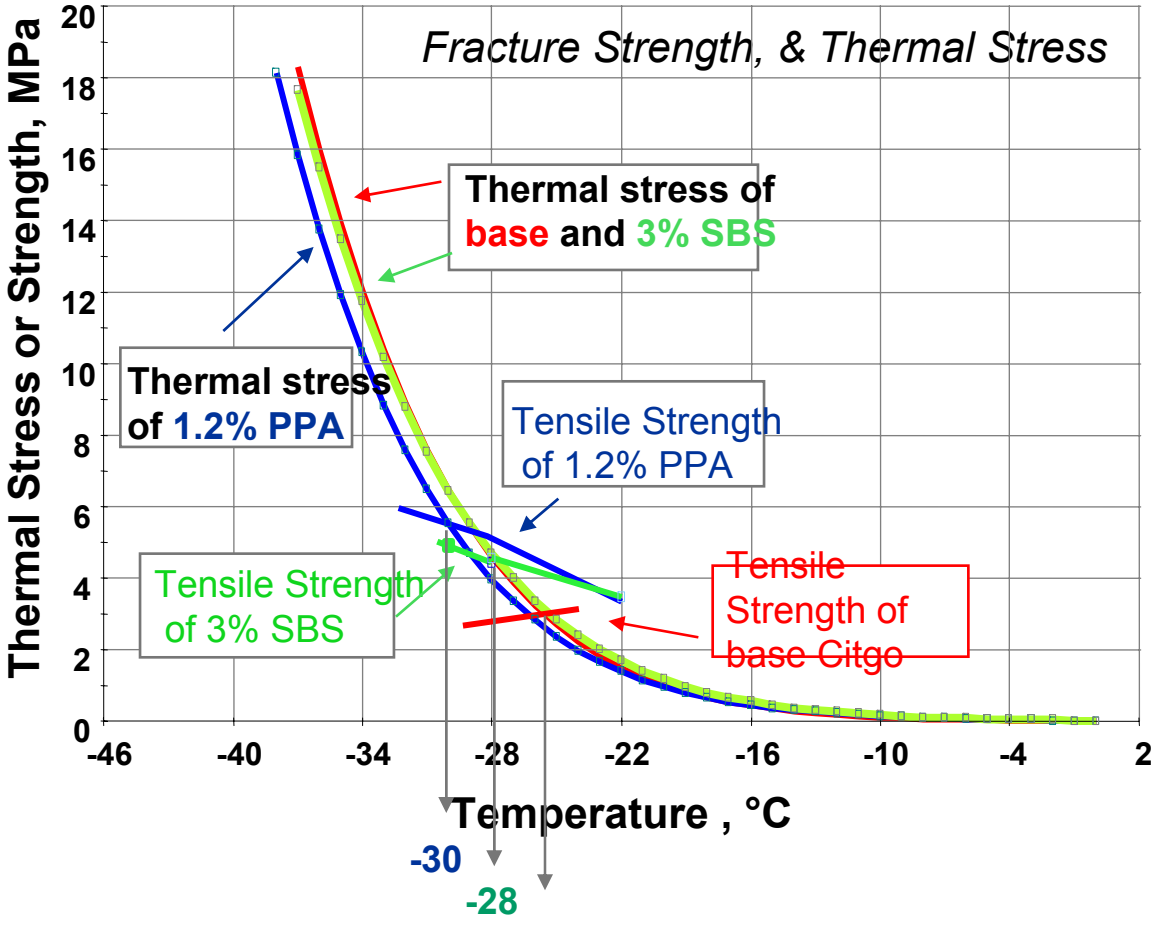
Low Temperature Fracture behavior : PPA modified asphalt

Naphthenic Asphalt (PG 67-22)

Aging treatment : PAV

PPA modification : 1.2%
SBS modification : 3%



BBR-DTT : AASHTO-MP1-A

- **Thermal stress** curve is shifted towards lower temperatures with PPA modification
- **Tensile strength** of neat asphalt is well improved with PPA (1.2%), similar to SBS (3%) modification
- **Cracking behavior**, according to MP1A, is improved with PPA modification

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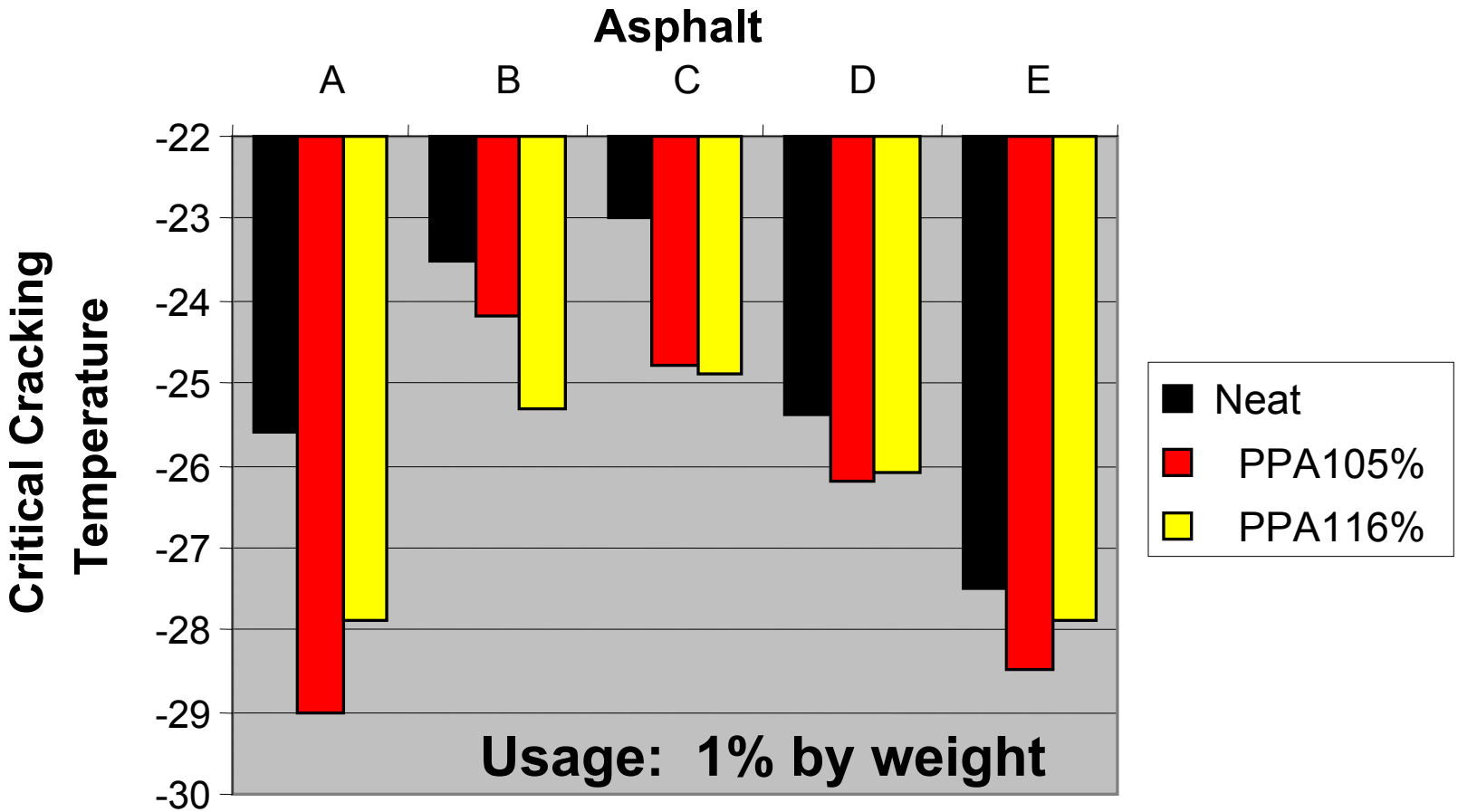
PPA : CRITICAL CRACKING TEMPERATURE

A = CITGO
B = BP Canada

C = TOSCO
D = Marathon

E = CHEVRON

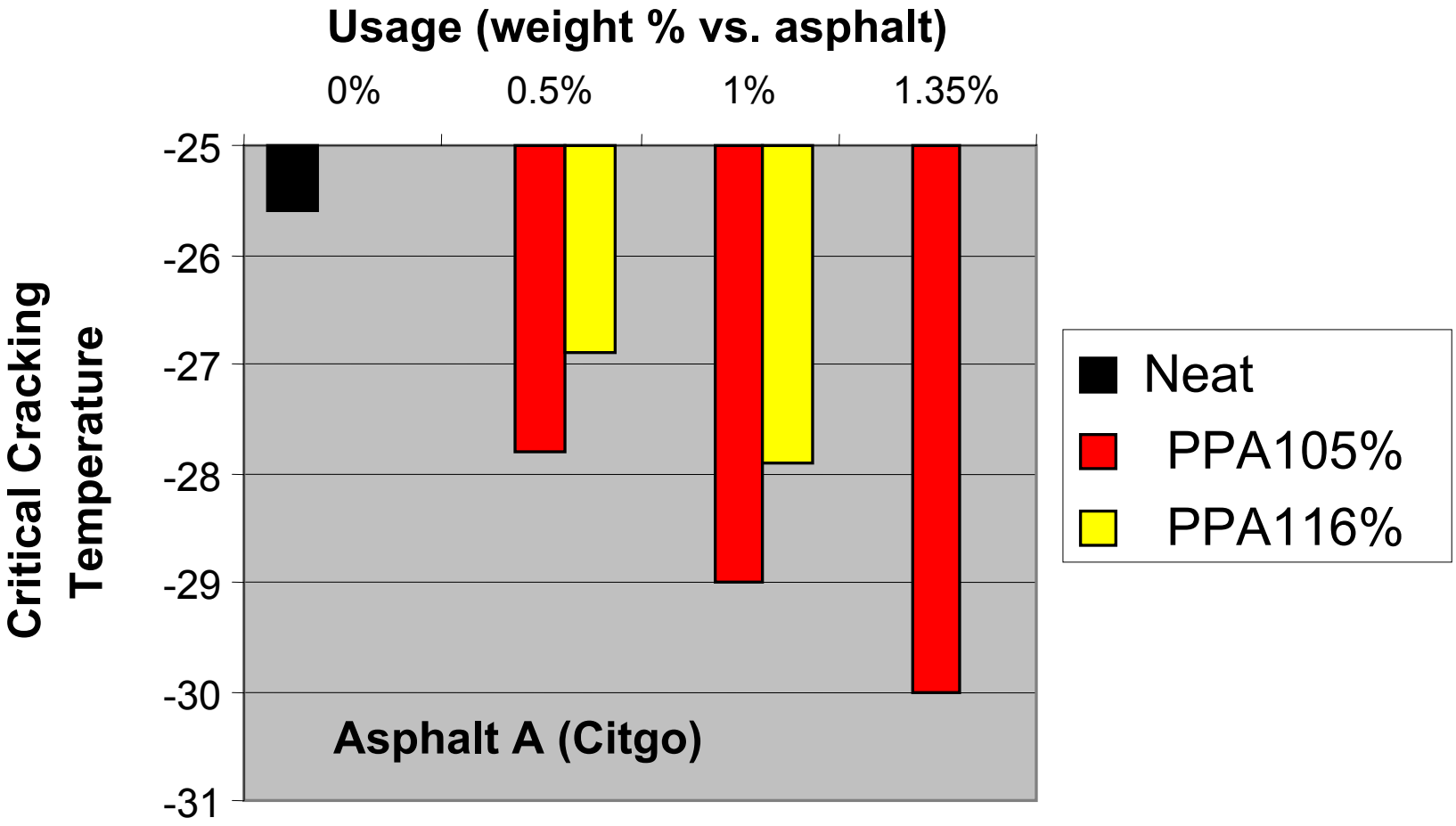
BBR/DTT (AASHTO MP1A) (PAV)



PPA improves the Low Critical Temperature Tc

PPA : CRITICAL CRACKING TEMPERATURE

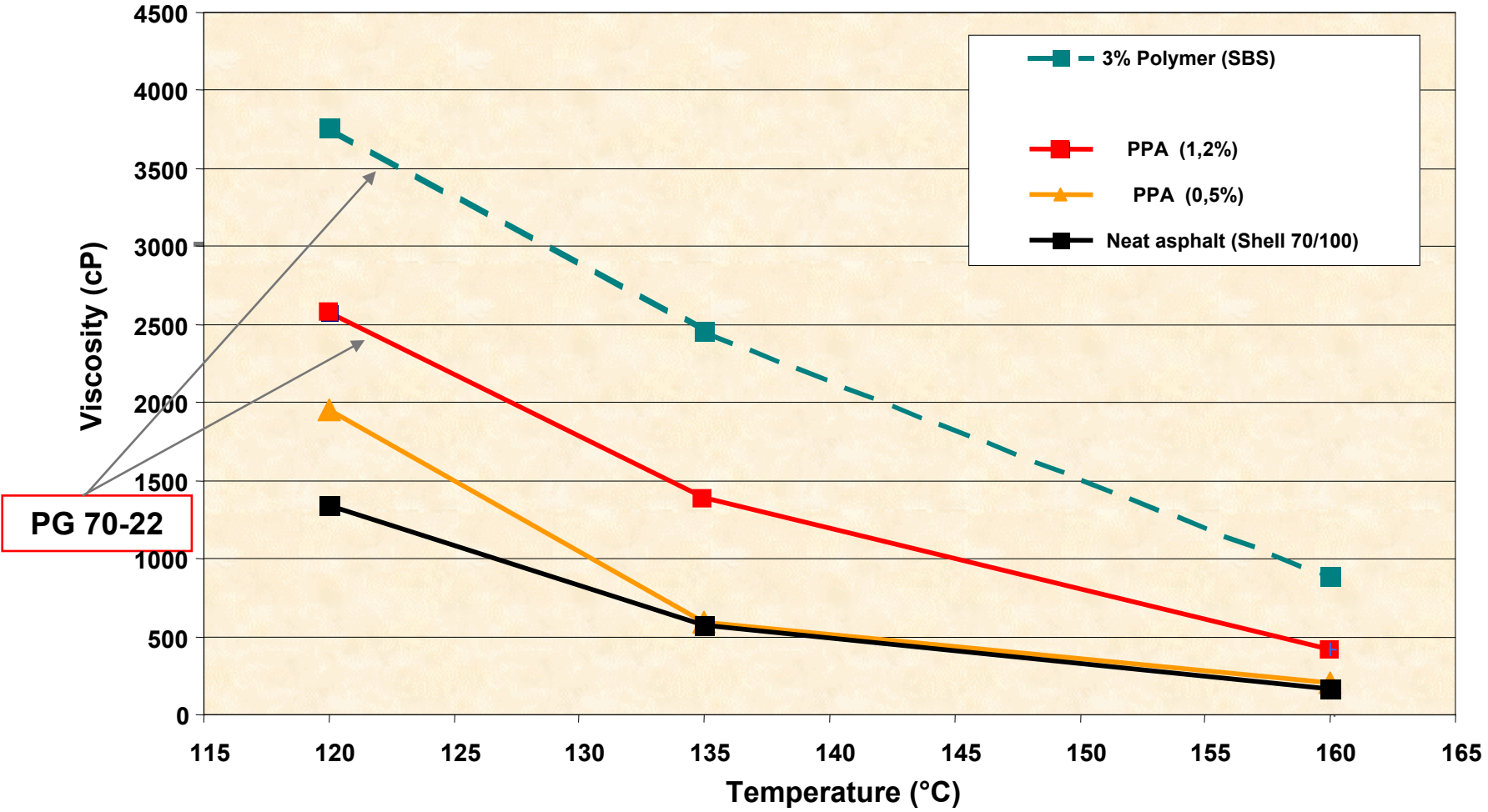
BBR/DTT (AASHTO MP1A) (PAV)



PPA improves the Low Critical Temperature Tc

PPA : High Temperature Viscosity

Shell 70/100 PC (France)



PPA reduced the viscosity resulting in reduced application temperature versus a polymer asphalt

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Adhesion-Moisture sensitivy evaluation

- **Boiling Water Test (BRRC Procedure ME65/91)**

  Stripping Resistance

  - Procedure defined by The Belgian Road Research Centre (BRRC), correlated with field results
  - Aggregates coated with binder (1.5%) at 160ºC and Coated aggregates suspended in boiling water for 10 minutes
  - The boiled sample is attacked by mineral acid. Acid is then consumed by decoated aggregates.
  - Remaining acid is then determine and Stripping Rate is obtained

- **TSR (AASHTO T 283)**

  Binder Cohesion – Stripping Resistance

  - Procedure on mixes, at fixed air voids content
  - Compression test : at dry, and water conditioned state
  - Determination of the compression strength ratio.

- **Cantabro**

  Binder Cohesion – Stripping Resistance

  - Procedure on mixes, at fixed air voids content
  - Abrasion test on dry, and water conditioned samples
  - Determination of the lost of sample weight after impact into Los Angeles drum

- **Hamburg (+Rutting)**

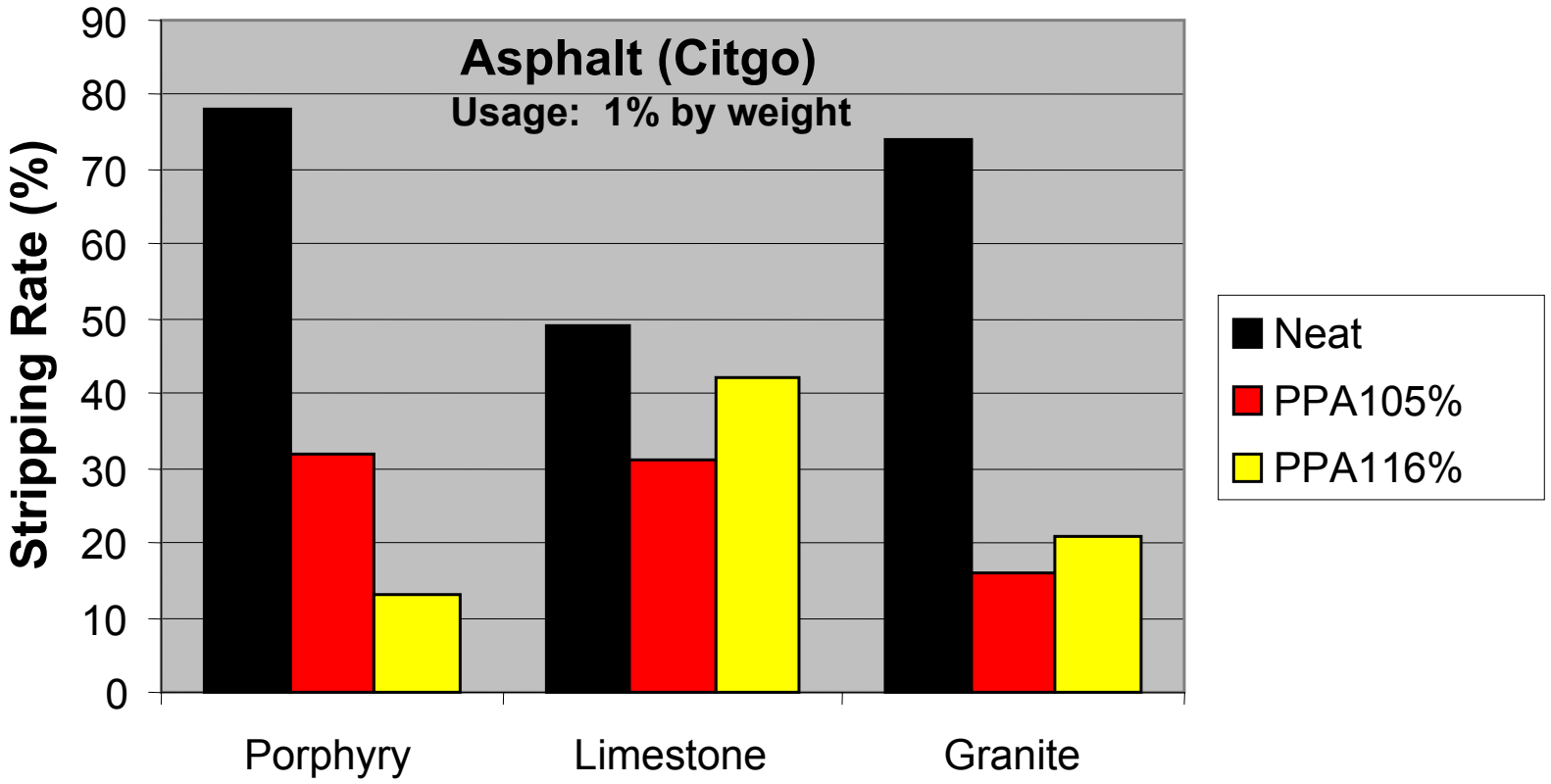
  Binder Cohesion – Stripping Resistance

  - Procedure on mixes, at fixed air void content
  - Rutting measurement under hot water conditions

PPA Improve mix moisture resistance in case of silicious aggregates

Naphtenic Asphalt (Venezuelian)

Boiling Water Stripping : BRRC test



PPA provides improved antistrip properties (except with this Limestone in this asphalt case (which is already very acidic)

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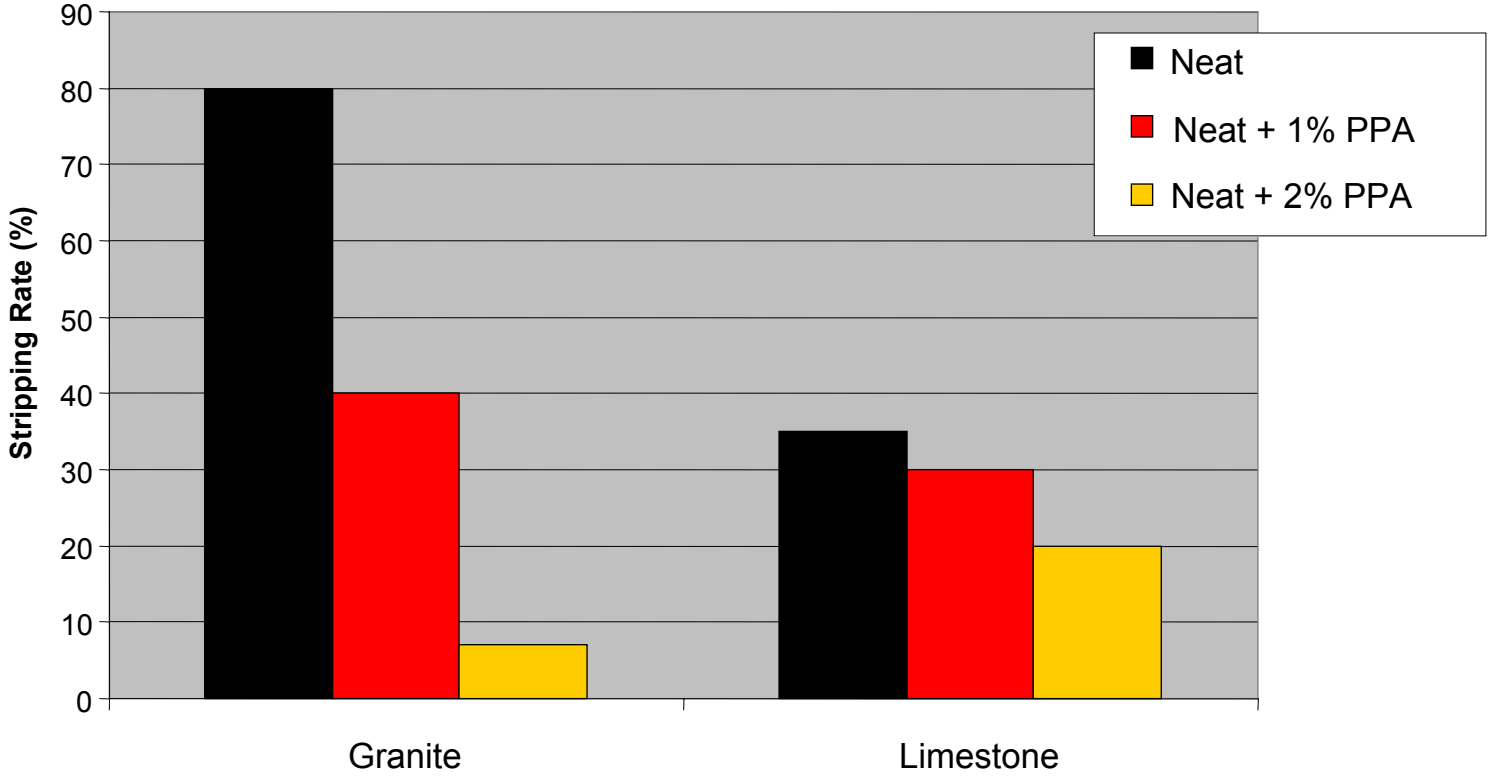
PPA Improve mix moisture resistance in case of silicious aggregates and limestone

Paraffinic Asphalt (Middle East)

Boiling Water Stripping : BRRC test



PPA provides improved antistrip properties in case of silicious aggregates .
Moisture sensitivity in case of limestone could be improved depending about the nature of the asphalt and aggregate

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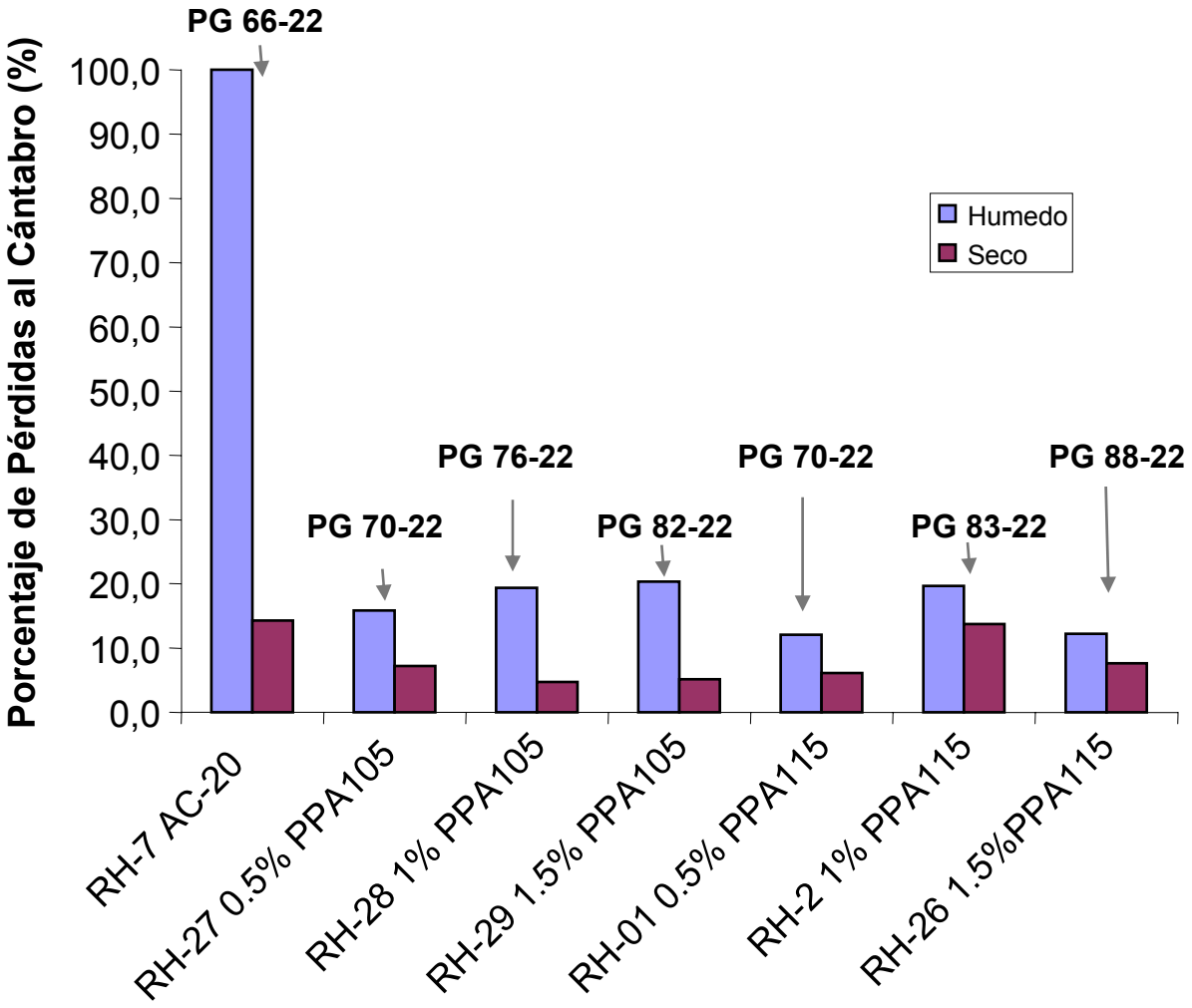
Cantabro test : Moisture sensitivity as well as cohesion are improved with PPA

Basalt aggregates

Mayan asphalt



Cohesion of binder is improved with Innovalt modification

Moisture sensitivity is improved due to PPA modification of asphalt

- **T=25°C**
- **Binder rate = 4,5%**
- **Air Void = 20%**
- **Average of 3 measures**

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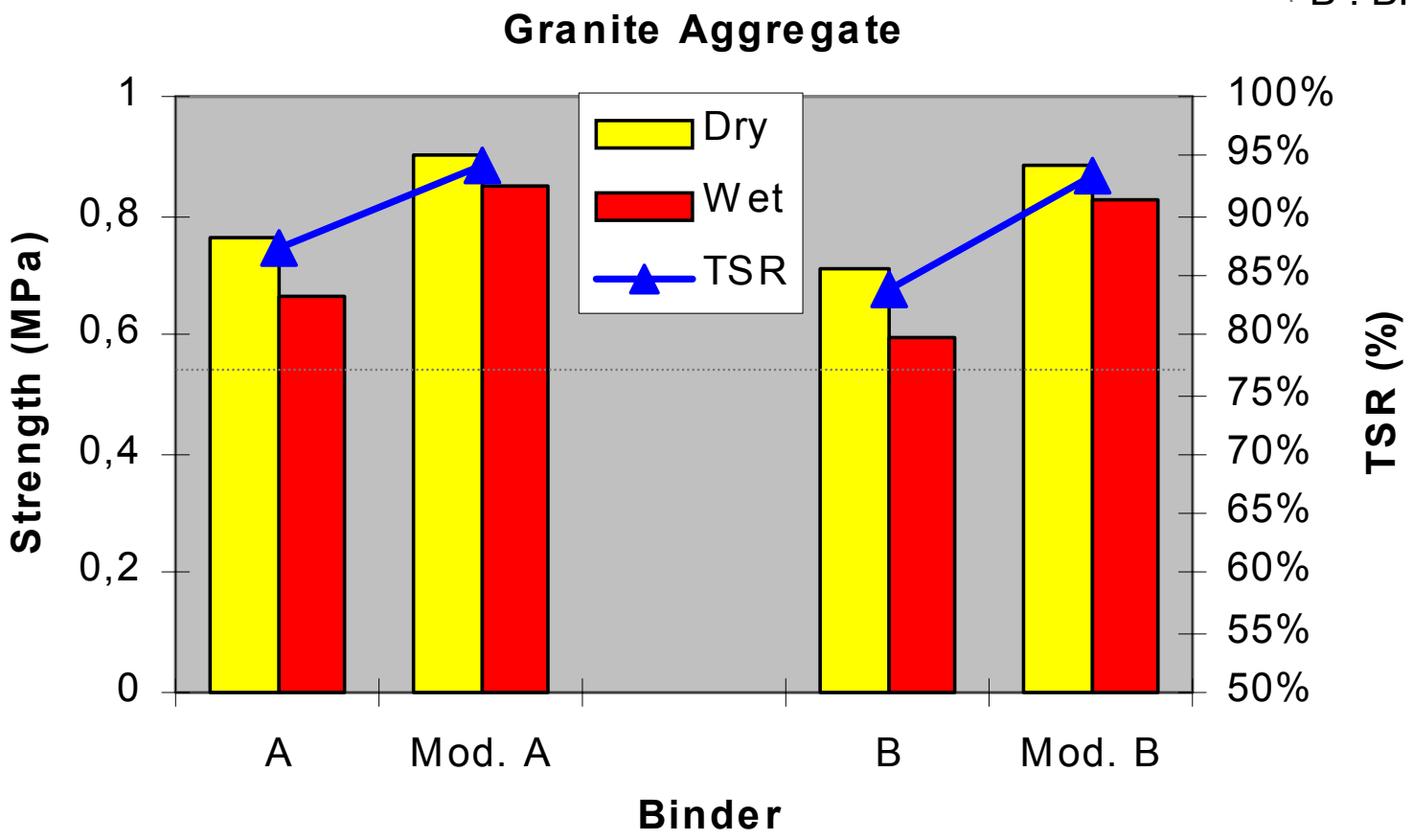
PPA Improve mix moisture resistance in case of silicious aggregates

TSR RESULTS : Granite Aggregates (Cisler)

A : CITGO 67-22
B : BP 64-22



No need for antistrip additives with granite aggregate

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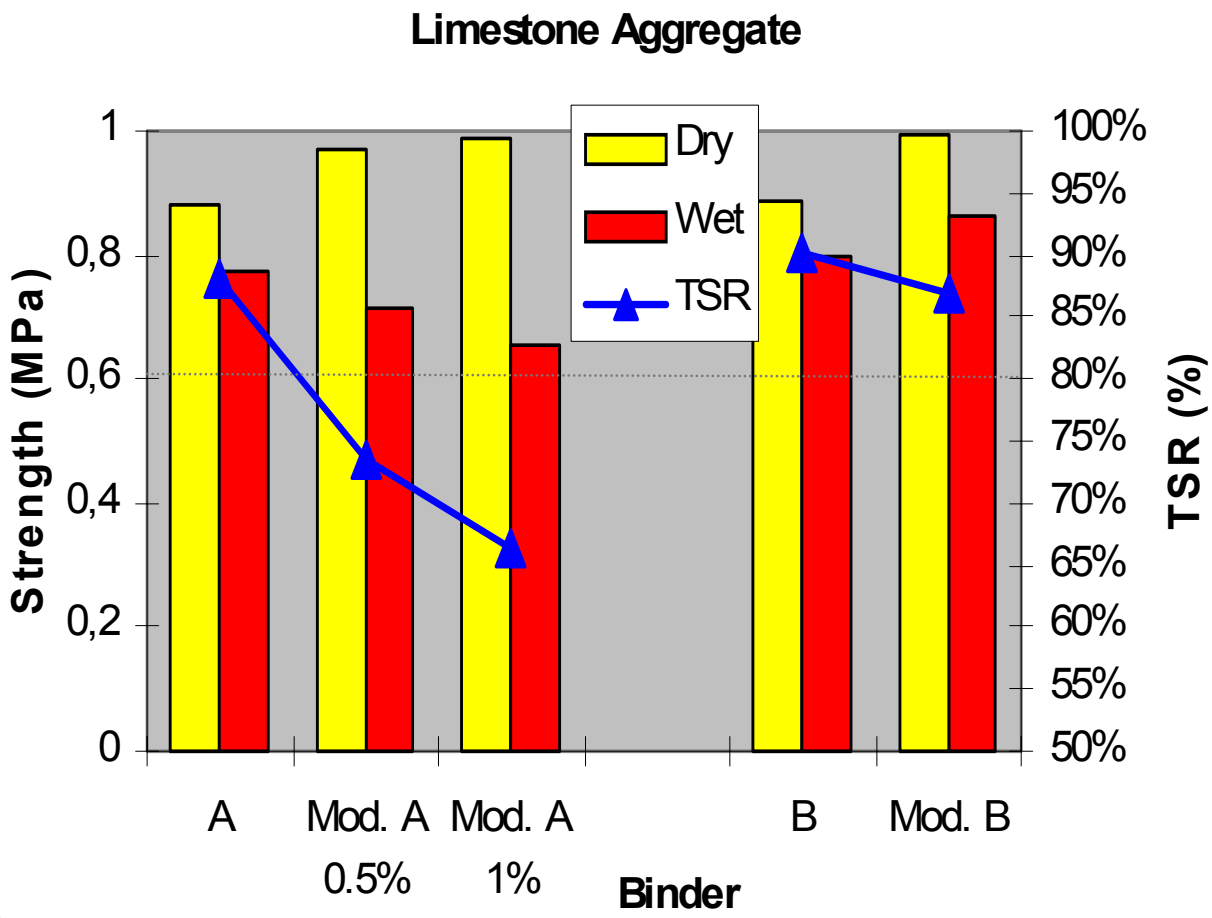
Depending on the nature of the asphalt and the aggregates , antistrip additive could be required in combination with PPA

TSR RESULTS : Limestone Aggregates (Medary)



A : CITGO
B : BP

Consistent results with Boilling Tests observations

<u>In case of Naphtenic</u>

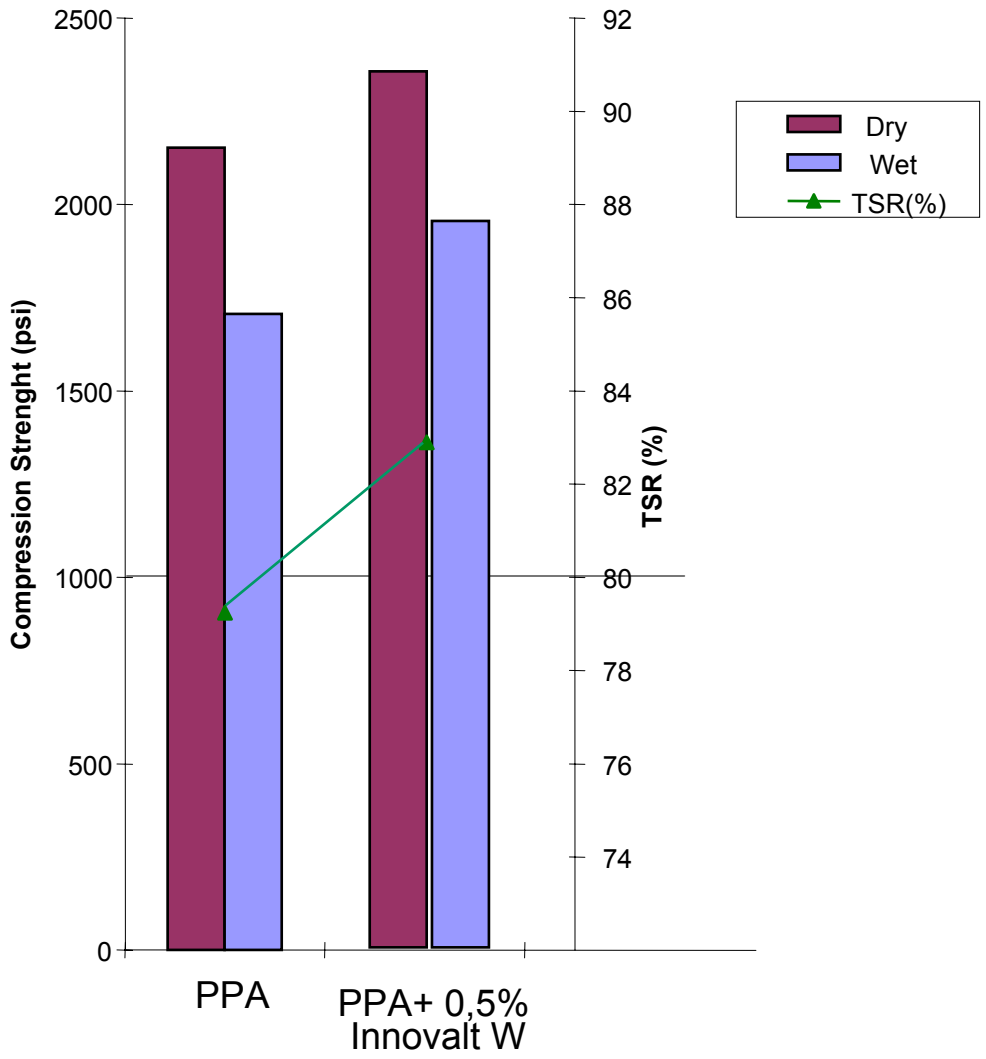
- Higher moisture sensitivity in presence of PPA is observed

A compatible antstrip is requested

<u>In case of Paraffinic :</u>

- Dry and wet sample tension strength are improved in presence of PPA, but the improvement is higher in dry condition than for the wet one

Combination of PPA + Compatible antistrip improves TSR



Limestone
(Ergon Asphalt)

Combination of PPA + Compatible antistrip improves TSR

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Conclusion on Asphalt Modification with PPA

- In case of granite aggregates :
  - PPA improved the cohesion of the mix
  - PPA improved the resistance of mix to moisture

- In case of limestone aggregate
  - For a Naphtenic asphalt (high acidity level) the combination with PPA reduces the resistance to moisture
    - A compatible antistrip may be used to improve resistance to moisture
  - For a Paraffinic asphalt the combination with PPA does not impact the stripping and moisture resistance

PPA Modified Asphalt

Generally speaking the amount needed of **PPA** is within **0.5 to 1.5%**.

PG Grades : generally at least one **grade bump** in high temperature SHRP number with excellent low temperature properties, and durability.

At high PPA contents (>1,2%), a two grade bump is possible (according to asphalt composition)

Adhesion is maintained -or even improved - according to the type of aggregates used.

PPA is easily incorporated into asphalt (viscous liquid), with no large modification of **viscosity** (135°C) and **no storage** problem of modified asphalt.

Health Safety and Environment : OK (high temp. stable, **no emission**, and not classified)

PPA is an economical asphalt modifier

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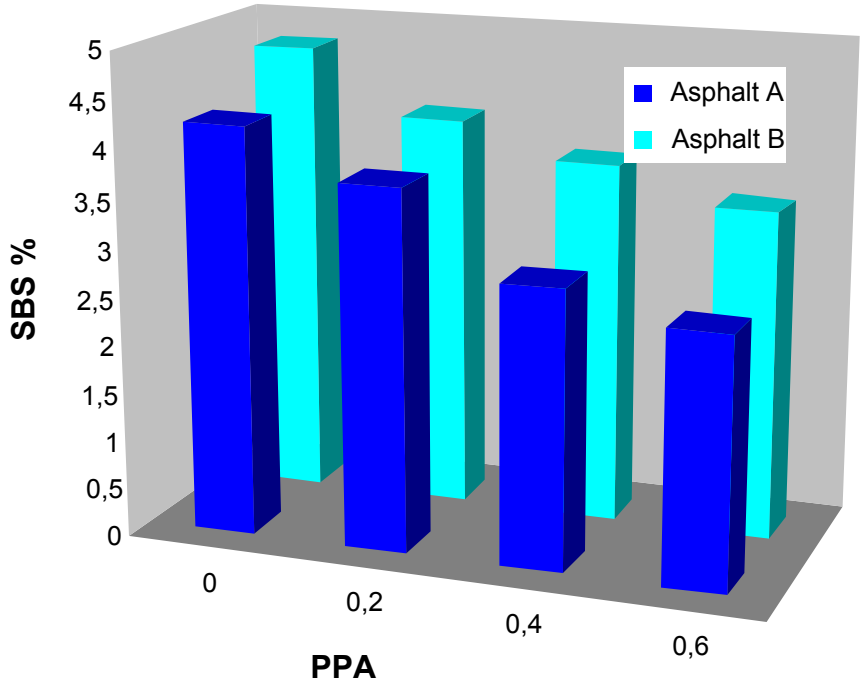
PPA + SBS : PG GRADING (PmB)

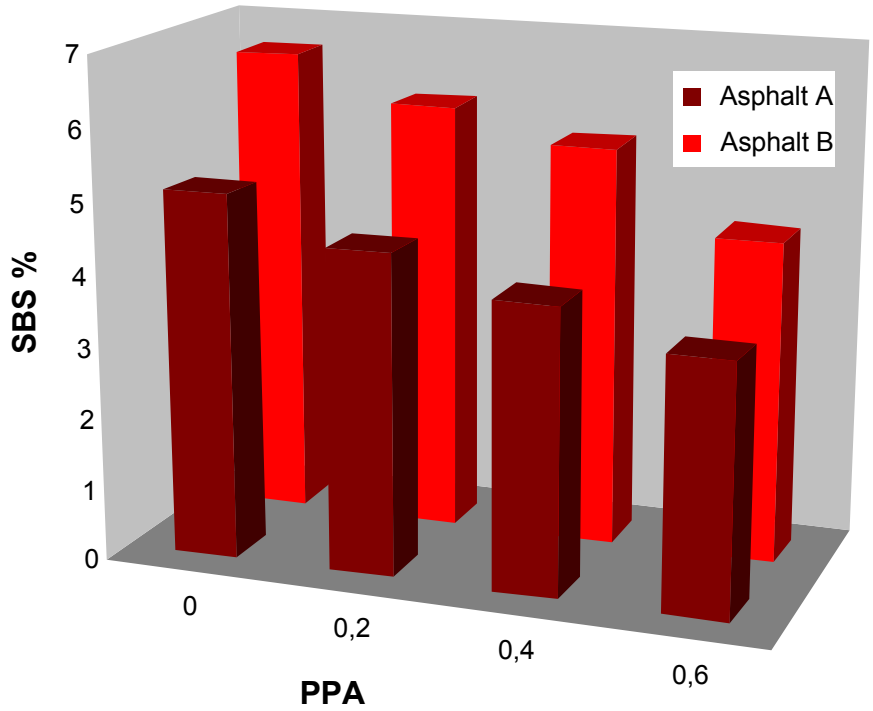
Partial Substitution of SBS with PPA at same PG grade

A : Ergon (Venezuela)

B : Lion Oil (Middle East)

SBS : Dexco Vector 2411 (radial)





76-22 PG

(4% SBS can be substituted with : 2.5% SBS + 0.6% PPA)

82-22 PG

(4.5% SBS can be substituted with : 3% SBS + 0.6% PPA)

1% PPA perform as well as 3% SBS

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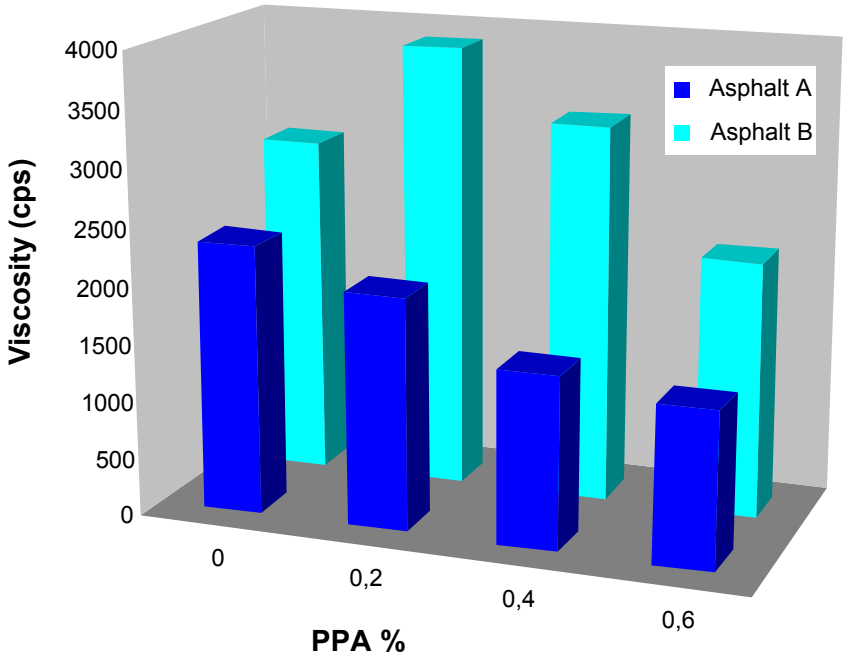
PPA + SBS : Brookfield VISCOSITY @ 135°C

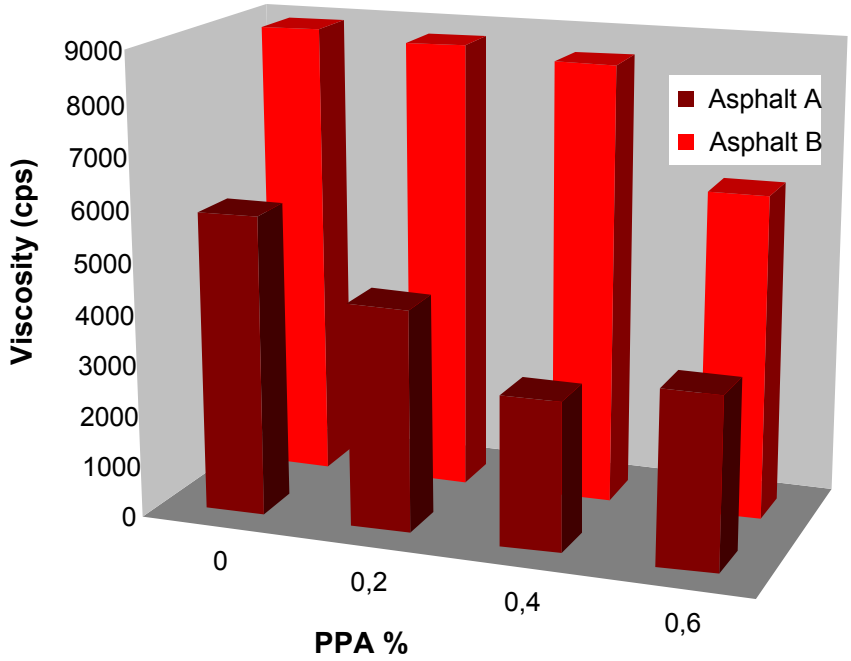
Partial Substitution of SBS with PPA at same PG grade

A : Ergon (Venezuela)

B : Lion Oil (Middel East)

SBS : Dexco Vector 2411 (radial)





76-22 PG

82-22 PG

→ **High temperature viscosity is reduced**

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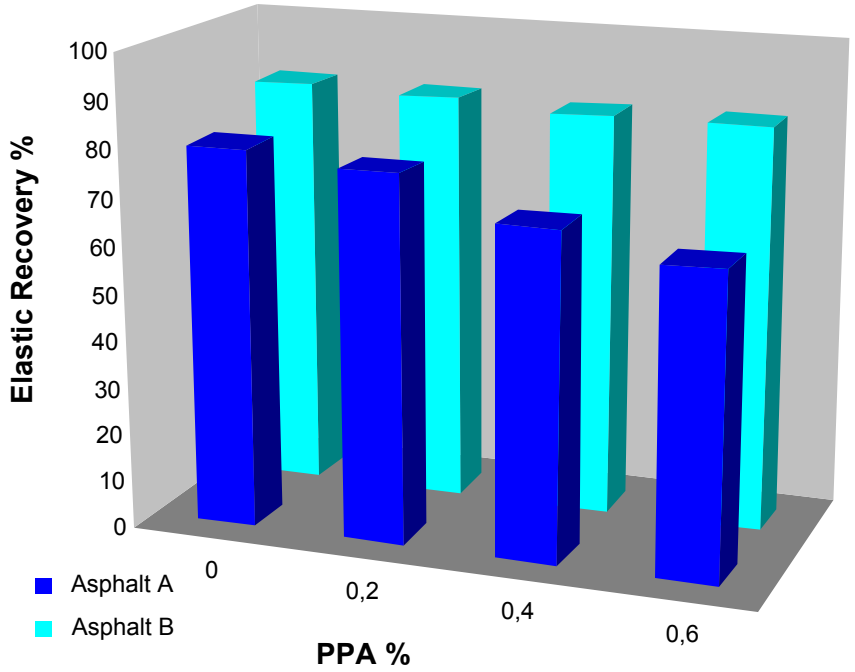
PPA+SBS : ELASTIC RECOVERY

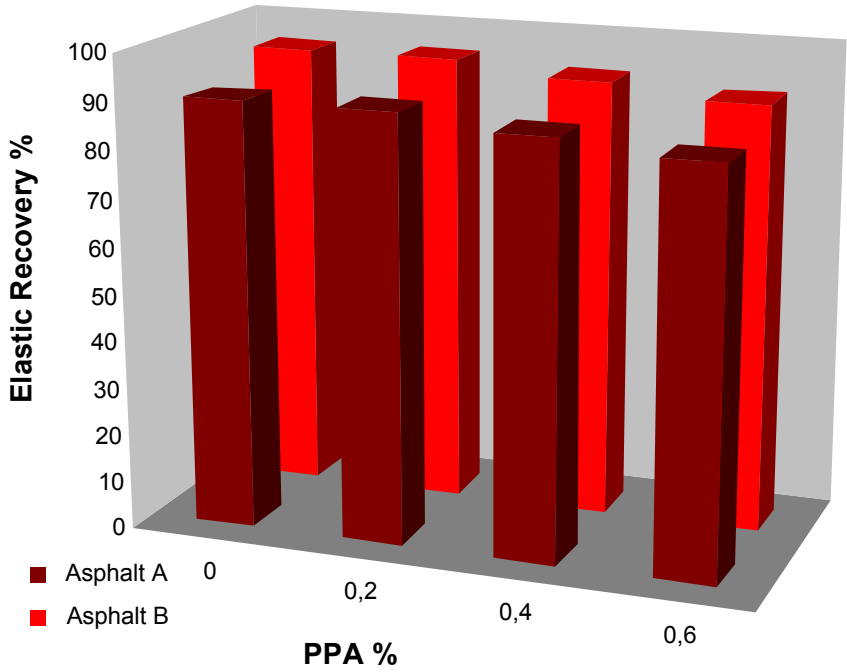
Partial Substitution of SBS with PPA at same PG grade

A : Ergon (Venezuela)

B : Lion Oil (Middel East)

SBS : Dexco Vector 2411 (radial)





76-22 PG

82-22 PG

→ **Elastic recovery is maintained**

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SBS+PPA : Most important point

Partial substitution of polymer (SBS) with PPA :

- Maintain the PG grade **(low Tc / High Tc)**
- Lower viscosity (0,4% PPA and higher)
- No or little decrease on elastic recovery
- Economical modifying cost : decrease the amount of modifier
- PPA + SBS (patented)

Polymer+PPA combination is an economical way to reach performance specifications.

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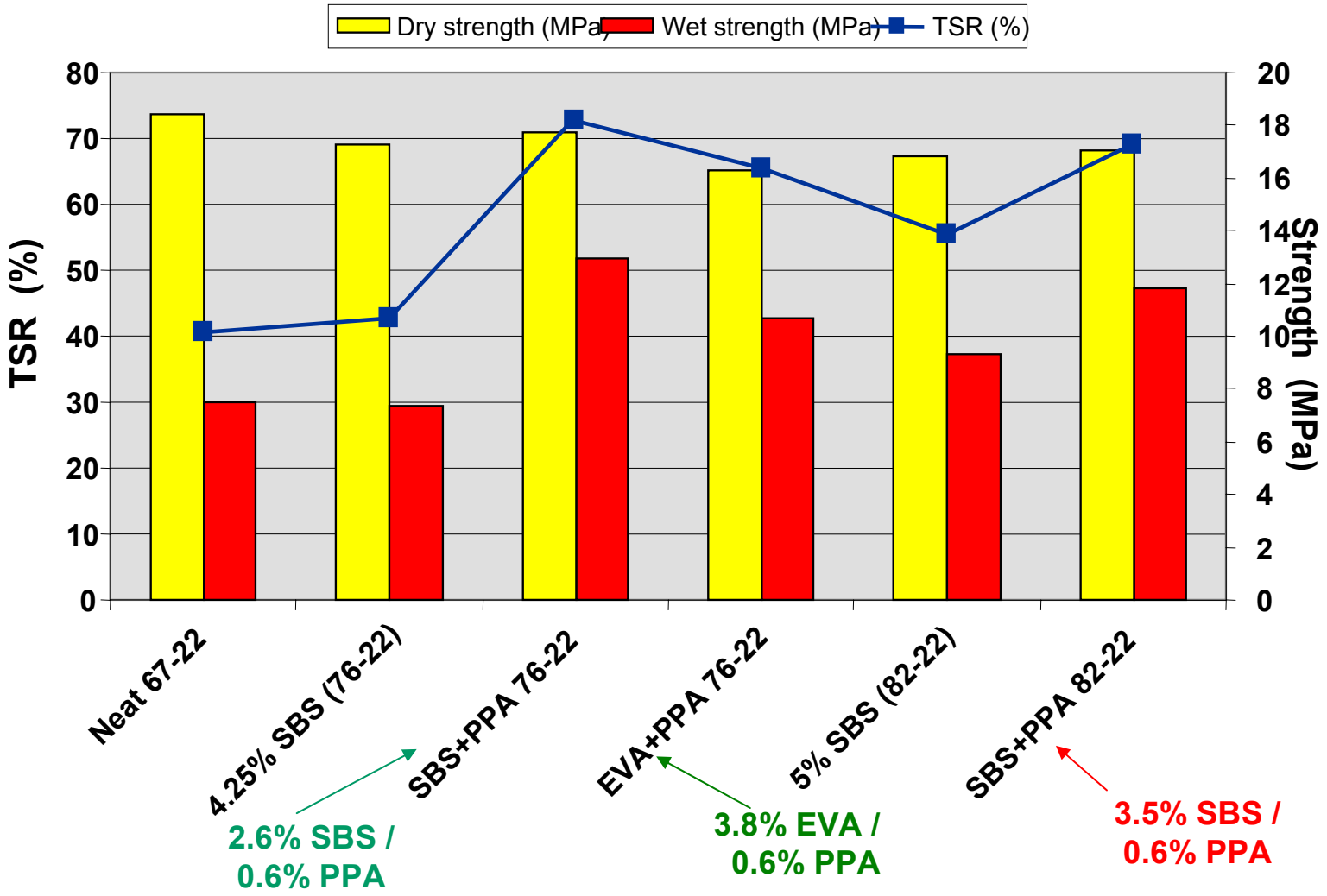
PPA+SBS : ASPHALT MODIFICATION

SBS : Dexco Vector 2411 (radial)
EVA : Exxon Polybilt 103C/Polybilt 152

TSR (Ergon asphalt - Granite)



→ **PPA improves TSR with granite (moisture resistance)**

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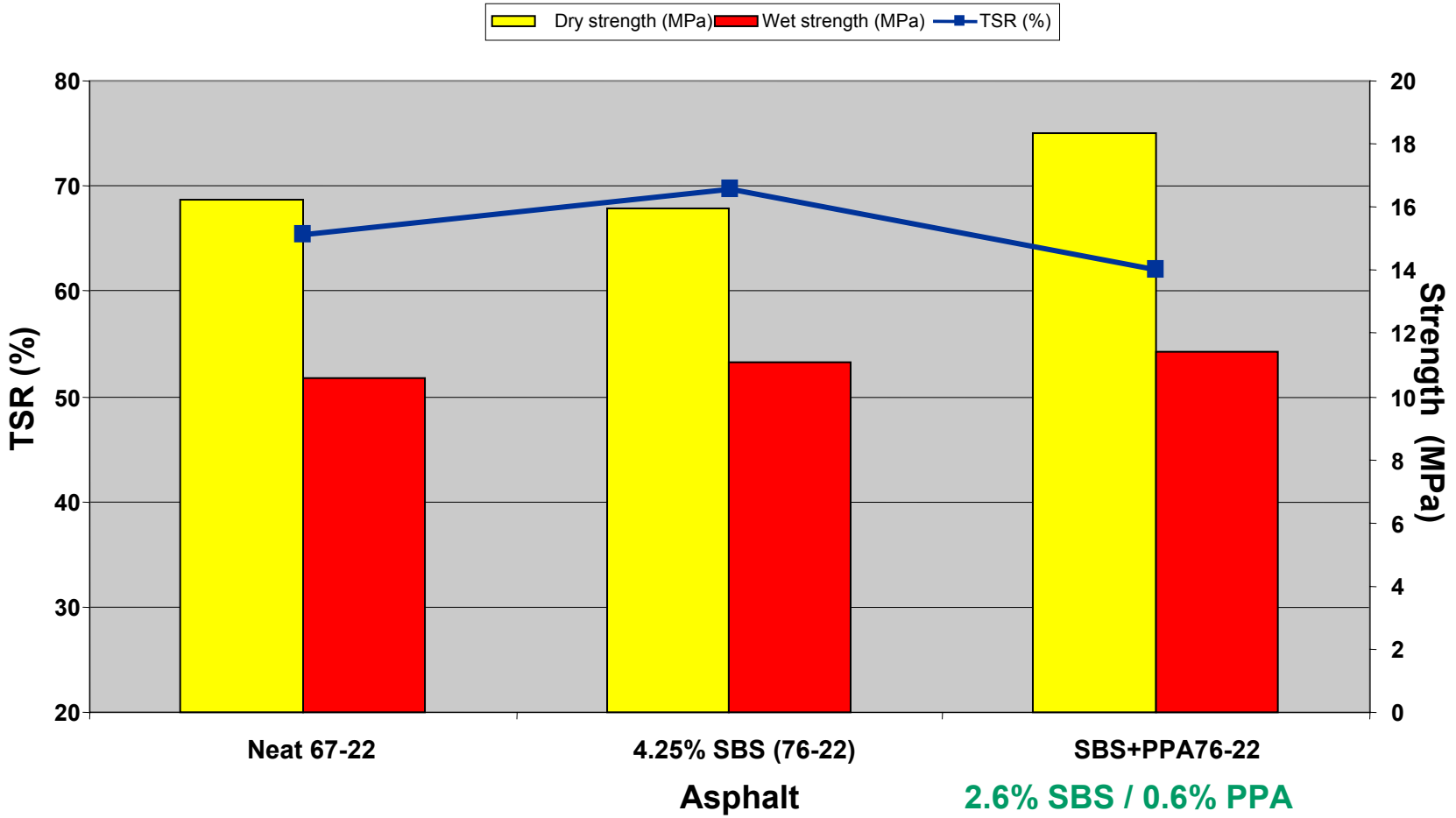
PPA + Polymer : Moisture Sensitivity

SBS : Dexco Vector 2411 (radial)

TSR (Ergon asphalt - Limestone)



→ **PPA doesn't affect TSR with limestone (moisture resistance)**

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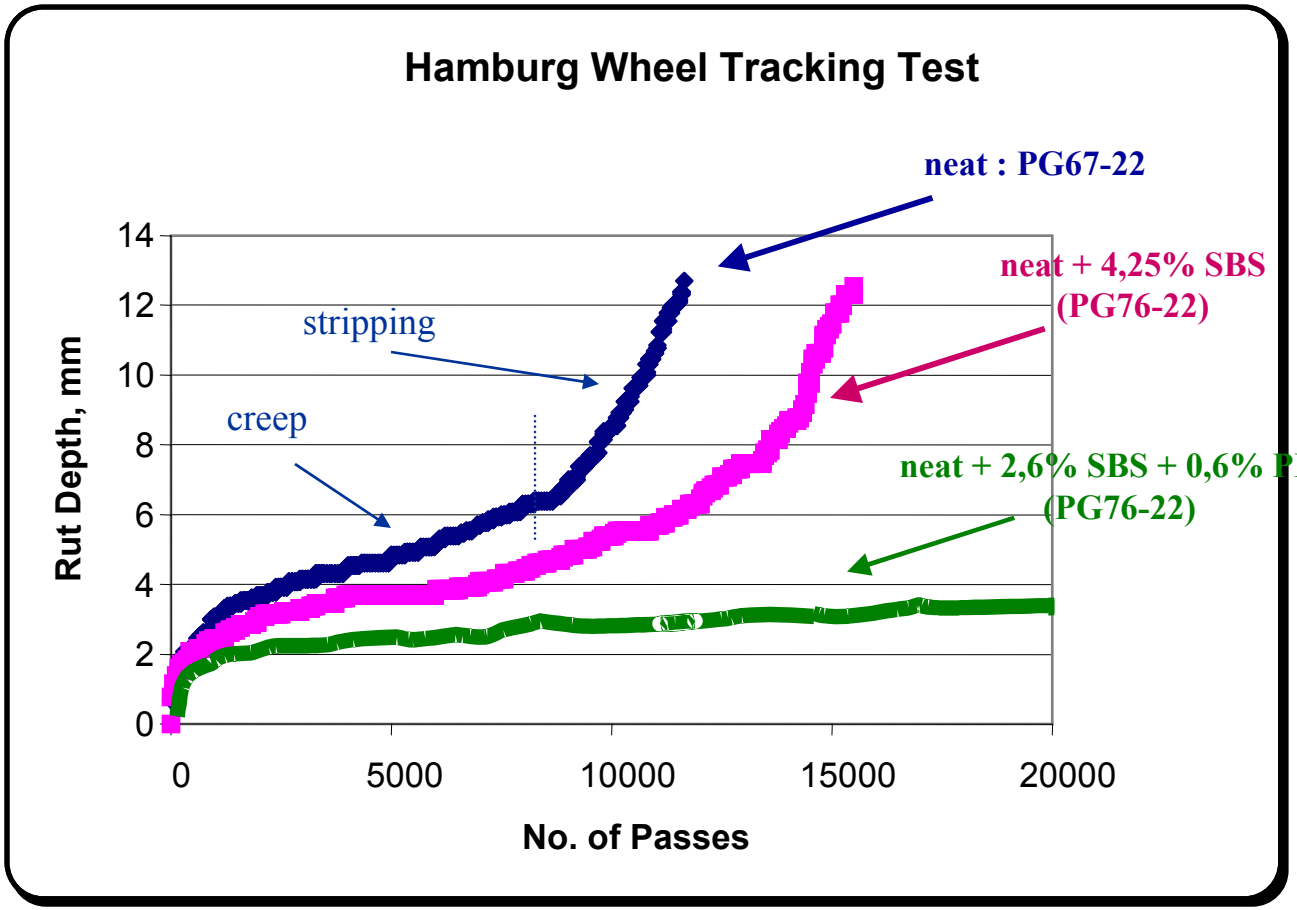
PPA + SBS : Better rutting+stripping bahavior than SBS alone

HAMBURG WHEELTRACKING (Asphalt A – Granite)



PPA+Polymer : Conclusion

- Compared to a 100% Polymer modified Mixture, a Polymer/ PPA modified mix at the **same PG** grade shows :

_____- Equivalent or higher moisture resistance (stripping resistance)

_____- Equivalent or higher resistance to permanent deformation (rutting)

General conclusion:

Asphalt has to reach several specifications that does not translate in the same amount of modifier.

Polymer/PPA combination is a good way to reach all specifications at the optimized cost.

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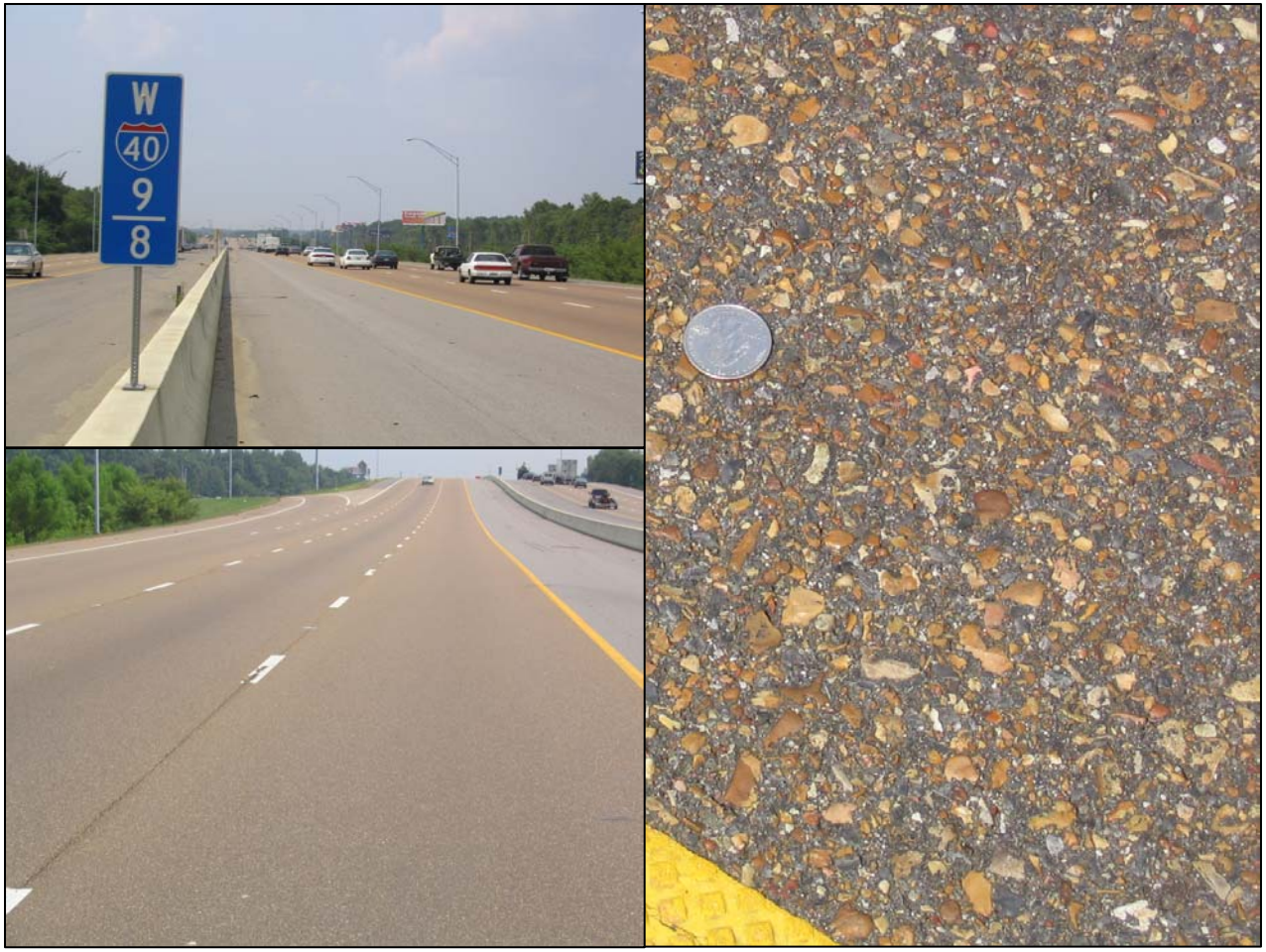
Association of Modified Asphalt Producers

- **I. POSITION STATEMENTS**:
- The Association of Modified Asphalt Producers (AMAP) supports the responsible use of modification of asphalt materials for improved performance. AMAP believes that through the innovation of material suppliers, new and improved products will be made available that will improve life cycle costs. AMAP does not endorse any specific form of modification.
- Acid Modification
- After a review of the available information on the use of polyphosphoric acid in the modification of paving grade asphalts, it is the position of AMAP that the correct use of polyphosphoric acid in the appropriate amount can improve the physical properties of bituminous paving grade binders. AMAP endorses appropriate testing on the modified asphalt binder after the addition of any and all additives to determine the final product specification is met. However, incorrect application of the technology, as with many additives, can result in problems associated with construction and/or performance.

INNOVALT™ is used since 97 in North America

I-40 Memphis, TN

- Paved in 1998
- PG 76-22
- Base asphalt PG 64-22
- 2.8% radial SBS
- **0.5% Innovalt E**



MERCI BEAUCOUP POUR VOTRE ATTENTION !

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