ISAP 2014

# Insights into Binder Chemistry, Microstructure, Properties Relationships
# -
# Usage in the Real World

Jean-Pascal Planche, PHD

jplanche@uwyo.edu

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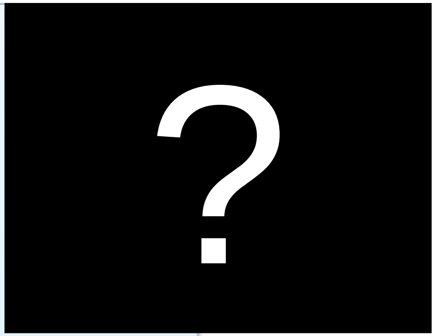
# Outline

- Background - Context
- Chemical-physical and structural properties of asphalt
  - Impact on asphalt mechanical properties
- Asphalt modification
  - Impact on structure and mechanical properties
- Summary
- Perspectives

# Context




- **Asphalt binders behavior dependency**
  - Crude oil origin and process
  - Temperature and time dependency of molecular interactions and asphalt structure
  - Aging impact
    - Chemical Oxidation – Plant and in-service aging
    - Physical aging – testing and in-service
  - Additives chemistry / physical properties and their interactions / compatibility with asphalt
- **Importance of understanding the relationships between composition–structure-properties**
  - Refiner / asphalt binder-additive supplier: crude selection / binder formulation and process
  - Applicator / contractor: mix design and application
  - Owner: specification and pavement performance

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# Background

- **A challenge**
  - ***So much knowledge acquired, worldwide***
  - ***But so much unknown, still!...***
- **Focus**
  - **Some particular aspects of asphalt structure – influence of additives**
  - **Examples of some innovative binder characterization methods**
  - **Meaning of the results in the real world – testing and performance**
  - **Not meant to be exhaustive, but to reconnect some dots**
- **A long trip through history, present time and… the future?**
  - **My deepest acknowledgements to fine researchers / technologists:**
    - **Anderson, Bahia, Brule, Claudy, D'Angelo, Di Benedetto, Jones, King, Kluttz, Lapalu, Lesueur, Letoffe, Little, Mouillet, Schabron. Pauli, Petersen, Redelius, Rowe, Such, Turner, Youtcheff, …**
    - **WRI, TU Delft, Nottingham, ENTPE, KTH, IFFSTAR (LCPC), FHWA, and BP, Kraton Polymers, Nynas, Shell, Total (Elf)…**

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# Asphalt chemical composition

- **Asphalt = a blend of complex hydrocarbons**
  - **Viscous and black**
  - **Complex composition = the chemistry supermarket!**
    - **Ten-Hundred Thousands of different molecules**
    - **Polarity and aromatic continuum**
    - **Associated species**
- **Elemental composition**

| | |
|---|---|
| • **Carbon** | **83-87%** |
| • **Hydrogen** | **10-14%** |
| • **Heteroatoms: Sulfur, Oxygen, Nitrogen** | **1-9%** |
| • **Vanadium, Nickel, Iron** | **1-2000 ppm** |

- **Specificities**
  - ➢ **Hydrogen deficient hydrocarbons**
  - ➢ **Ni/V and C/H sometimes used as crude oil or process tracers**

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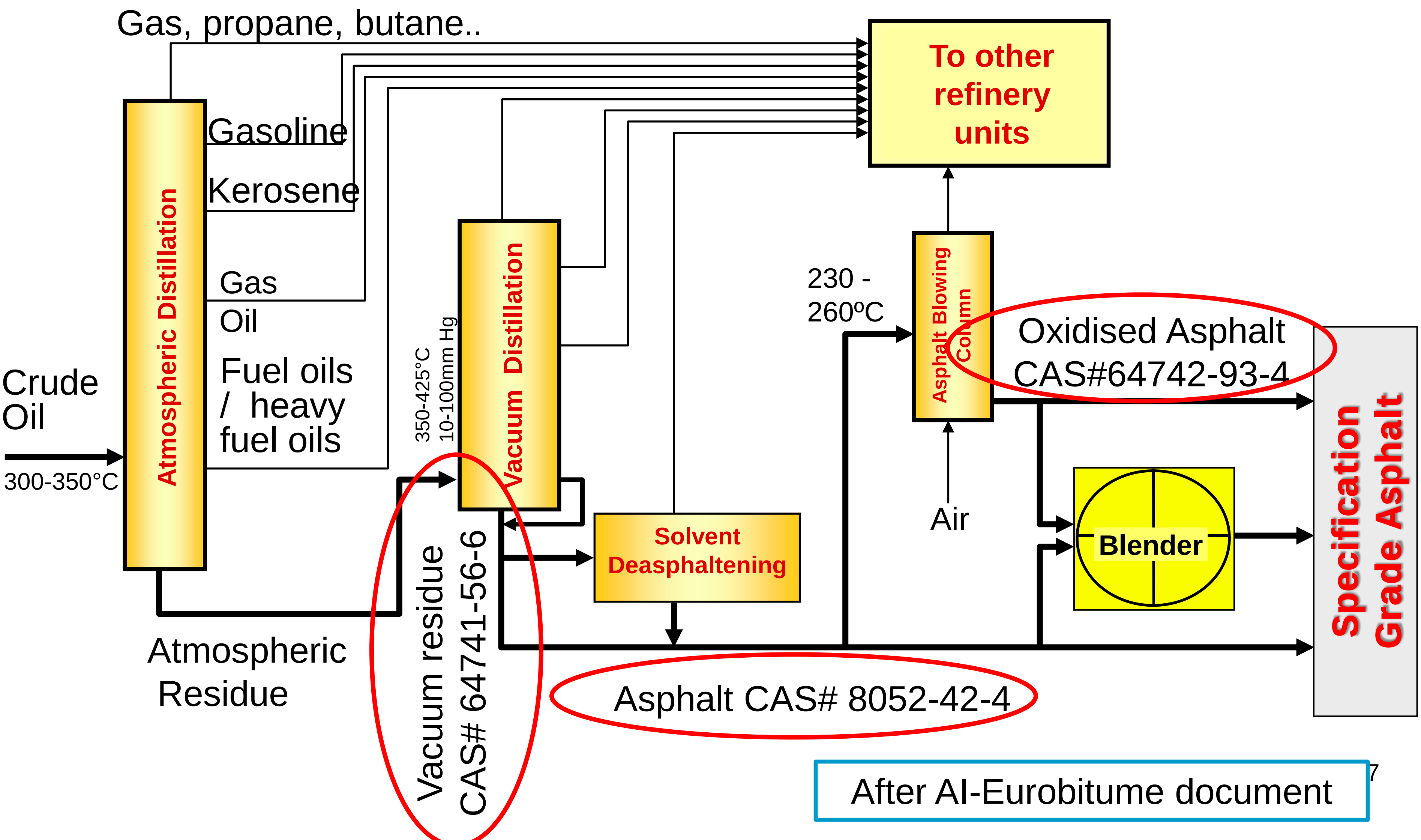
# Refinery Block Diagram






- **Complex Asphalt production process (Europe-US)**

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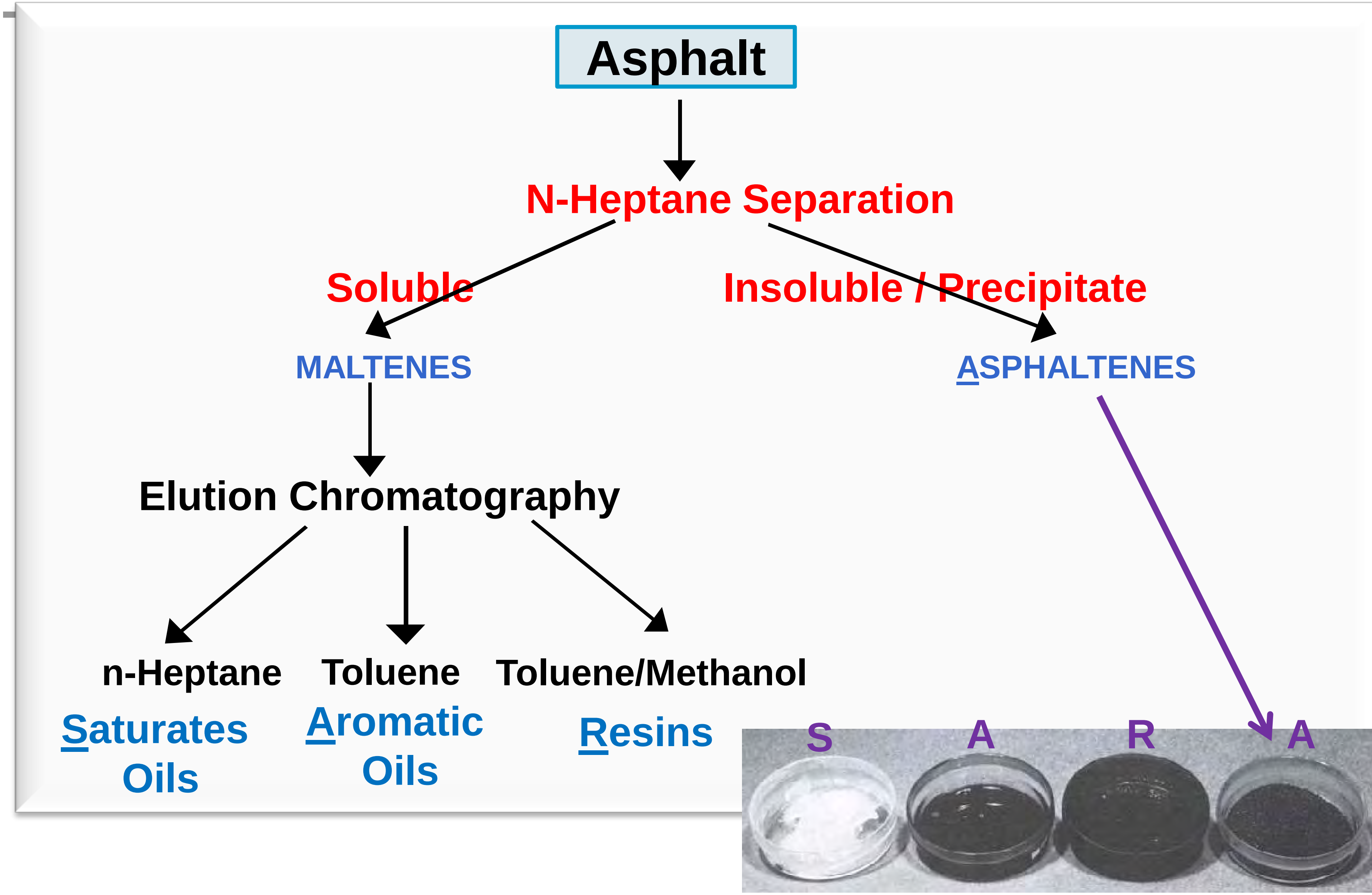
# Asphalt chemical composition

- **Examples from the SHRP AMRL library**

| MRL Code | AAA-1 | AAA-2 | AAB-1 | AAB-2 | AAC-1 | AAC-2 | AAD-1 |
|---|---|---|---|---|---|---|---|
| Crude Oil Source | Lloydminster | | WY Sour | | Redwater | | Ca Coast |
| Elemental Analysis | | | | | | | |
| C, % | 83.9 | 84.12 | 82.3 | 85.7 | 86.5 | 86.6 | 81.6 |
| H, % | 10.0 | 10.59 | 10.6 | 10.59 | 11.3 | 10.6 | 10.8 |
| O, % | 0.6 | | 0.8 | | 0.9 | 1.0 | 0.9 |
| Nitrogen, % | 0.50 | 0.50 | 0.54 | 0.54 | 0.66 | 0.90 | 0.77 |
| Sulfur, % | 5.50 | 6.00 | 4.70 | 5.40 | 1.90 | 1.90 | 6.90 |
| Vanadium, ppm | 174 | 138 | 220 | 163 | 146 | 100 | 310 |
| Nickel, ppm | 86 | 77 | 56 | 36 | 63 | 55 | 145 |
| Fe, ppm | <1 | | 16 | | | 29 | 13 |

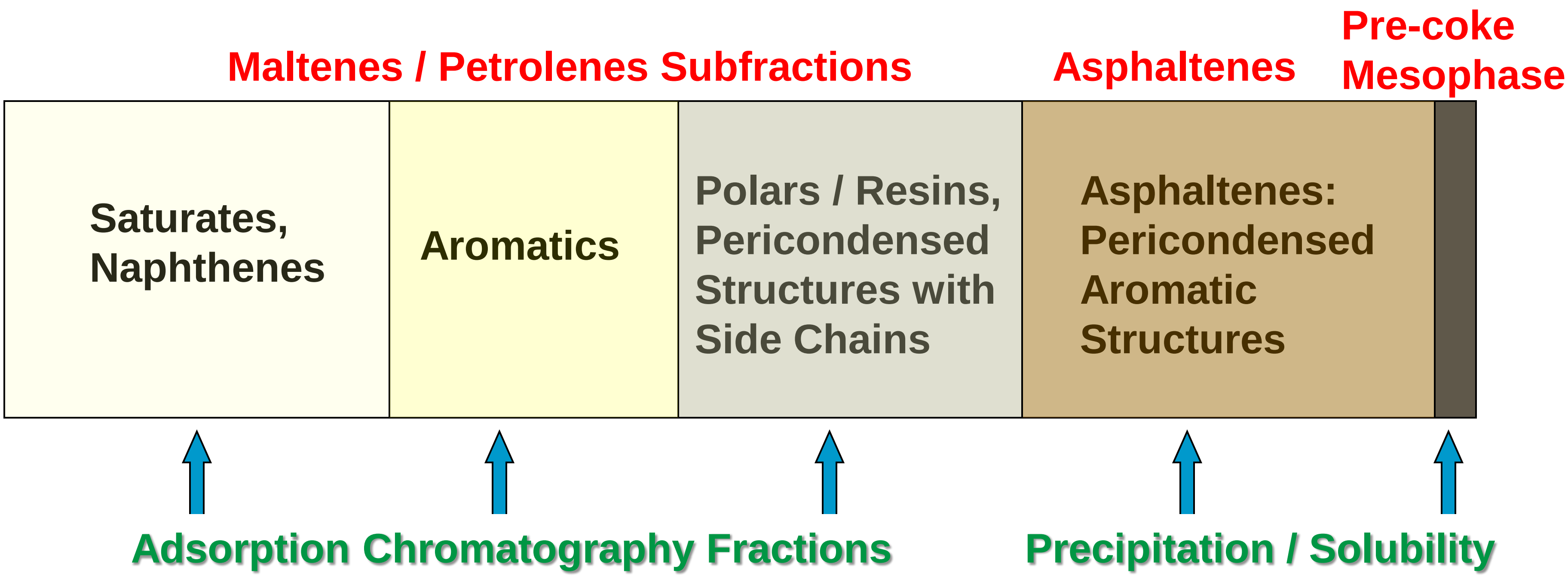
- **Dependence on crude oil origin & process**
  - **Only 10% all crude oils yield asphalt!**
- **Generic fraction composition to overcome the complexity**

# Generic fractions of Asphalt



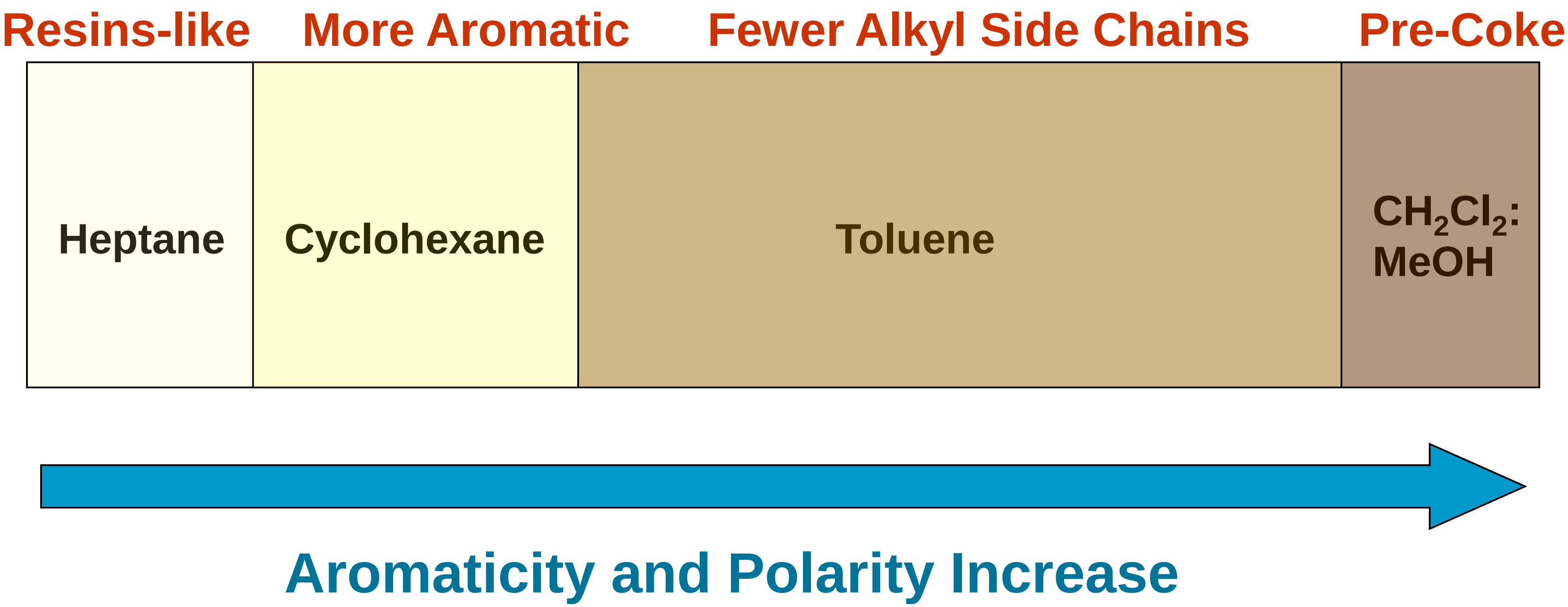
# Generic fractions of Asphalt

- Asphalt SARA separation in fractions of a <u>continuum</u>
- Fraction chemistry defined by the particular methods and/or solvents used




# Generic fractions of Asphalt

- Asphaltenes are also part of the continuum
- Asphaltene subfractions can also be defined / separated according to their solubility in solvents




- **Some of the fractions consist of associated species**

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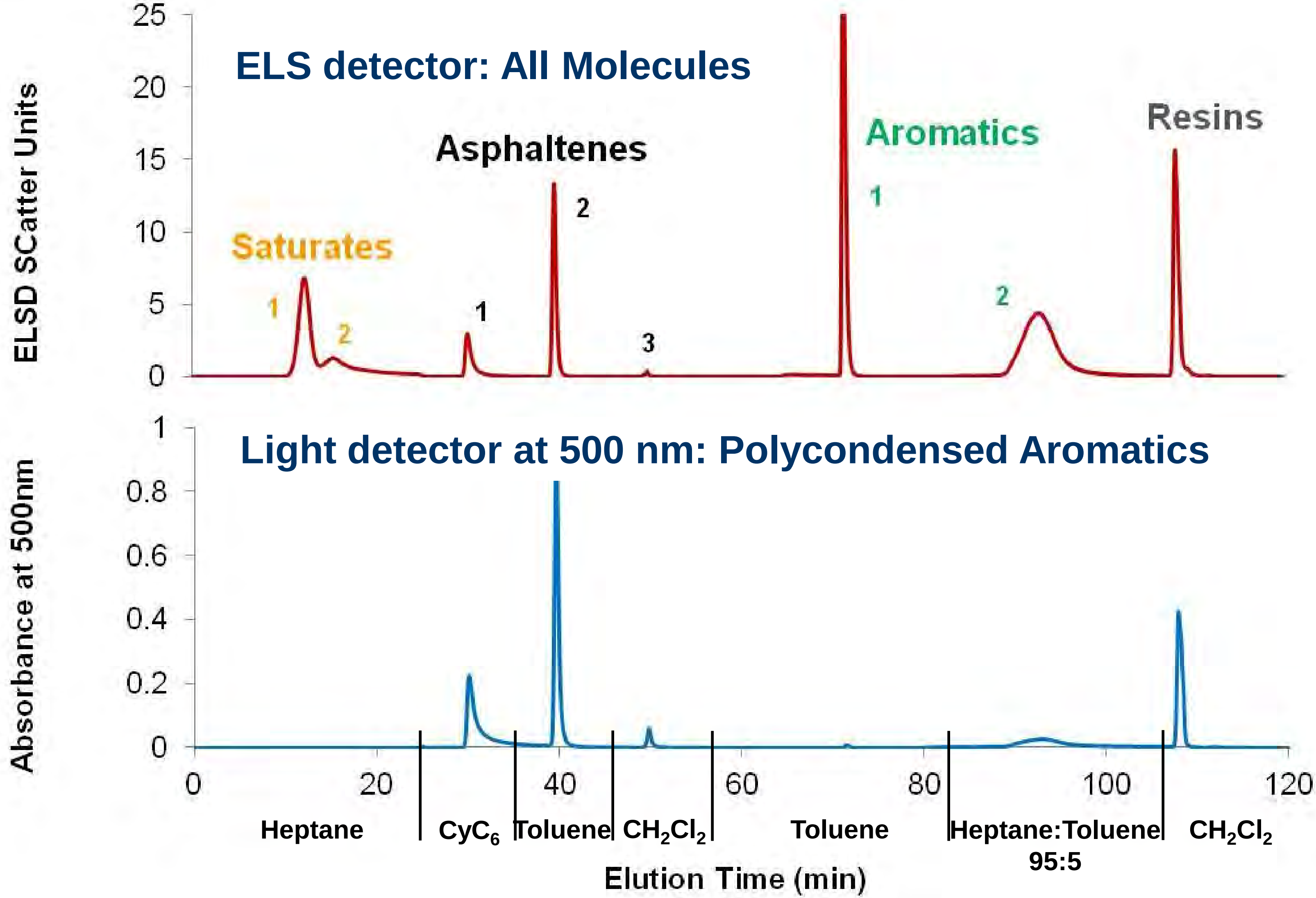
# Generic fractions of asphalt

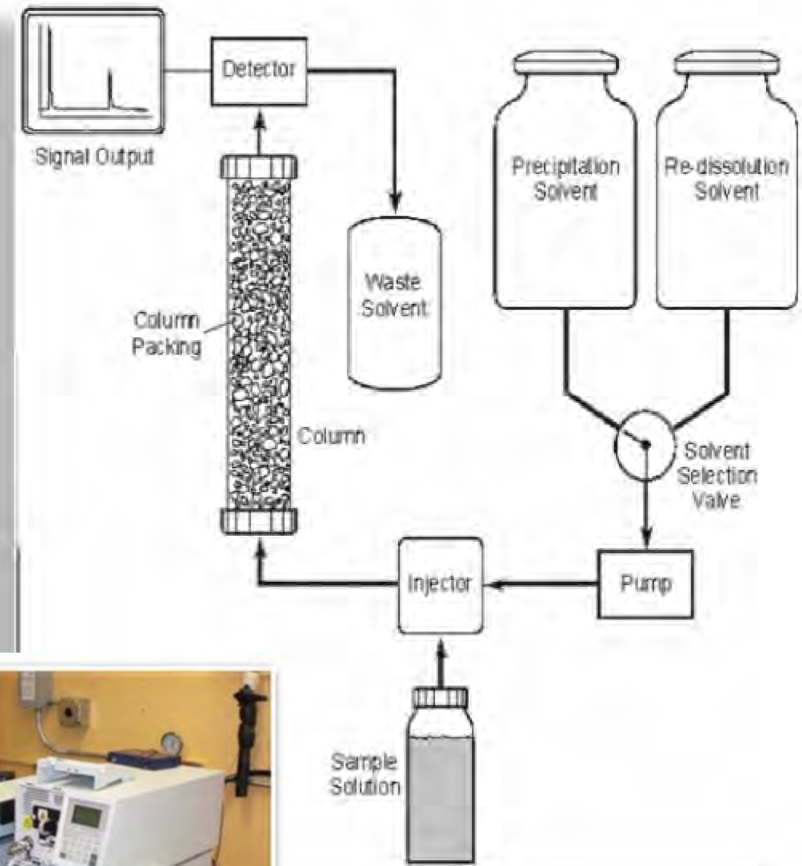
- ***SAR-AD™*** ***separates asphalt into 8 fractions***



# Generic fractions of asphalt

- **Asphalts & Heavy Oils separation by SAR-AD™**
- **Rapid & Relevant analytical tool developed by WRI**

- **Whole product injected (2 mg) separated in 4hrs**
- **4 separation columns**
  - **Maltenes & varnish**
  - **Polars/resins**
  - **Saturates and aromatics**
  - **Asphaltene subfractions**
- **Dual detection by ELSD and Light**
- **Repeated injections**




***SAR-AD™ patented***

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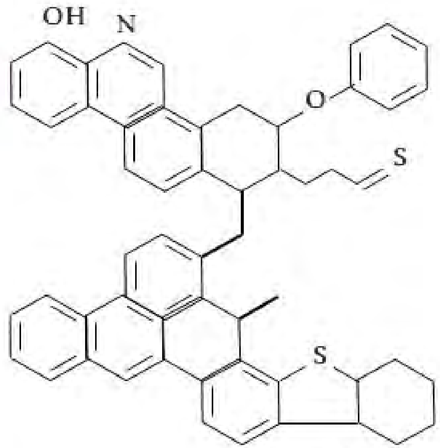
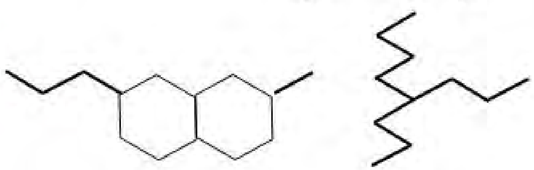
# *Asphalt generic fractions*
# *Model molecules and structures*

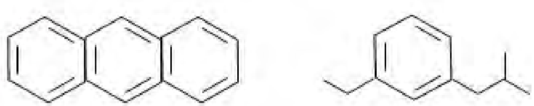
**Asphaltenes**



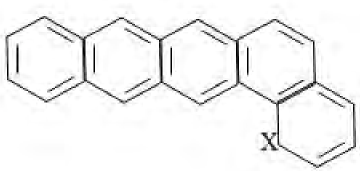

**Saturates**

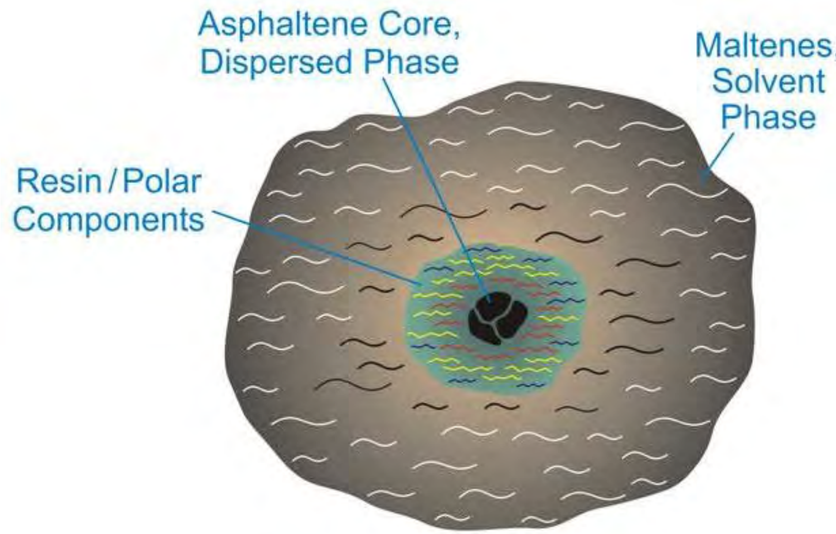


**Aromatics**



**Resins**




**Asphalt Colloidal structure model**

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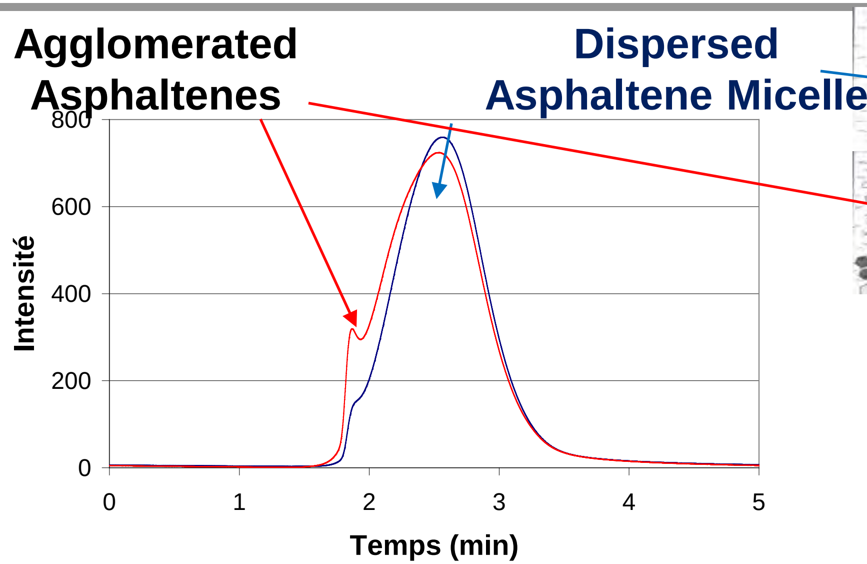
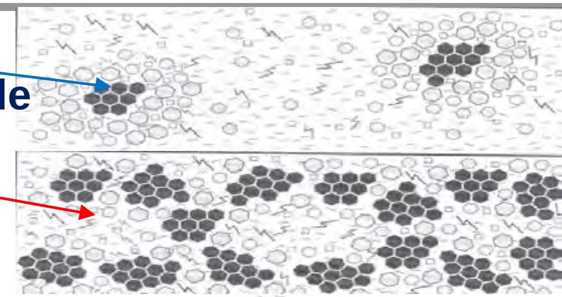
# Structural Model of Asphalt

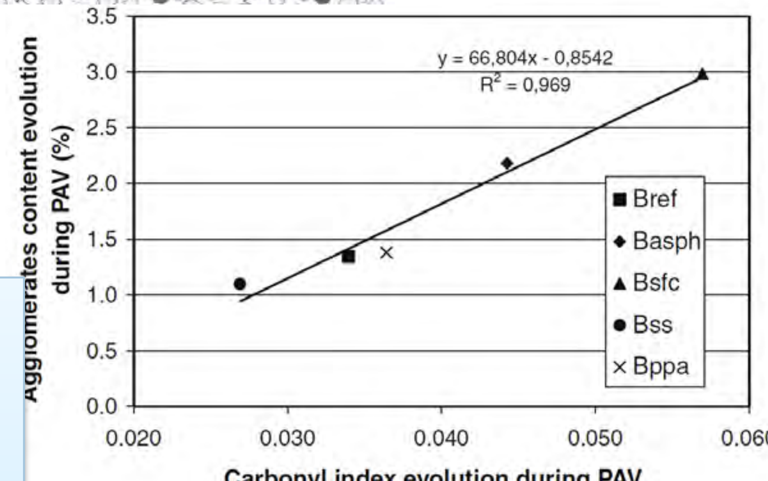
- **Hypothesis: Asphalt molecules assembly in a colloidal structure – temperature dependent**
- **SOL = Asphaltene micelles well «peptized» / dispersed in the maltene "solvent" matrix**
  - **Low content in asphaltenes and saturates**
  - **High content in aromatics and resins**
- **GEL = Asphaltene micelles poorly « peptized »**
  - **High content in asphaltenes and saturates**
  - **Low content in aromatics and resins**
- **At high temperature: homogeneous SOL structure**
  - **Brownian relaxation above about 80C where interactions, polar, H-Bonds… in asphaltenes and resins are destroyed**
- **Boussingault (1837), Nellensteyn (1923), Pfeiffer (1940), Yen, Storm, Pal-Rhodes, Lesueur (1996),… revisited**

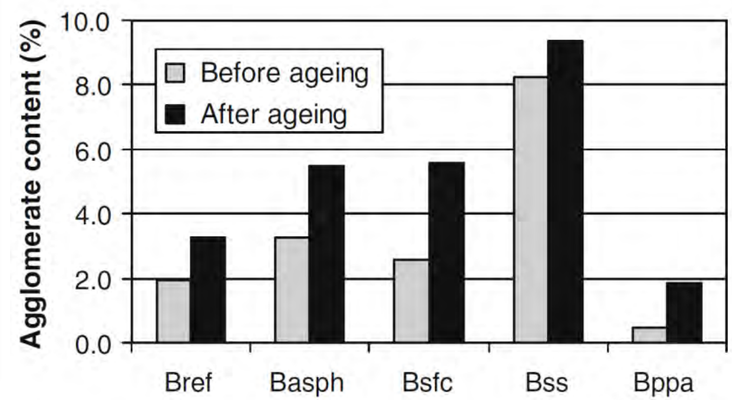
# Structural Model of Asphalt



**SOL/GEL Shell Model**




- **Sol-Gel asphaltene molecular association (peak) evaluated by High speed SEC**
  - **Increase during aging - Correlated with carbonyl and sulfoxide formation**
  - **Asphalt source, additive and process dependant**
- ***Works: Brule, Such (80's), Jennings, Pribanic (90's), Chailleux, Mouillet (2010's)***

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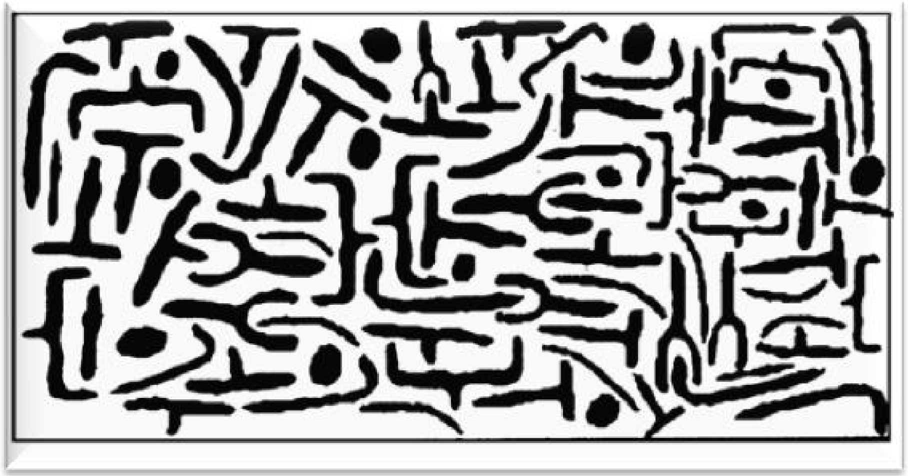
# Dispersed Polar Fluid Model

- **Developed under SHRP - based on fluid polarity**
- **Asphalts: homogeneous concentrated mixtures of polar materials dispersed in neutral materials**
  - **Polars in a continuous, rather homogeneous, 3-D network**
  - **No asphaltene but a range of polar compounds - strong/weak acid/bases through amphoterics**
  - **Oxidation effect: molecular species sensitive to oxidation, increase the polar content, the size and strength of the 3-D microstructure**

**After:**
**•Robertson et al**
**•Jones et al**

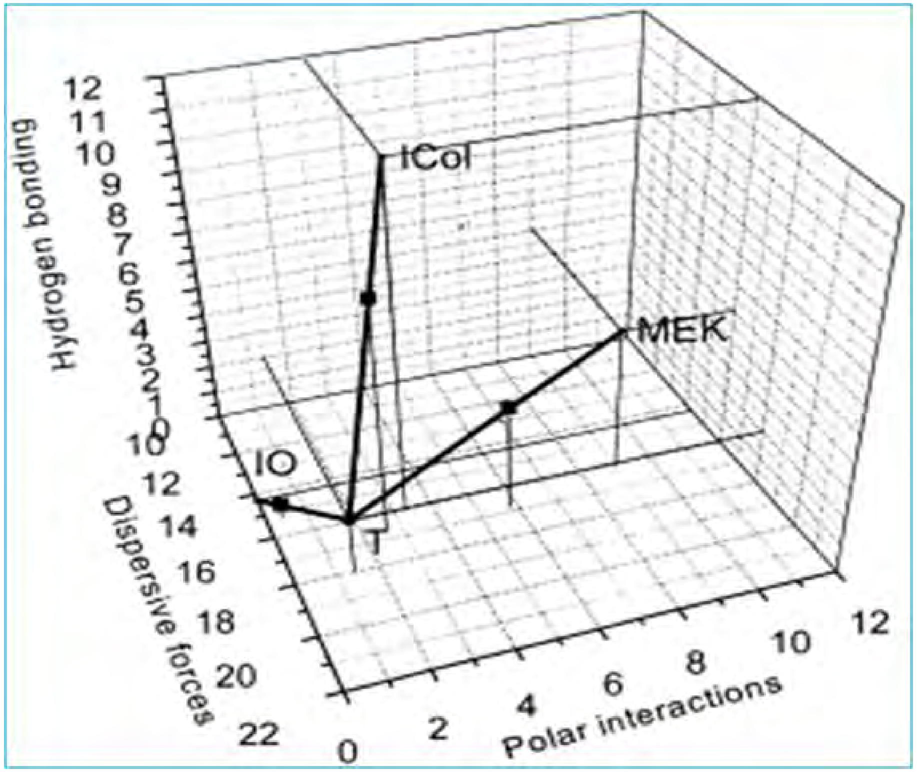


# Dispersed Polar Fluid Model

**3D Solubility parameter**

- Accounts for various interactions between the various bitumen molecules
  - •H-Bond
  - •Polar
  - •Wan der waals

- Dedicated to embrace solubility issues as a whole




Black Squares = Precipitation Points

Diagram of Titration of Venezuelan Bitumen

*By Redelius - Credit To Fuel 79 (2000)*

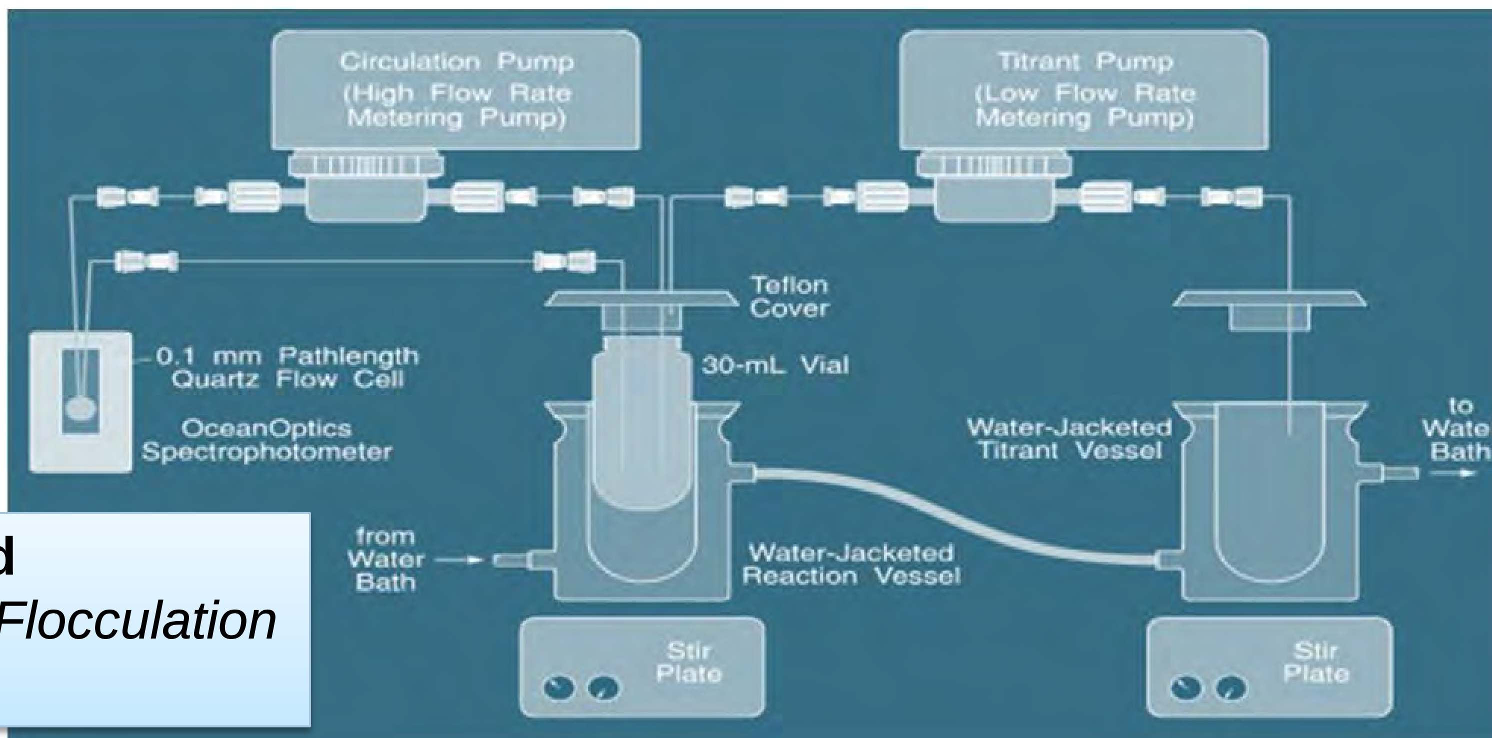
# *Asphalt Compatibility*

- **Compatibility concept - "Operational"**
  - **Mixing similar materials gives expected results - linear rule - blending**
  - **Consequently incompatibility is when mixing similar materials gives unexpected results - non-linear - like softer or stiffer than expected**
  - **Ex: mixing incompatible asphaltenes from different asphalts (study from Anderson, Petersen)**

| | | Neat | | | TFOT + PAV, 60°C, 144 hours | | |
|---|---|---|---|---|---|---|---|
| Mix # | Components of Mixture | Vis., Pa•s 25°C, 1 r/s | Tan ∂ 25°C, 1 r/s | R. S. Visc. 25°C, 1 r/s | Vis., Pa•s 25°C, 1 r/s | Tan ∂ 25°C, 1 r/s | Aging Index 60°C, 1 r/s |
| I (A) | AAD Maltenes (79%) AAD Asphaltenes (21%) | 49,011 | 3.2 | 705 | 550,650 | 1.5 | 15.4 |
| VII (B) | AAG Maltenes (94%) AAG Asphaltenes (6%) | 389,100 | 6.3 | 64 | 1,086,400 | 1.6 | 4.2 |
| Cross Blends | | | | | | | |
| V (C) | AAG Maltenes (79%) AAD Asphaltenes (21%) | 4,970,900 | 1.5 | 287 (?)* | 20,662,000 | 0.8 | 15.5 |
| III (A) (C) | AAD Maltenes (79%) AAG Asphaltenes (21%) | 62, 908 | 3.7 | 906 | 552,310 | 1.8 | 9.0 |

## Asphalt Compatibility

- **Compatibility: function of the maltene solvent power and the asphaltene dispersion (ref. Heithaus)**
  - Measured by Asphaltene Flocculation Titration
  - $P_a$ and $P_o$ peptizability of the asphaltenes and maltenes
  - P-value: state of peptization of the Asphalt (or the oil)




**WRI method**
*Automated Flocculation Titrimeter®*

# Asphalt compatibility Consequences

- **Colloidal structure parameters from SAR-AD, AFT, DSC and SEC can / could be used to assess compatibility, blending rules and aging effects**
  - Blends of various asphalt bases available in refineries
  - Virgin asphalt and RAP or RAS blends
  - Polymers / additives for asphalt modification
  - Binder oxidative and physical aging
  - No standard to identify the borderline between "compatible" and "incompatible" asphalt
- **Example 1 - compatibility of SBS PMBs assessed using the instability index**
  - Gaestel index $I_C$ = (Saturates+Asphaltenes)/(Aromatics+Resins)
    - When $I_C$ increases, the colloidal stability decreases
  - Rule of thumb: the lower the $I_c$ (higher aromatics), the more compatible the SBS-Asphalt system (after Airey UNOTT, Brule LCPC,…)

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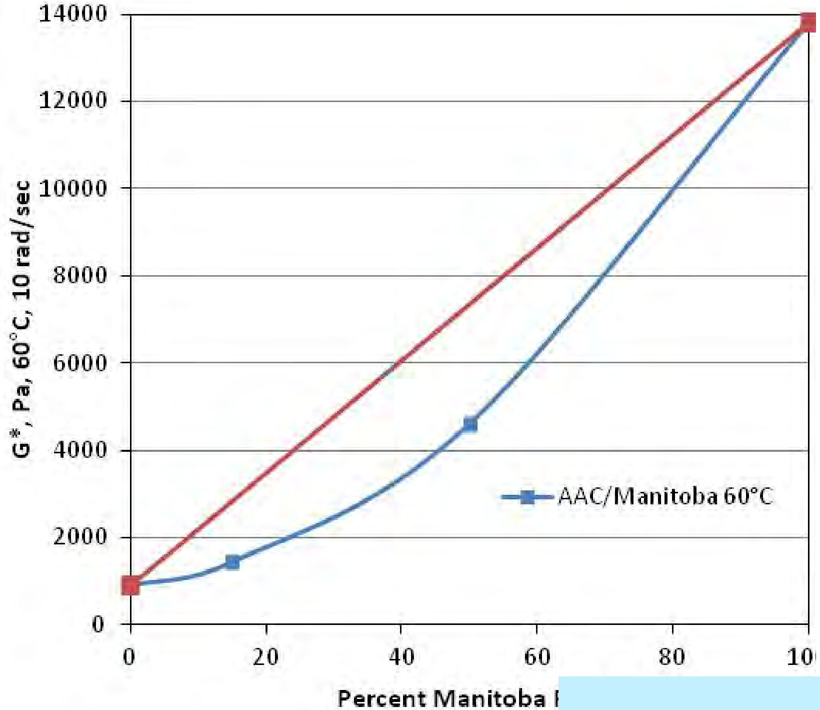
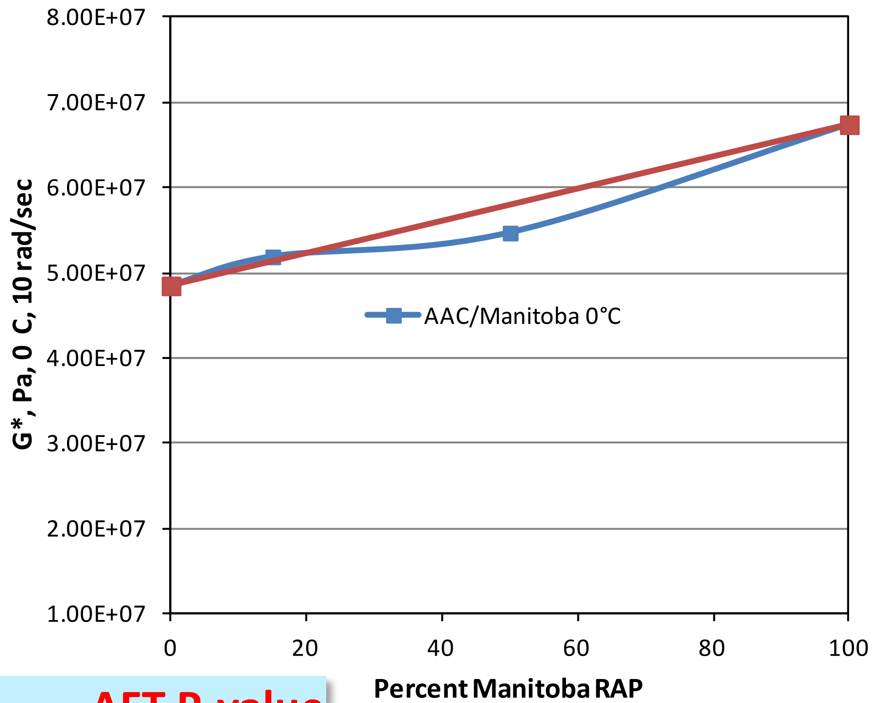
# Asphalt compatibility consequences

## Example 2: Virgin binder + RAP – lab blends

- AAC-1 – Manitoba RAP / G* measured at 60 and 0C / 10 rad/sec




| | AFT P-value |
|---|---|
| AAC-1 | 4.58 |
| +50% Man RAP | 3.86 |
| 100% Man RAP | 3.78 |

**Unpredictable blend**

**Semi Predictable blend**

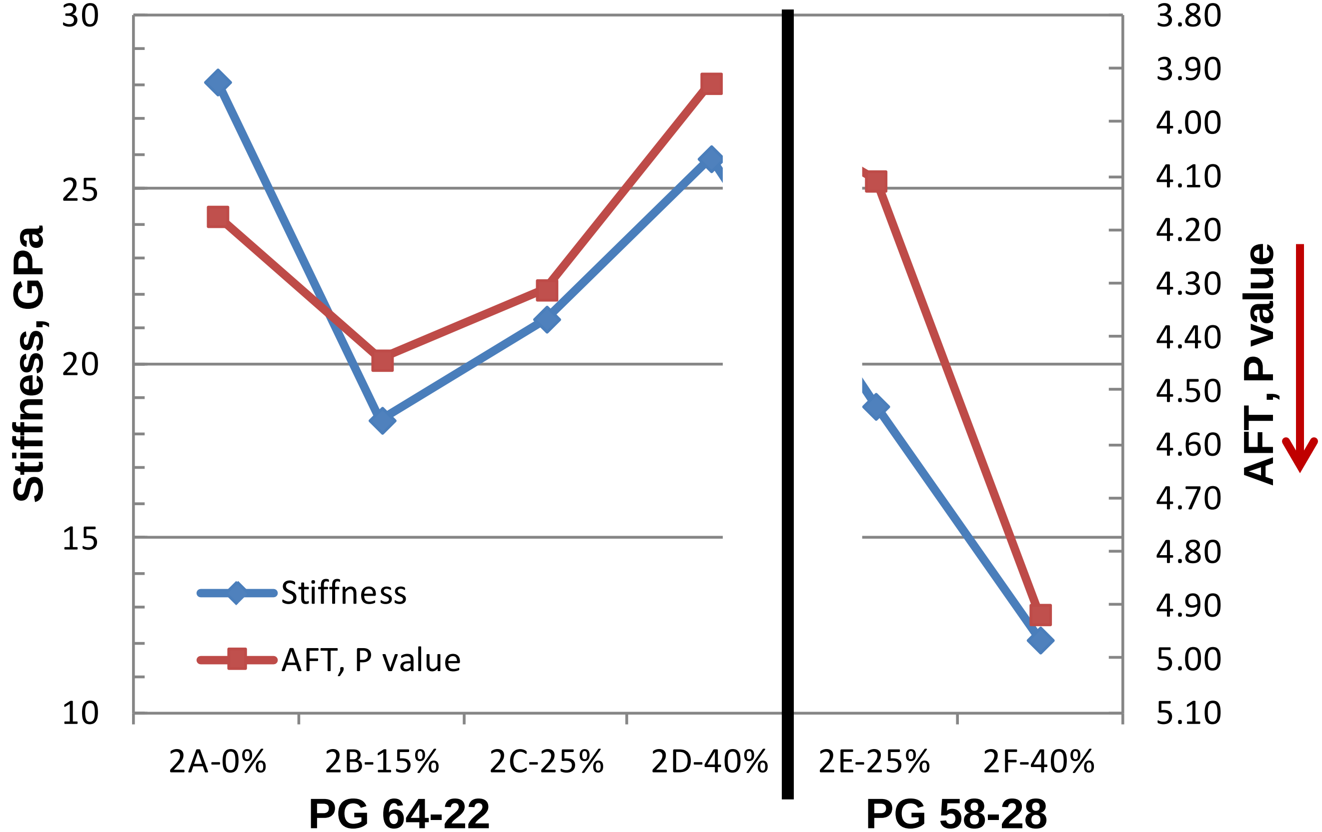
**Lower p-value = bad compatibility**

**Anti-synergy in G***

# Asphalt compatibility consequences

## Example3 : Virgin binder + RAP – Plant blends – IDT mix testing

- **PG 64-22 and PG 58-28 with up to 40% RAP / low Temp. E***

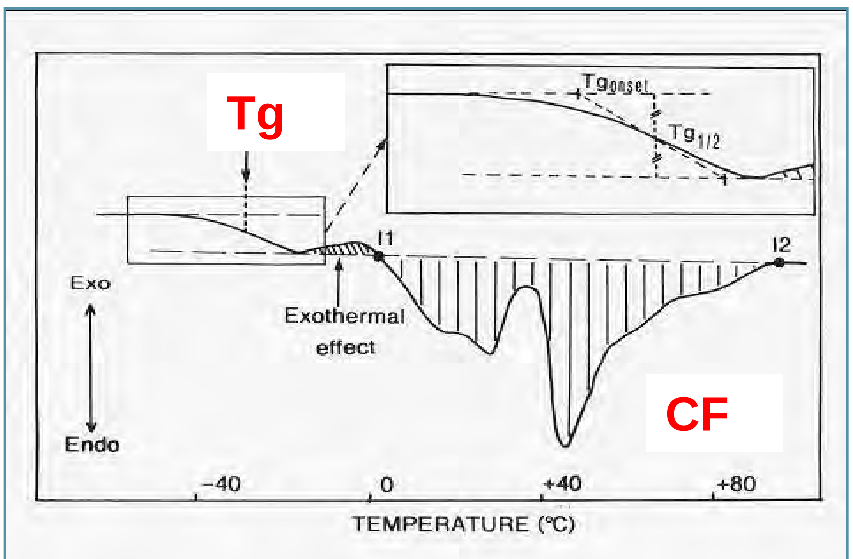


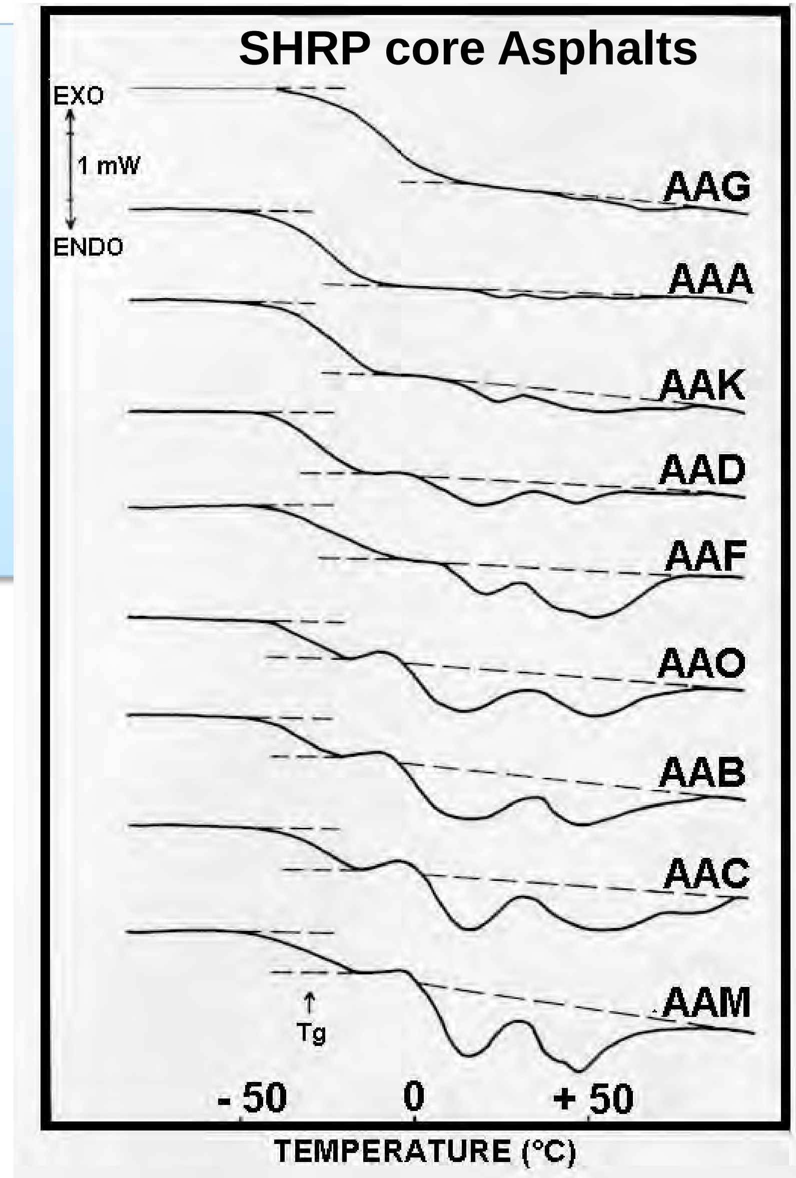

➢**Mix low temperature stiffness evolution follows AFT p-value**

Data from: *Investigation of Low and High Temperature Properties of Plant-Produced RAP Mixtures Phase II,* McDaniel and Huber

# Additions to the colloidal model

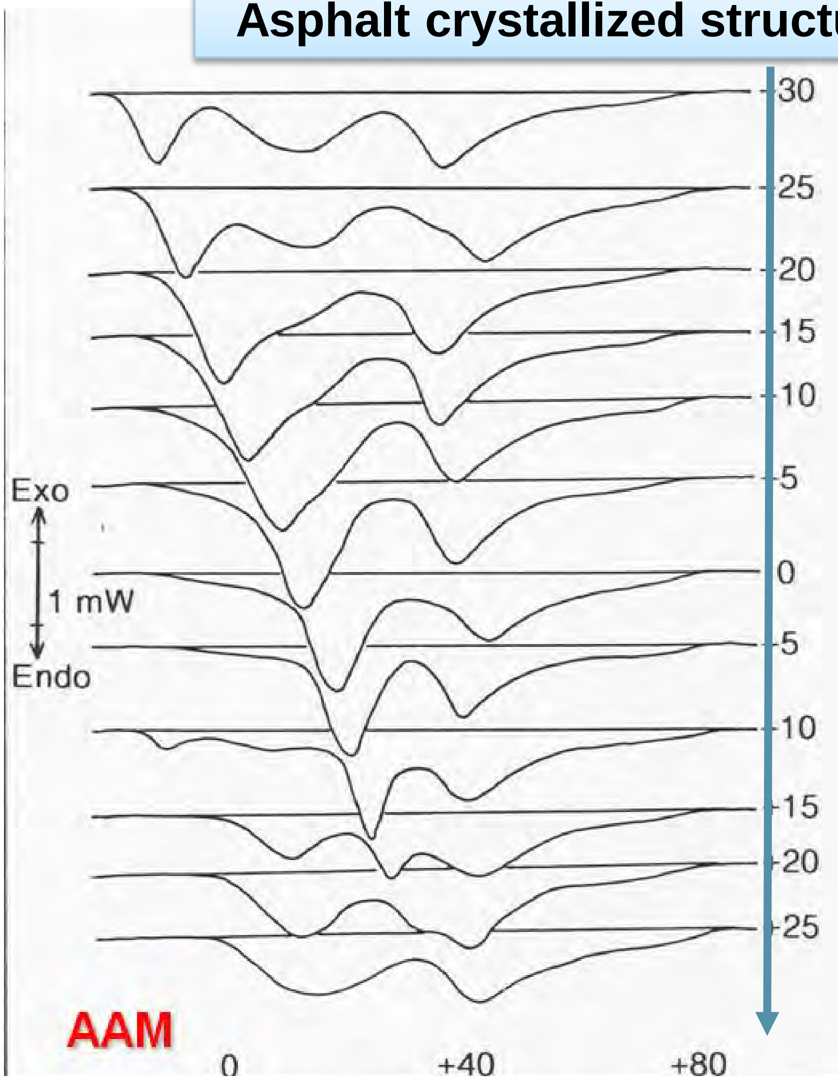
- ***Crystallized fraction (CF) present in most Asphalts*** **not accounted for in the Colloidal model**
- ***Glass transition temperature not directly used in asphalt models***
- **Differential Scanning Calorimetry**
- ***Work by: Claudy and ELF in the 90's and Ensley (80's), Turner at WRI, Masson…***



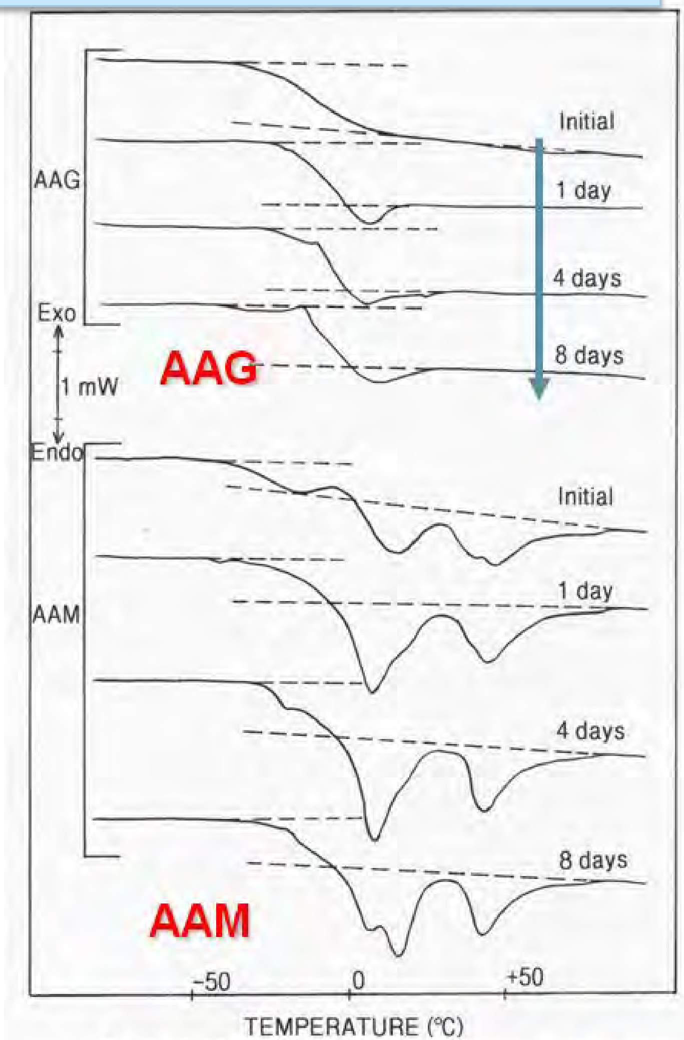



# Additions to the colloidal model

**Asphalt crystallized structure is thermal history dependant**




Conditioning temperature, deg C




Conditioning time, days

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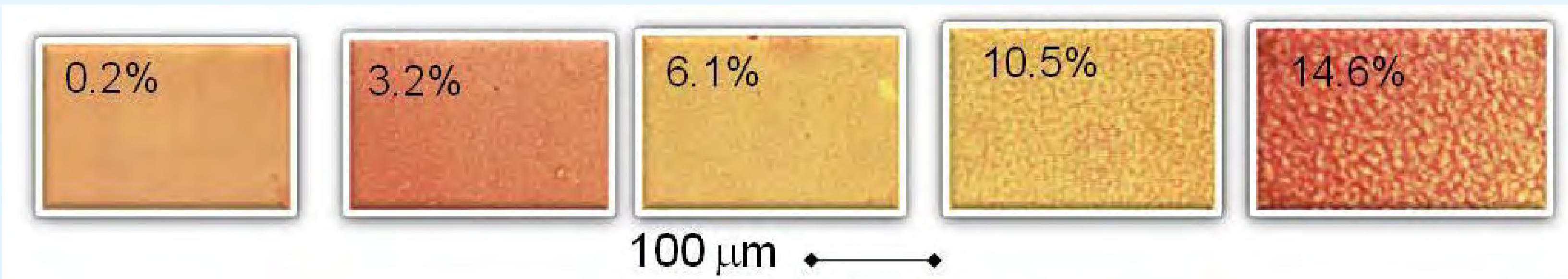
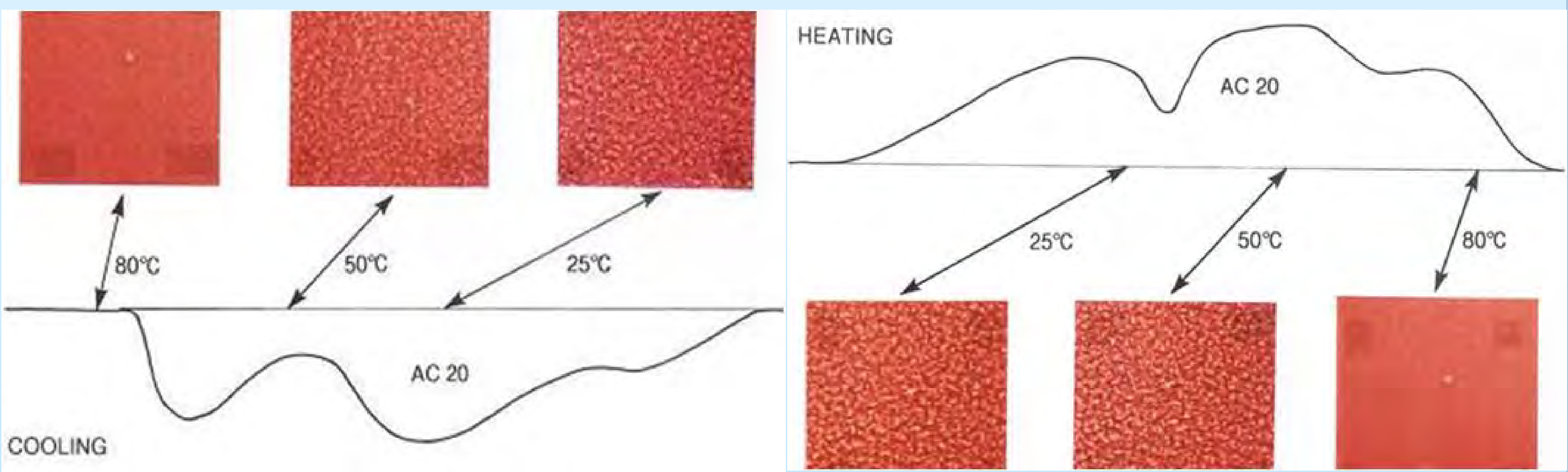
# *Additions to the colloidal model*

- **Crystallized Fraction - Phase contrast microscopy observation at 25°C for different asphalts**



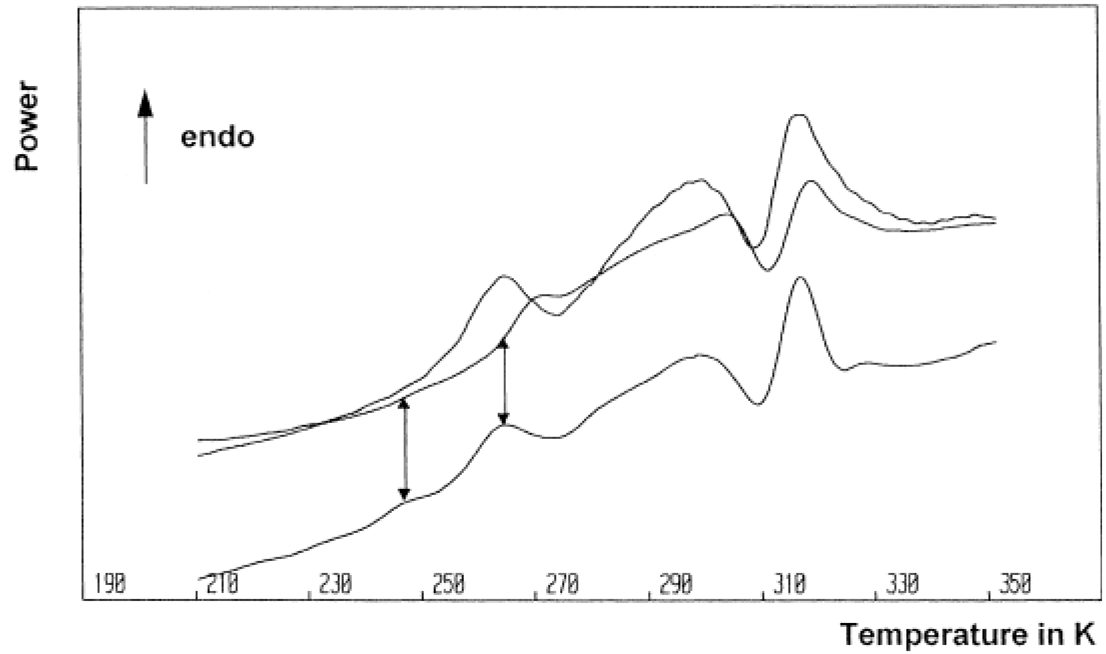

- **Crystallized Fraction varies as a function of temperature upon cooling or heating - Phase contrast microscopy and DSC**



# Additions to the colloidal model

**Modulated DSC shows 2 Tg's**

- **Asphalt conditioning**
  - **-30C for 16 hrs**
- **Heat capacity from phase shift (b), amplitude (m), Average signal (t)**




- **What's happening?**
- **At room temperature: asphalt made of two liquids and some crystallized fractions**
- **At lower temp: CF increase due to lower solubility in the liquids**
  - **Two glasses are formed depending on temperature**
  - **Their proportion depends on the thermal history**



Claudy et al, Thermochimica Acta 324 (1998)

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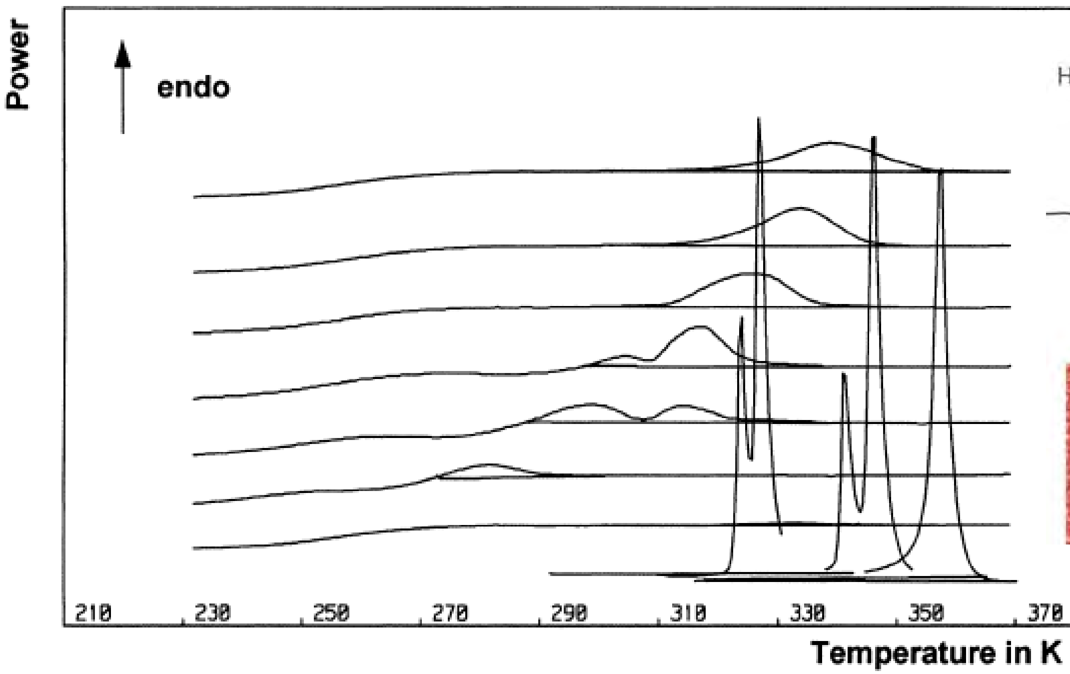
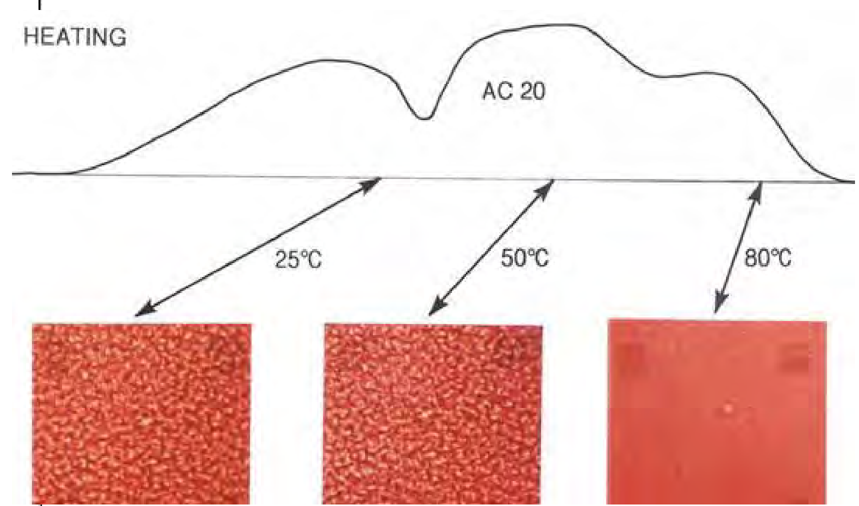
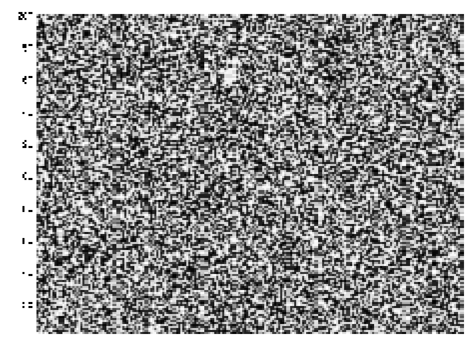
# Additions to the colloidal model



- ✓ **Proof of concept by doping n-paraffins in a non waxy asphalt - C20 to C40**
- ➢ **Dissolution endotherm at much lower temperature than melting**
- ➢ **Crystallized fraction makes asphalt phase separate into 2 liquids as in a spinnodal decomposition –Temp. dependant**

**Claudy, Thermochimica Acta (1998)**
**Wikipedia**

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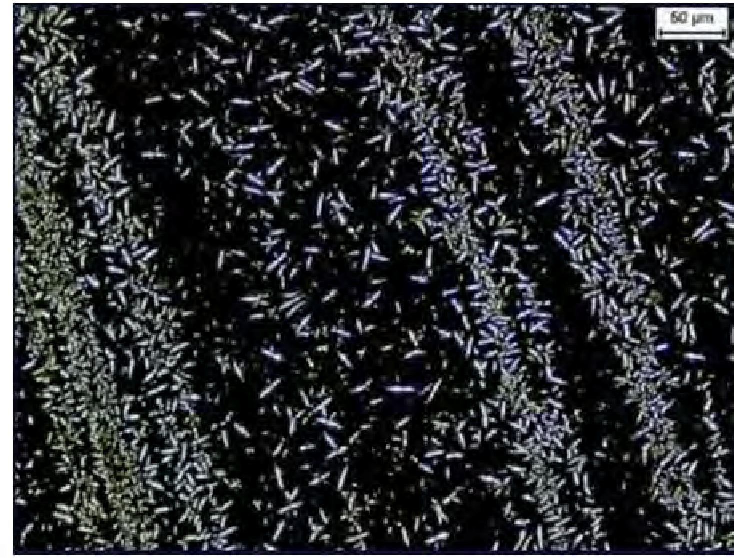
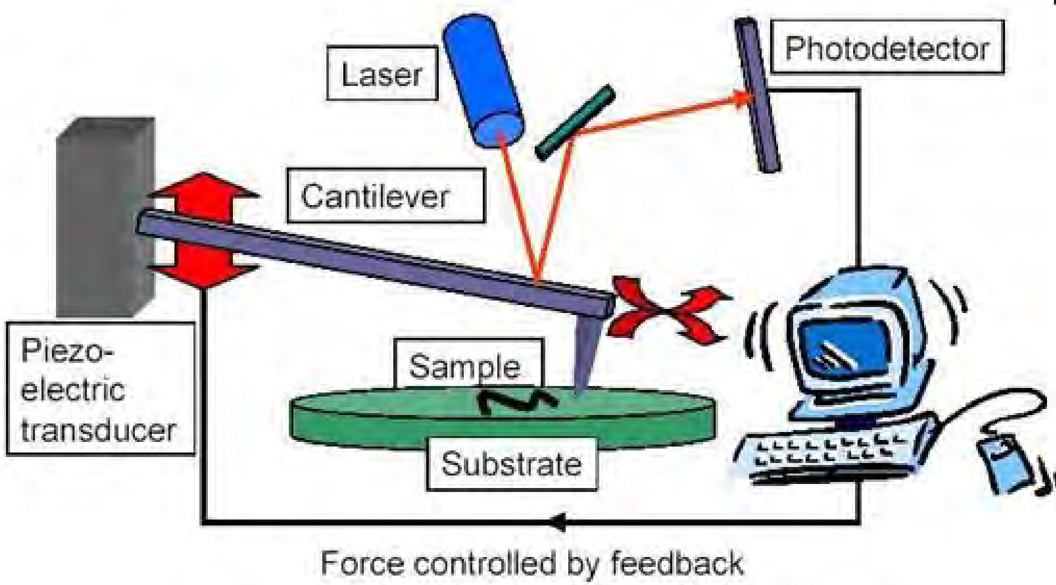
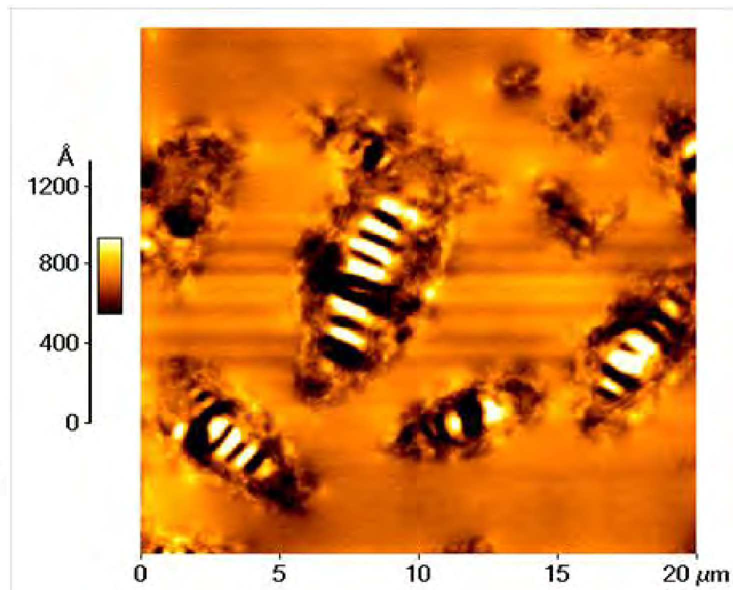
# Additions to the colloidal model

- **Cold surface crystallization of waxes observation**
  - **Dark Field Optical Microscopy**
    **500 μm level: Crystals**
  - **Atomic Force Microscopy**
    **20 μm level: Bee structure**



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# *Additions to the colloidal model*

- **Interactions between crystallizing paraffin waxes and the non-wax asphalt components are responsible for much of the structuring**
  - **Including the bee-structures observed on the surface of asphalt thin-film samples by AFM**
- **AFM a powerful tool to visualize surfaces at very small scale – BUT tricky…**
  - **Sample preparation / Film thickness**
  - **Thermal conditioning prior and during imaging - Cool rates / Time / Temperature**
  - **Wax concentration in the bulk**
  - **Molecular weight distribution of wax**
  - **Properties of the medium from which wax crystallizes from (e.g., asphalt crude source or asphalt fraction)**
- ***Troy Pauli's dissertation, March 2014***

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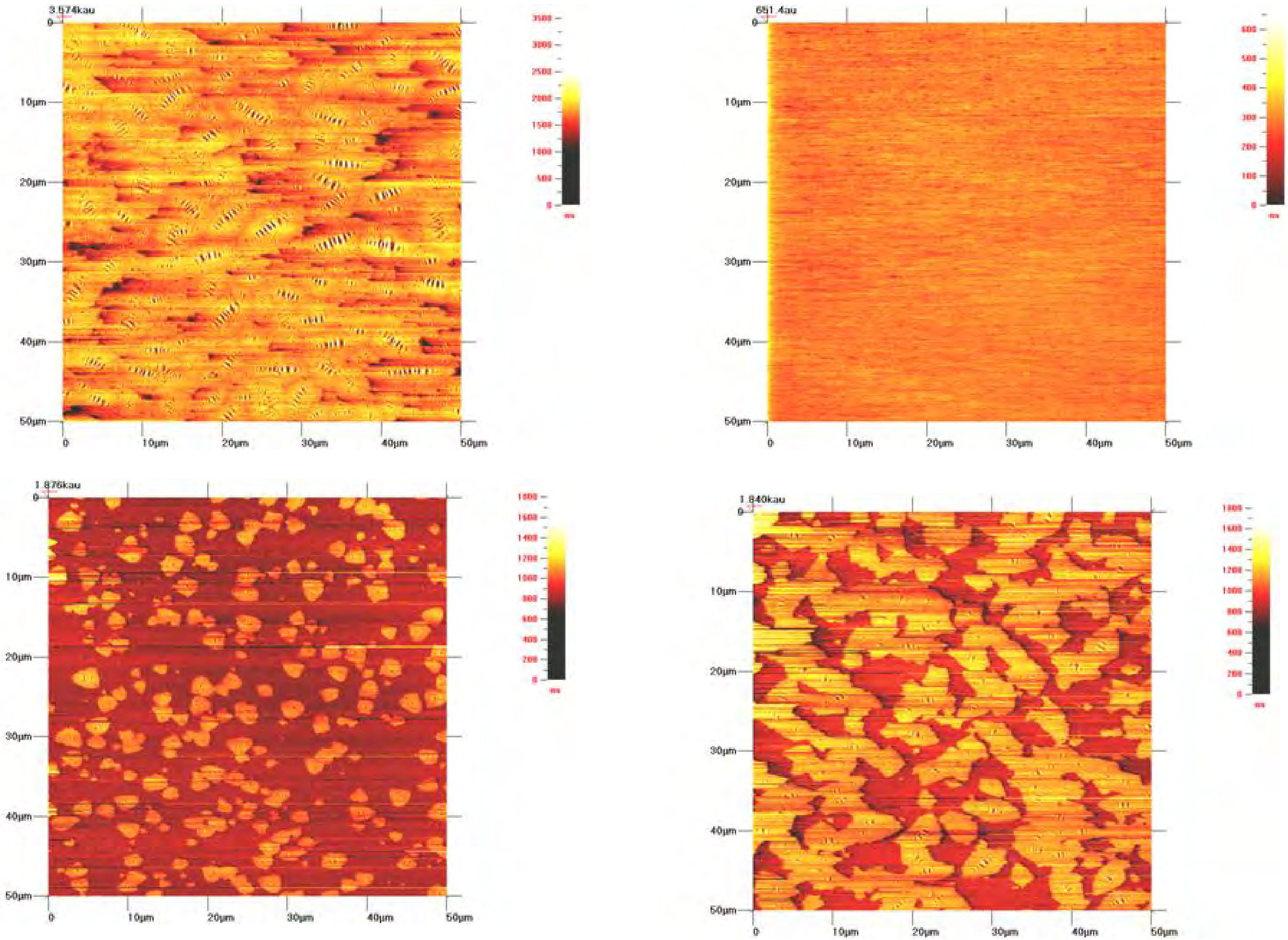
# Additions to the colloidal model

## Bee Structuring as a function of crude source



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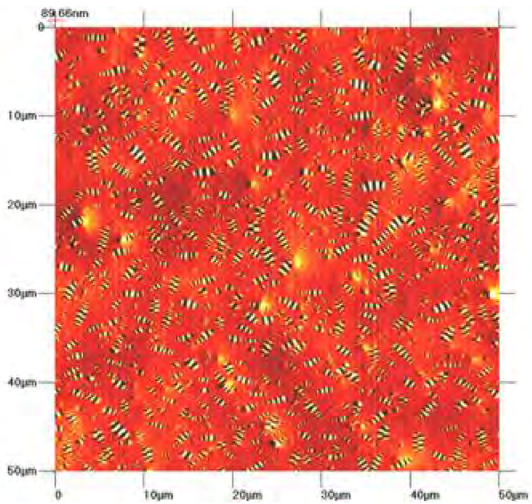
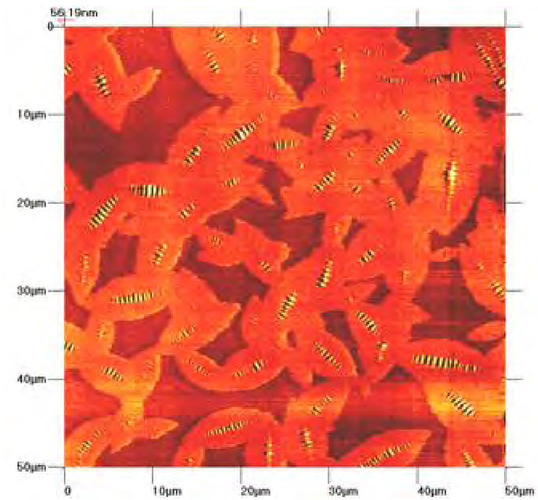
# *Additions to the colloidal model*

## Bee Structuring as a function of chromatographic fraction – interactions with the various fractions

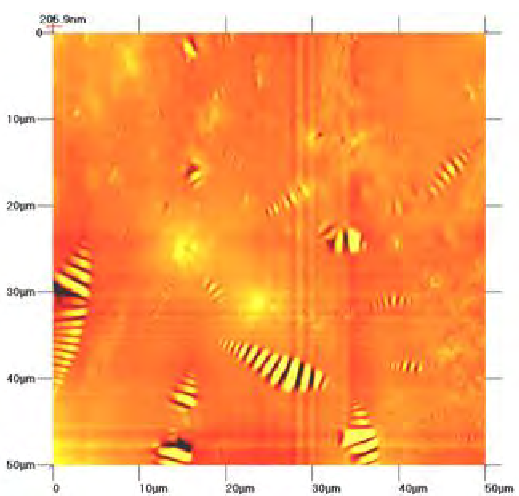



**AAB-1-Neat**

**At 25°C**



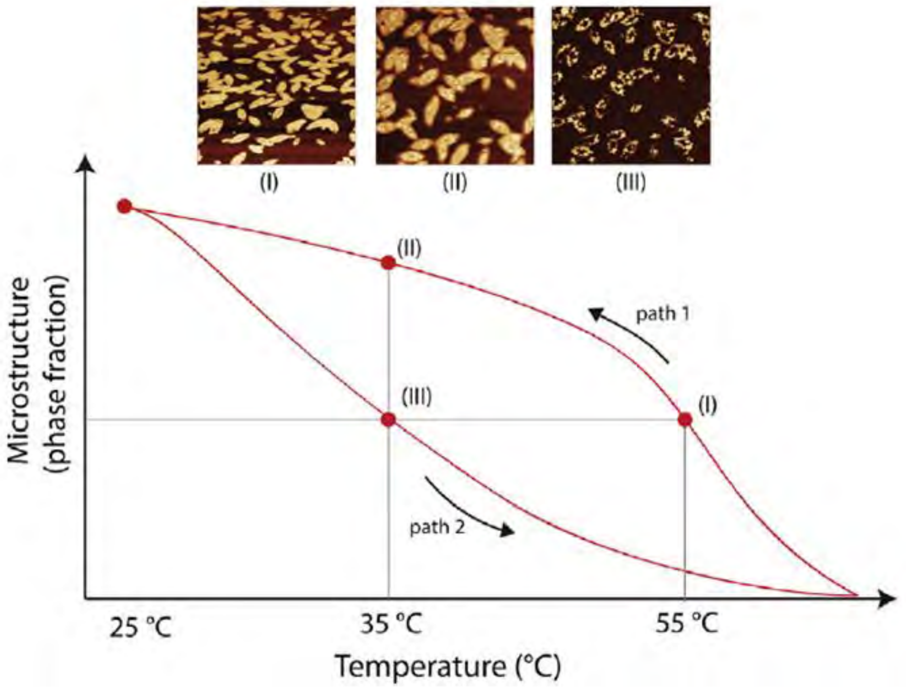

**AAB-1-Maltenes**




**AAB-1-Neutrals**

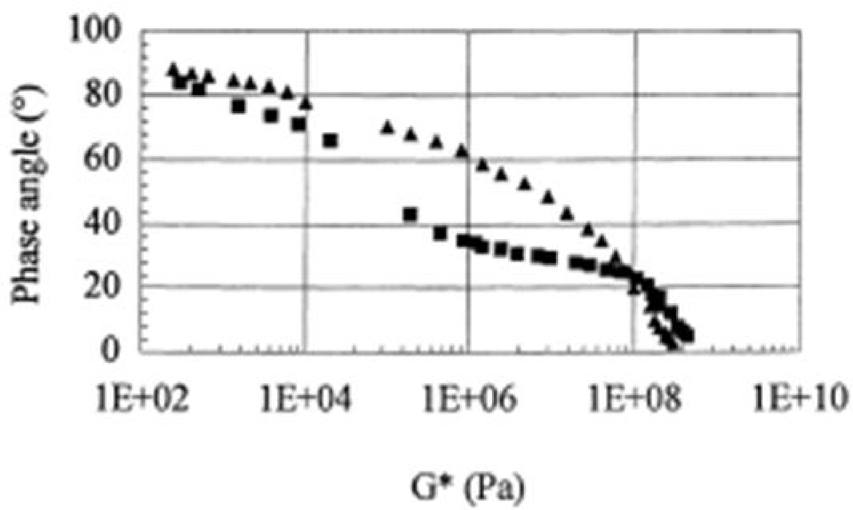
# Additions to the colloidal model

**Thermal hysteresis of the microstructure morphology of bitumen**




**TU-Delft Works (2010's)**

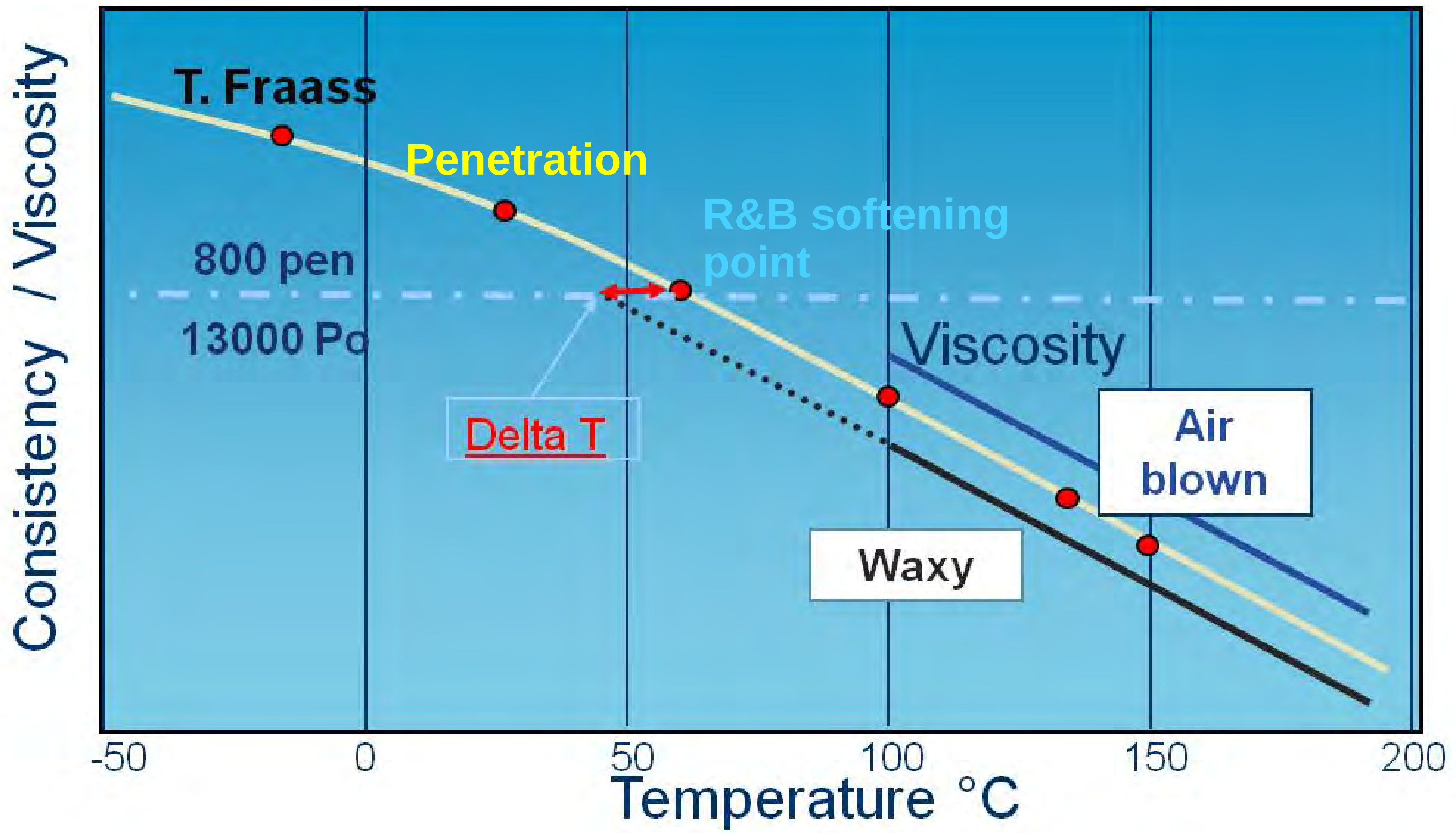
**Thermal hysteresis of the rheology of waxy asphalts (comparison 3% vs. 10% CF asphalts)**




**TOTAL (Elf) Works (1990's)**

# Relationships between Asphalt Structure & Mechanical properties

W. Heukelom, 1973



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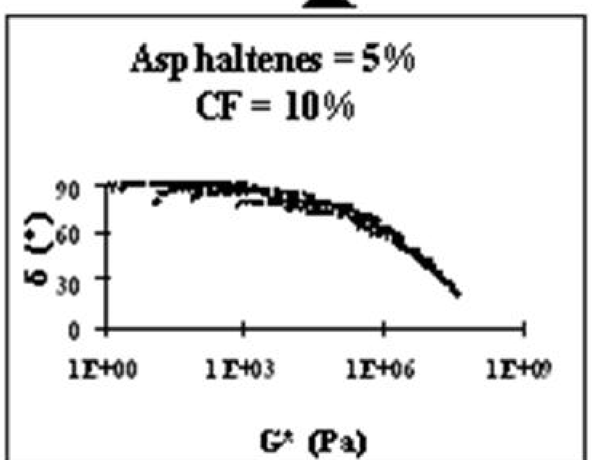
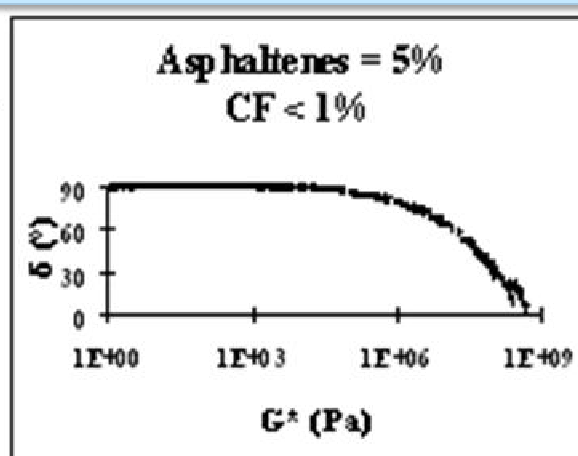
# *Relationships between Asphalt Structure & Mechanical properties*

- **Time Temp Superposition Principle applicability ?**
  - **YES: single curve in case of “Sol” structures**
  - **NO: “Gel” structure / high wax or high asphaltene contents**
- **Dynamic Shear Rheology using Black space - no data shift**
  - **Phase angle as a function of the stiffness modulus**
- ***Works: Ramond, Such (LCPC) in the 80’s, Lesueur, Champion-Lapalu (Elf) in the 90’s***

**High Crystallized fraction**

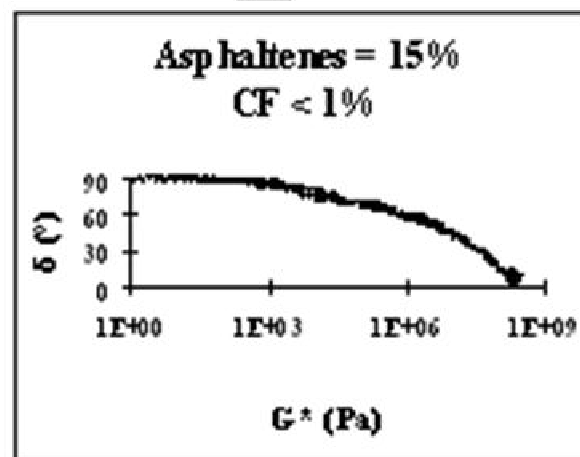



**Rheologically simple**

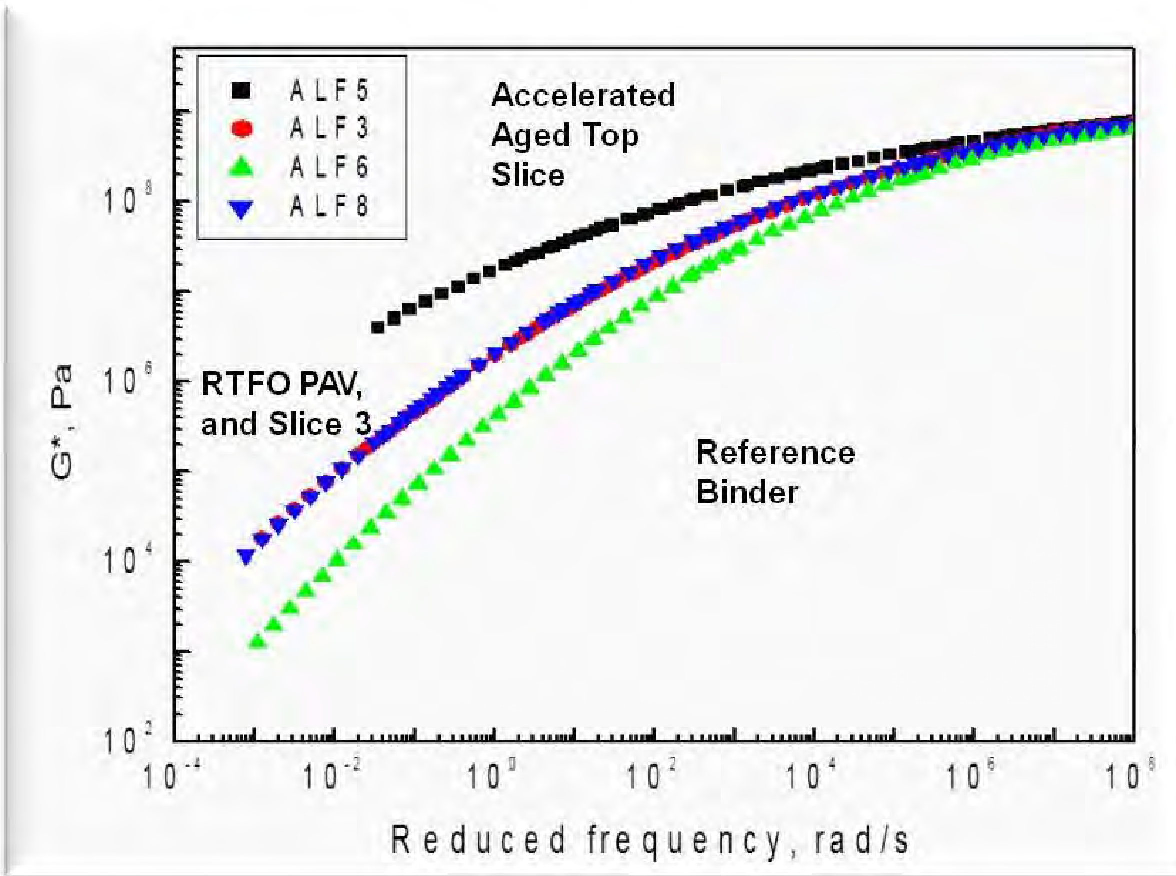
**-> Low Asphaltene & wax**

**High Asphaltene**



# Relationships between Asphalt Structure & Mechanical properties

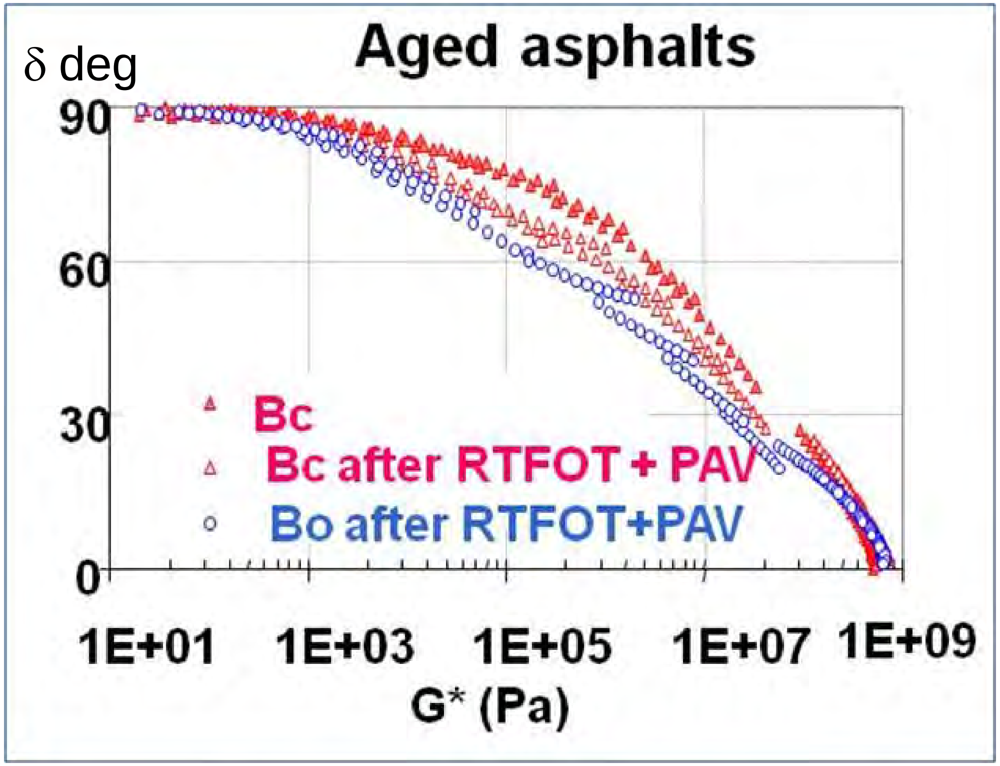
## Typical effect of ageing on asphalt rheological properties




**Stiffening: Increase in stiffness modulus**

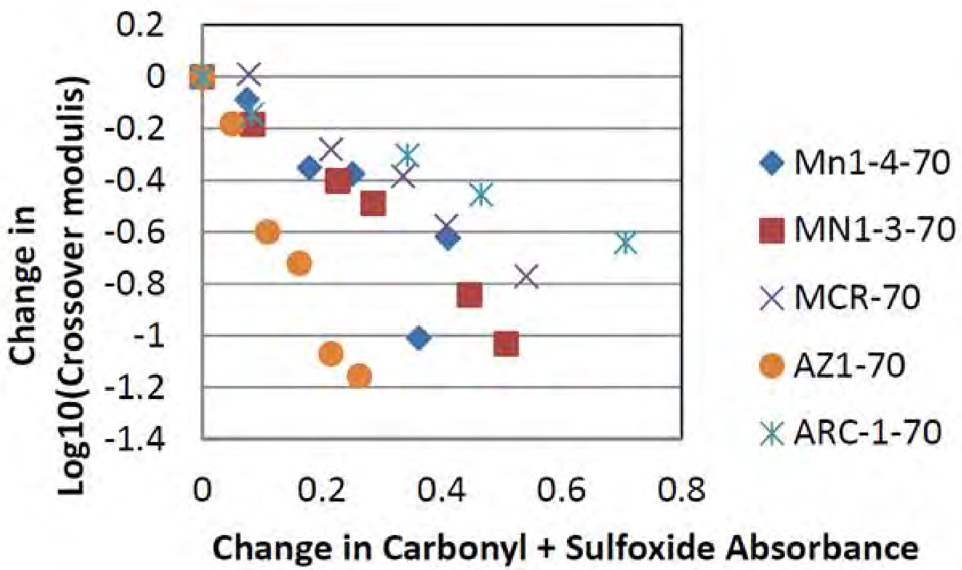
Case of ALF Lane 2, 4 mm Plate Master Curve Data (25 °C Reference Temperature) – FHWA/WRI FPIII

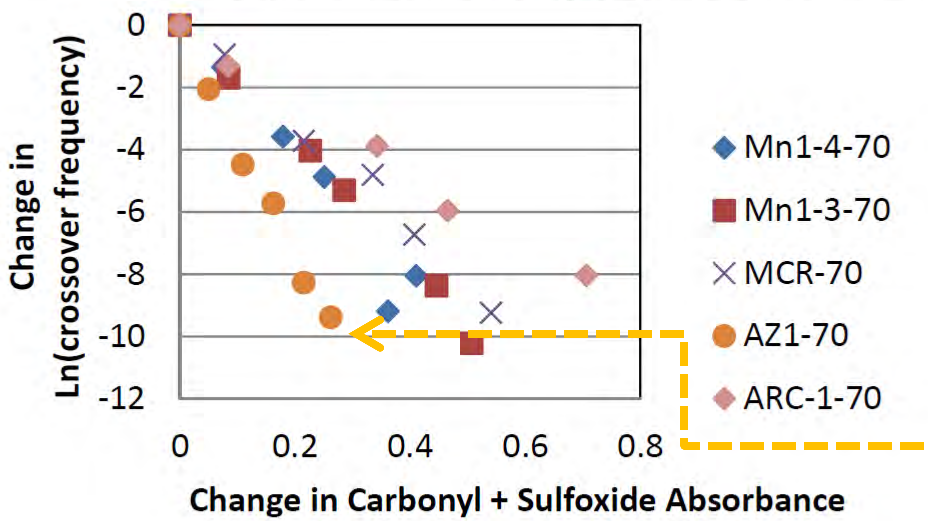
# Relationships between Asphalt Structure & Mechanical properties




- **More in depth effect of oxidative aging: stiffening, more elastic behavior, "flattening" and shift from TTSP**
  - **Black space visualization**
  - **Asphaltene increase due to aromatization and polarity**
- ***Works by: Mouillet / Lamontagne (TOTAL/LCPC) - early 2000***

# Relationships between Asphalt Structure & Mechanical properties



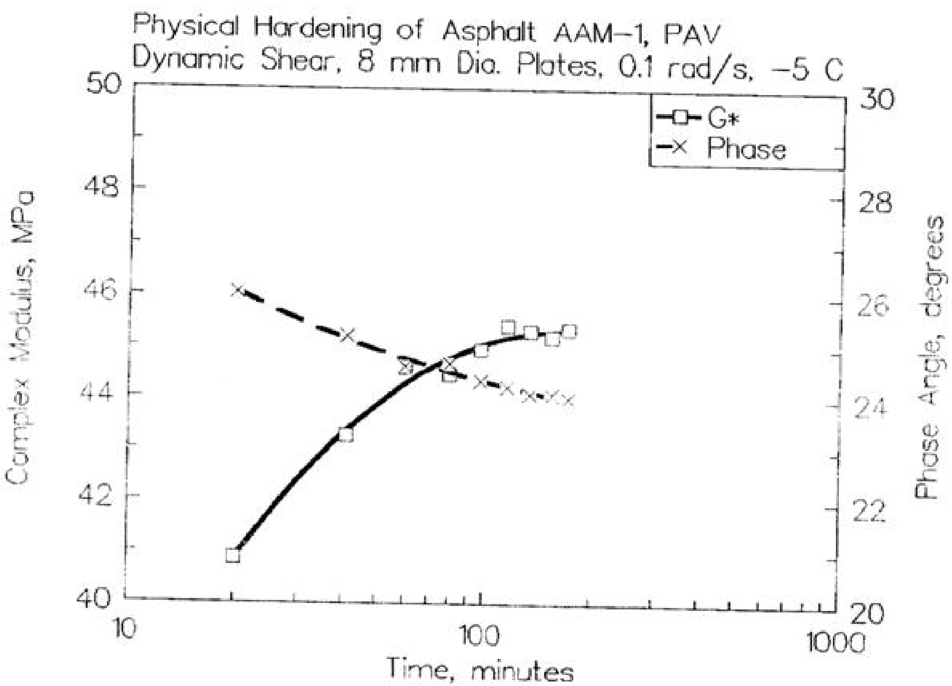




- **Binder stiffening upon oxidation tracked by the crossover modulus**
  - **Parameter where a material goes from elastic to viscous ($\delta$=45º)**
- **Stiffening rate with oxidation function of binder original state**
  - **Gel asphalts stiffen "faster" than sol**
- **Farrar and Glaser (WRI-FPIII)**

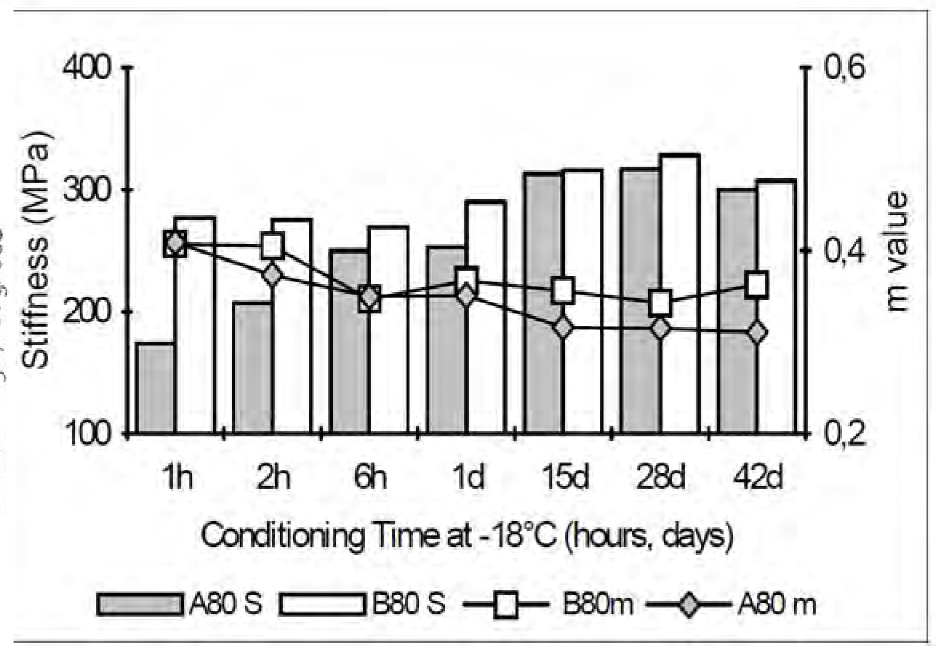
**AZ1-70 : Airblown bitumen with a gel structure**

# Relationships between Asphalt Structure & Mechanical properties

**Physical Hardening by D. Anderson, H. Bahia (PennState U) DSR and BBR – SHRP (early 90's)**



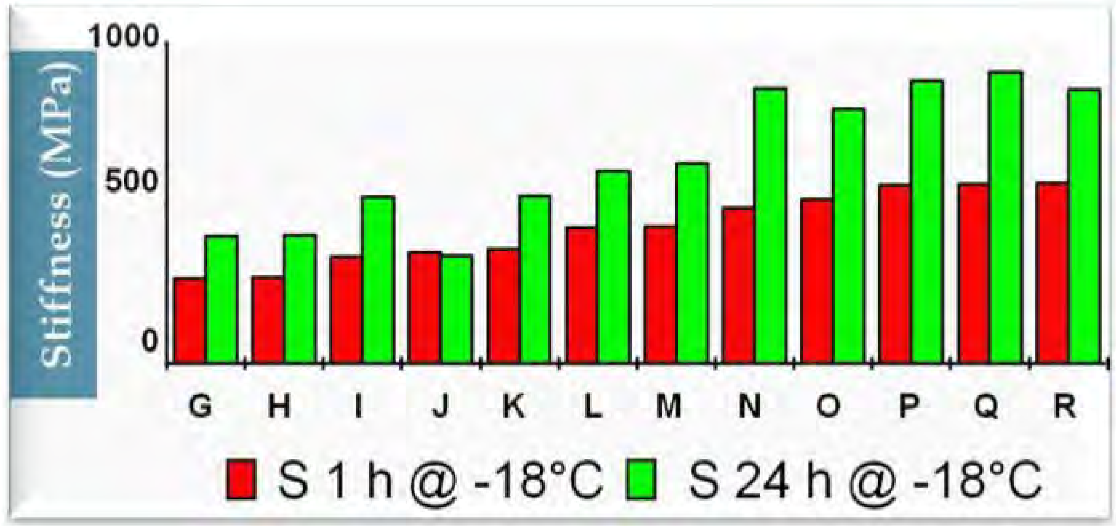

**Physical Hardening in the BBR confirmed by Elf (JP in the 1990's)**



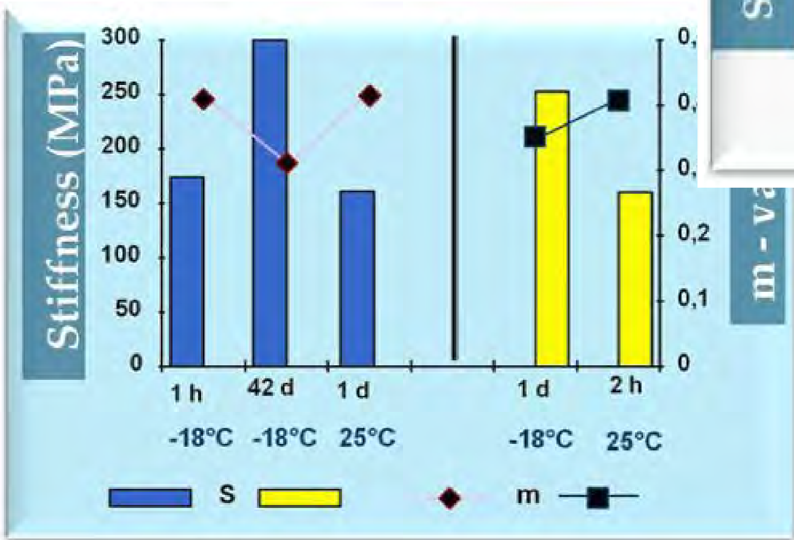

❖ **Physical Hardening occurs both in the BBR and the DSR... Intensity and duration may differ**

# Relationships between Asphalt Structure & Mechanical properties

## Physical hardening
- BBR ranking impact




Effect of physical hardening on Bitumen ranking (BBR)



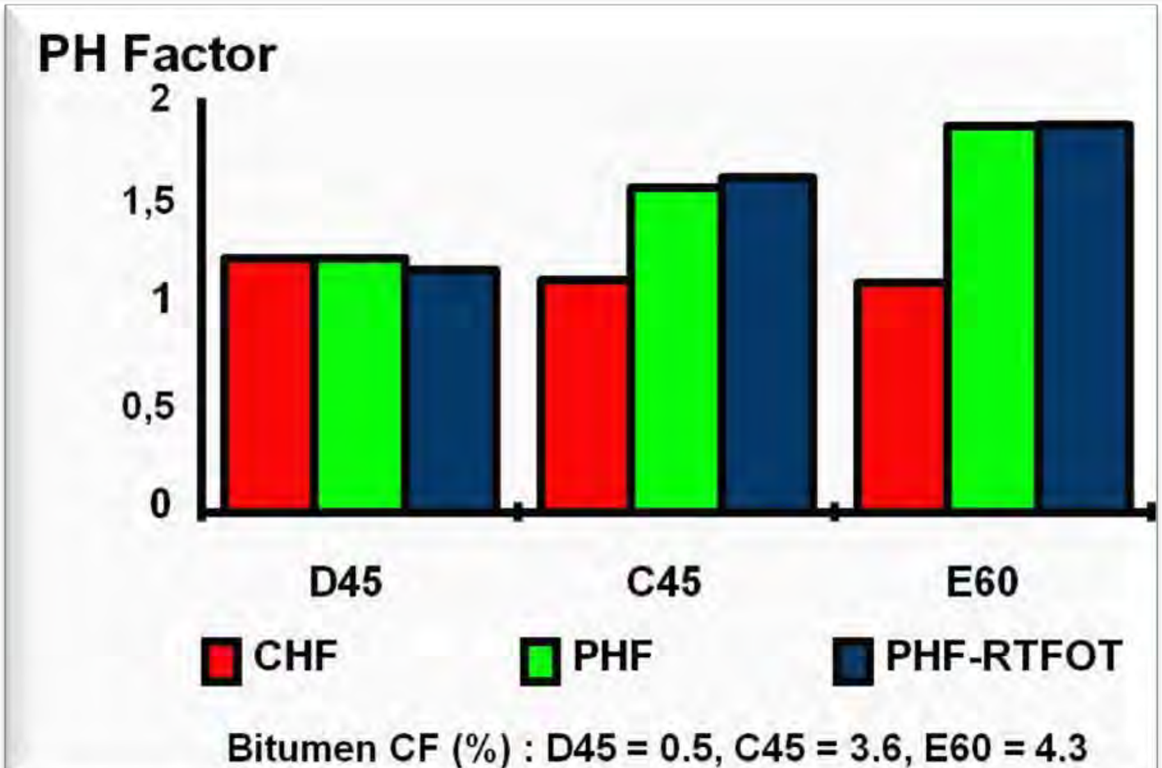

## Physical Hardening
- Reversibility at room temperature

Ref: Planche et al, RILEM 1997

# Physical hardening issues

**Comparison between Physical Hardening and RTFOT**

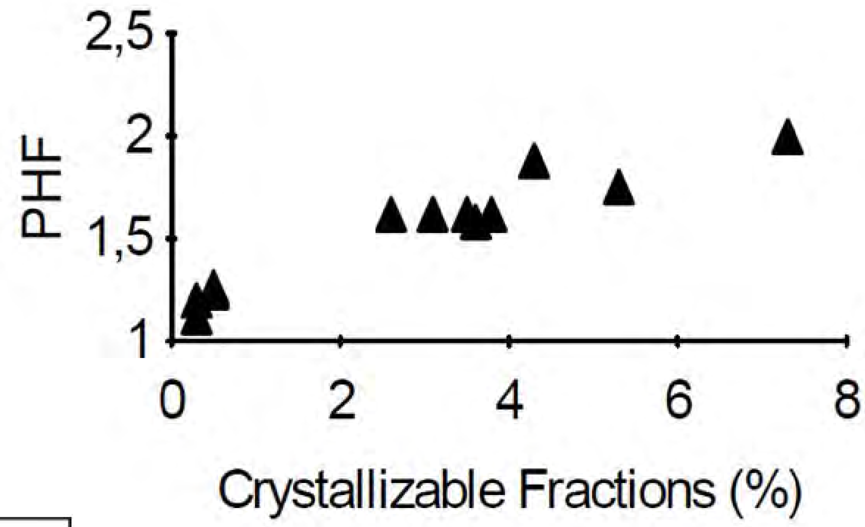
- Effect at the same level or higher than RTFOT
- Not affected by RTFOT

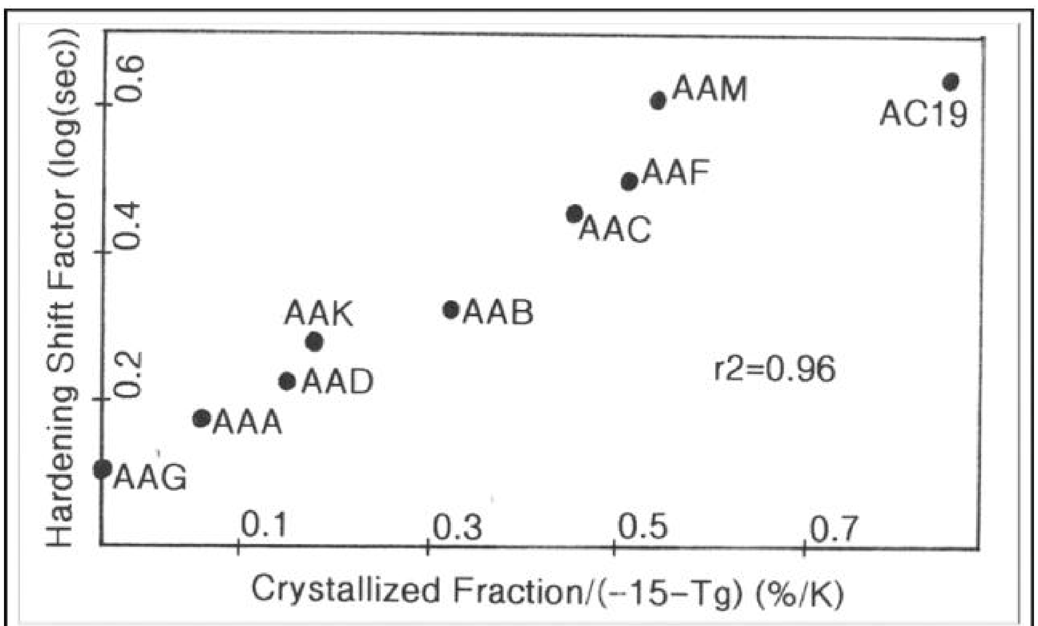



Ref: Planche et al, RILEM 1997

# Relationships between Asphalt Structure & Mechanical properties

- Physical hardening dependency
  - Crystallized fraction & Tg
  - Conditioning temperature & time
- Assessed by DSC and BBR
- *Works by Anderson, Bahia et al (US), Claudy, Planche, (FR) 90's*

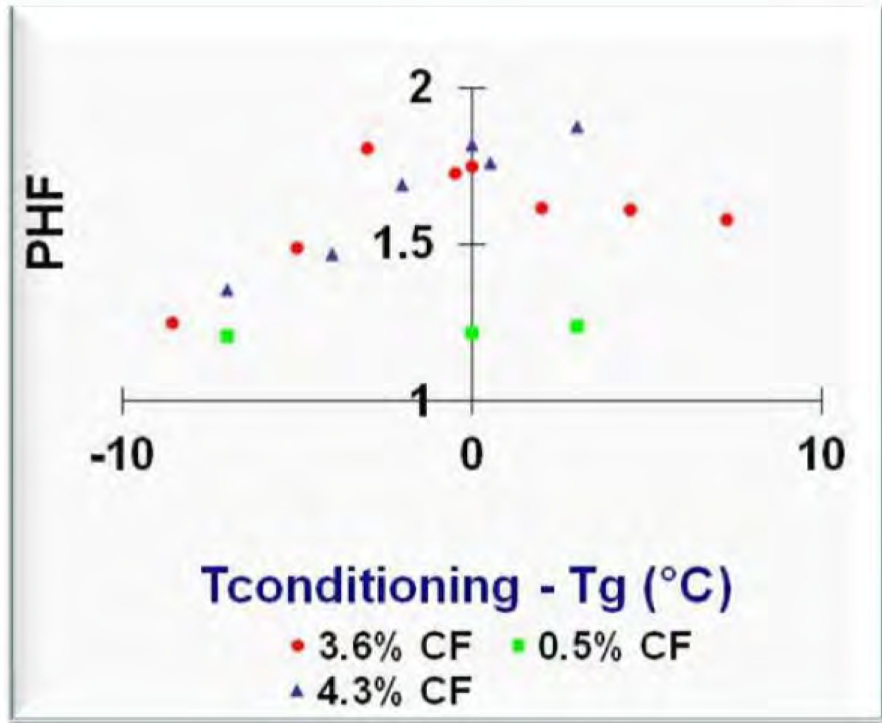



$$PHF = (S_{24h} / S_{1h})^{(m_{1h} / m_{24h})}$$

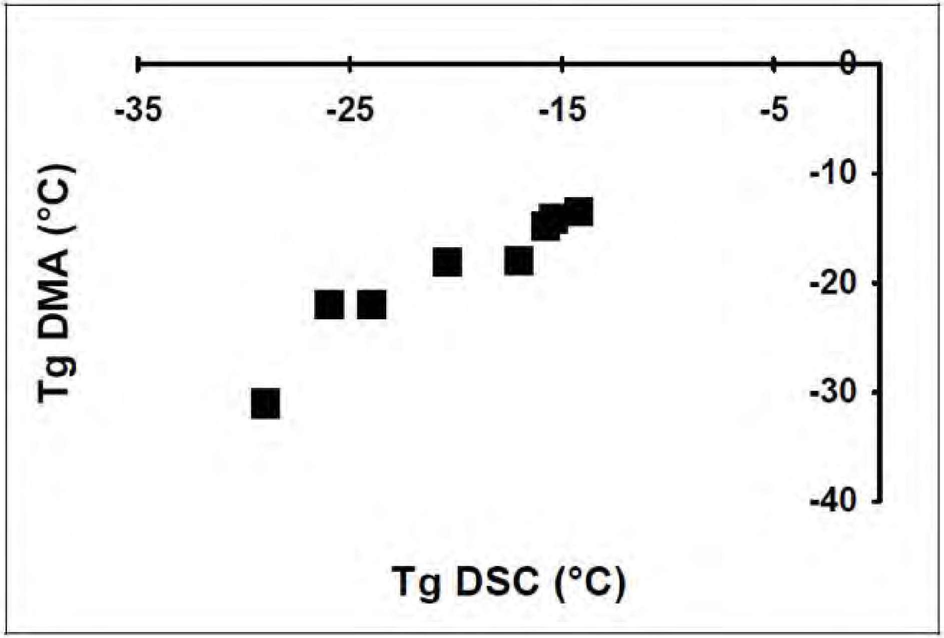
# Relationships between Asphalt Structure & Mechanical properties

- **Physical hardening dependency**
  - **Crystallized fraction & Tg**
  - **Conditioning temperature & time**
- **Physical hardening reaches maximum intensity around Tg, decreases to nil 10C below Tg**
  - **Free volume collapse and wax cold crystallization**
- **Assessed by DSC and BBR**
- ***Works by Anderson, Bahia et al (US), Claudy, Planche, (FR) 90's***




$$PHF = (S_{24h} / S_{1h})^{(m_{1h} / m_{24h})}$$

# Relationships between Asphalt Structure & Mechanical properties



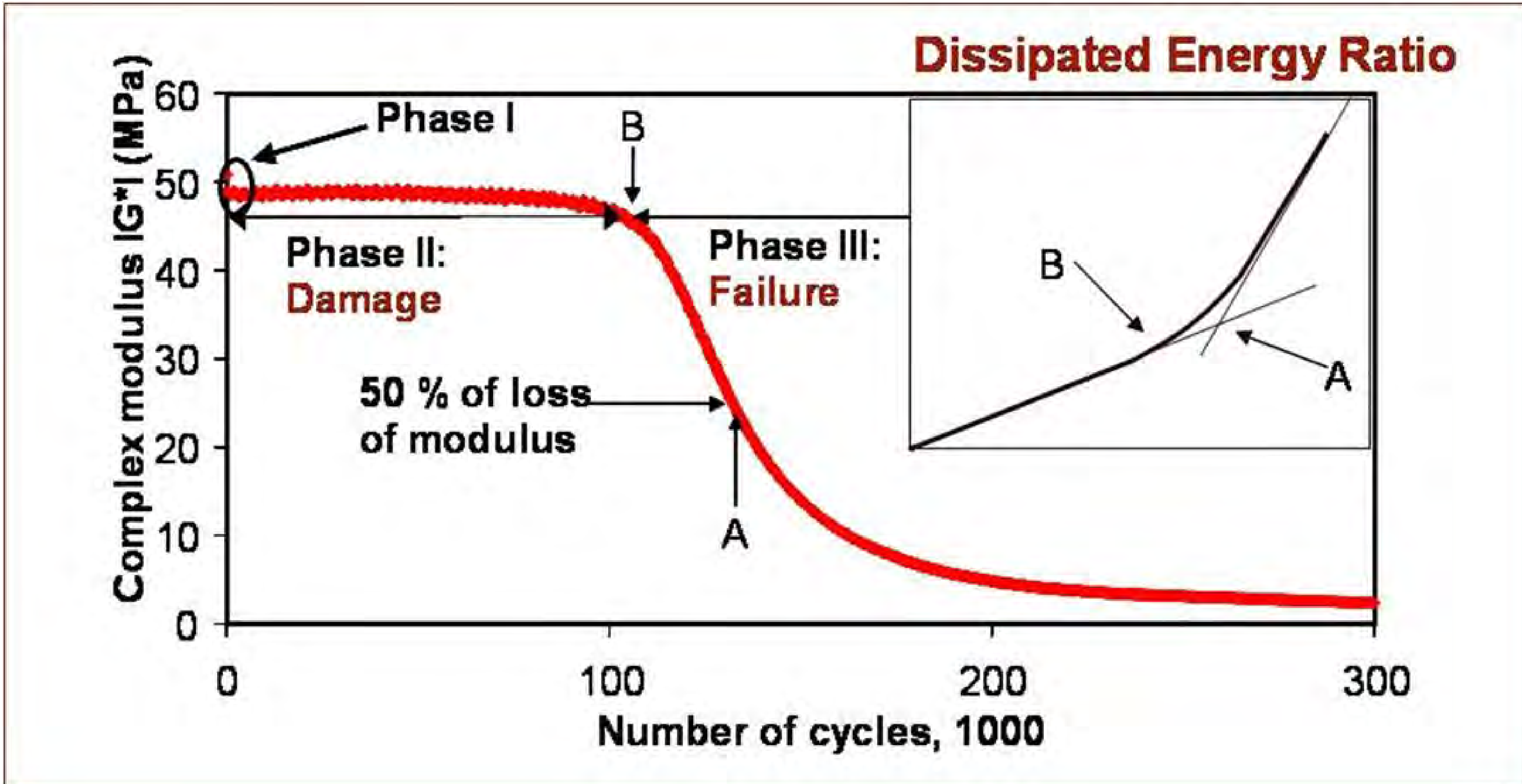

**Relationship Rheological Tg (DSR) vs. Thermal Tg (DSC)**

- ➢DSR Tg = loss modulus peaks at low frequency (5 rad/sec)
- ➢Compatibility related blending rules for PMA's and RAP blends
- ➢Related to TSRST critical cracking temperature
- ➢Changes with aging (widened temp. range)



**Works: King (AAPT 1993), Claudy, Lesueur (1990's), Huang, Turner (FPIII)**

# Relationships between Asphalt Structure & Mechanical properties




**Fatigue Testing of binders assessed by DSR Time sweep**

•Work by H. Bahia (UWM), D. Anderson (PennState) and Le Hir, Gauthier (TOTAL) late 90's (US-FR)

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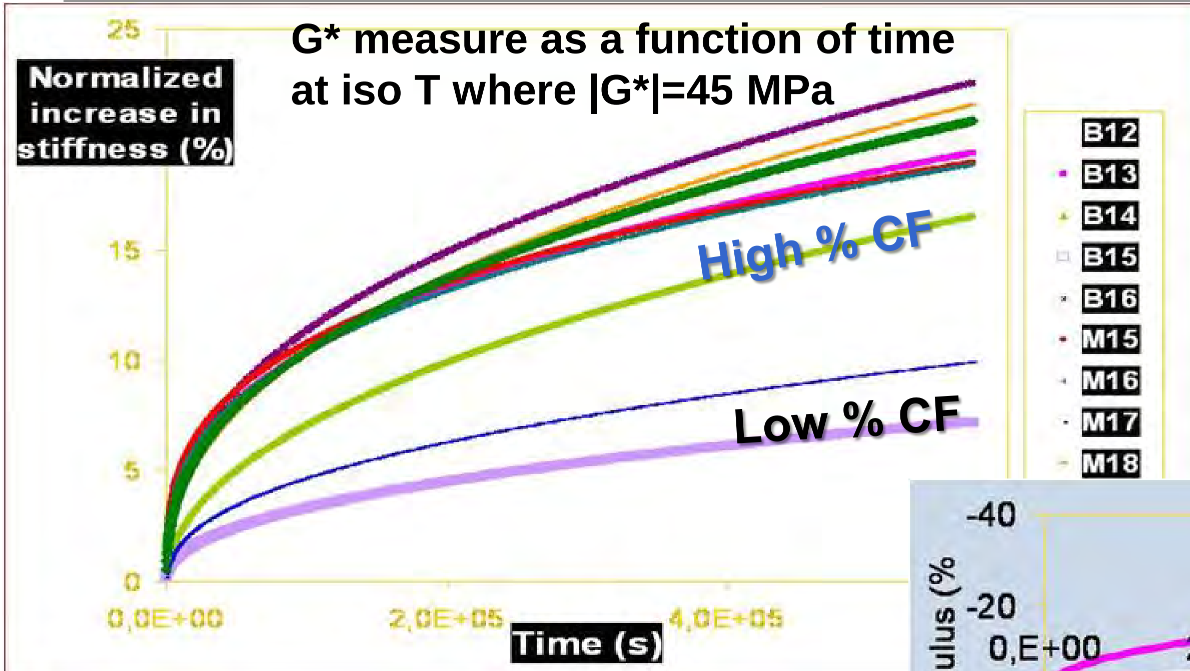
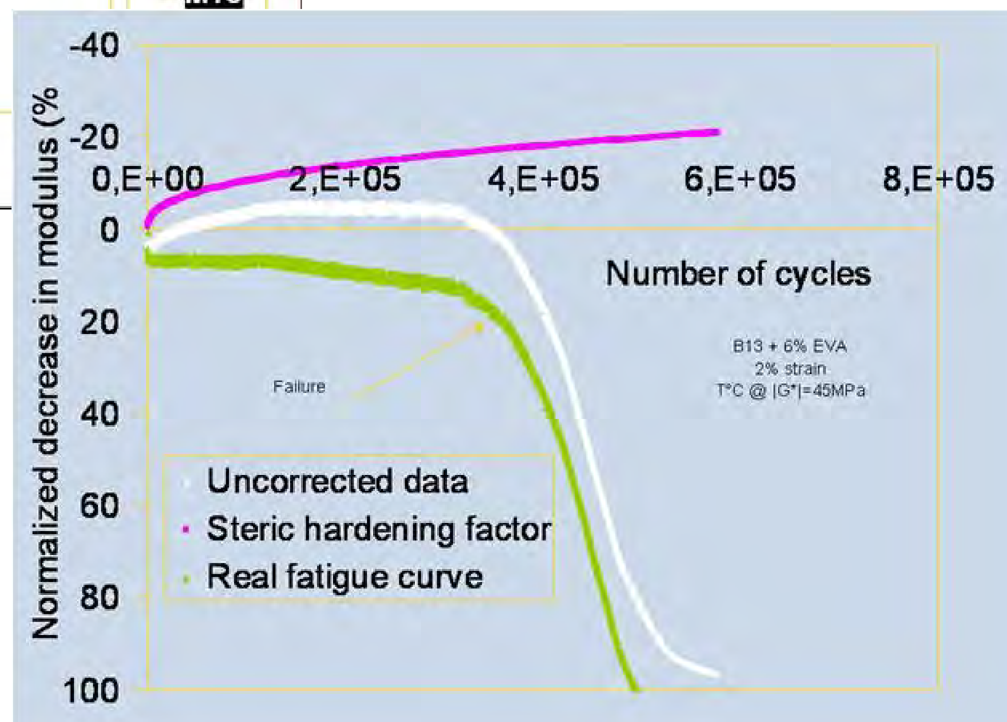
# Relationships between Asphalt Structure & Mechanical properties



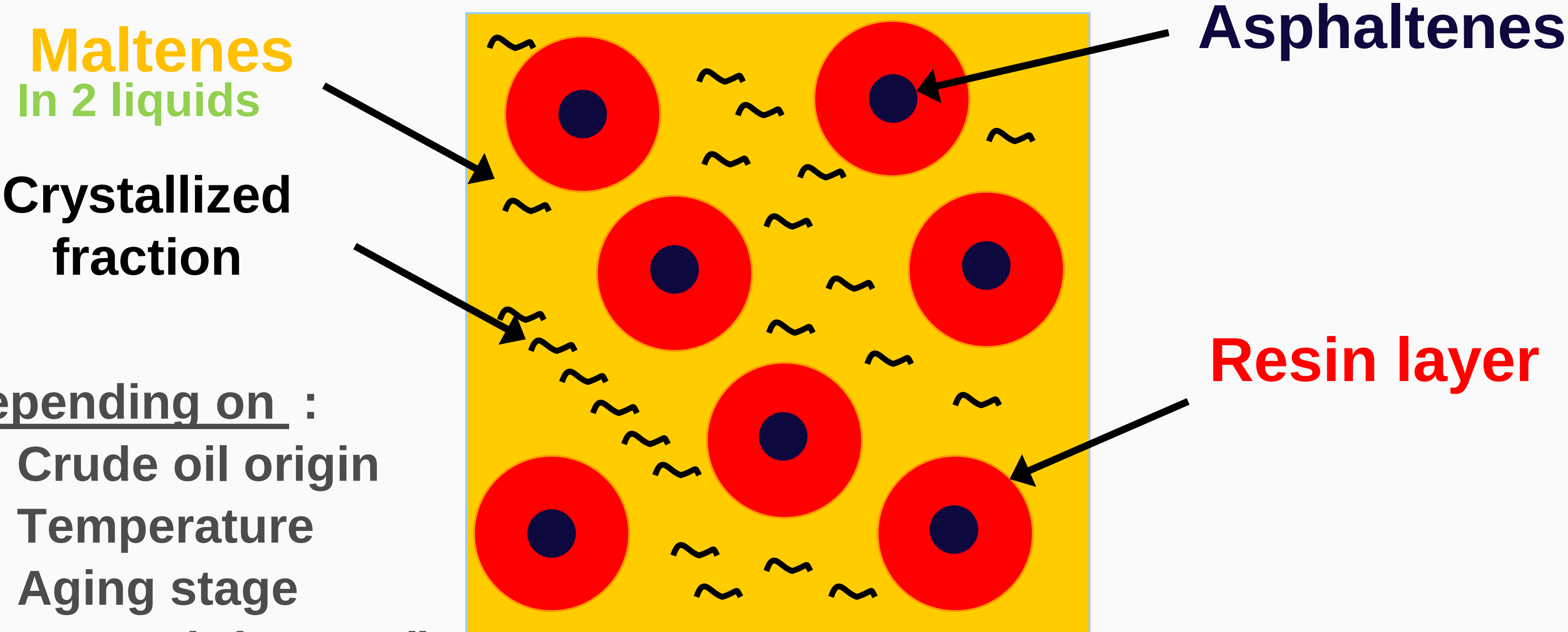

Time sweep at iso T storage where |G*|=45 MPa




- **Influence of Steric Hardening on DSR time sweep**
  - remains under shear
  - influences fatigue results
  - somehow related to crystallized components

# Summary
# Structural Model of Asphalt

## Colloidal suspension of asphaltenes in a maltene matrix




Depending on :

- Crude oil origin
- Temperature
- Aging stage
  - Tank (unaged)
  - Short Term (aggregate mixing)
  - Long term - in service in the pavement
- **Presence of an additive or a polymer**

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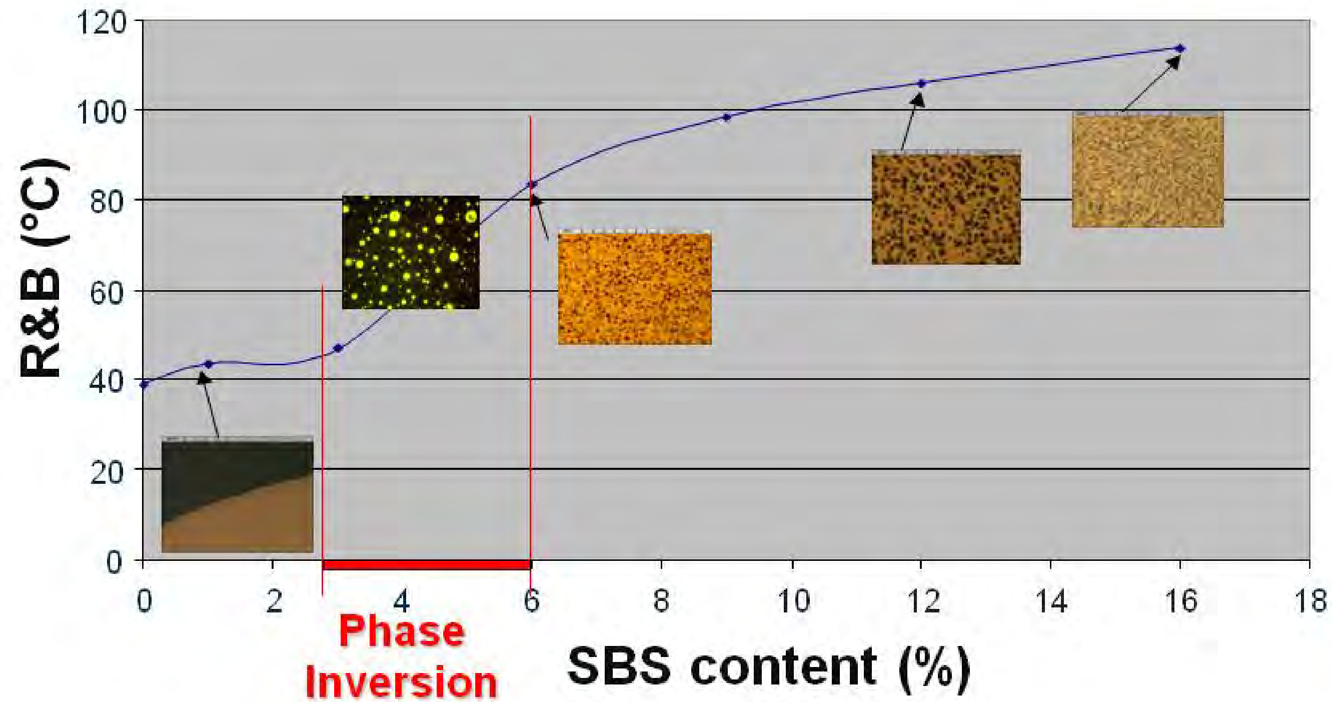
# Outline

- Background - Context
- Chemical-physical and structural properties of asphalt
  - Impact on asphalt mechanical properties
- **Asphalt modification**
  - **Impact on structure and mechanical properties**
- Summary
- Perspectives

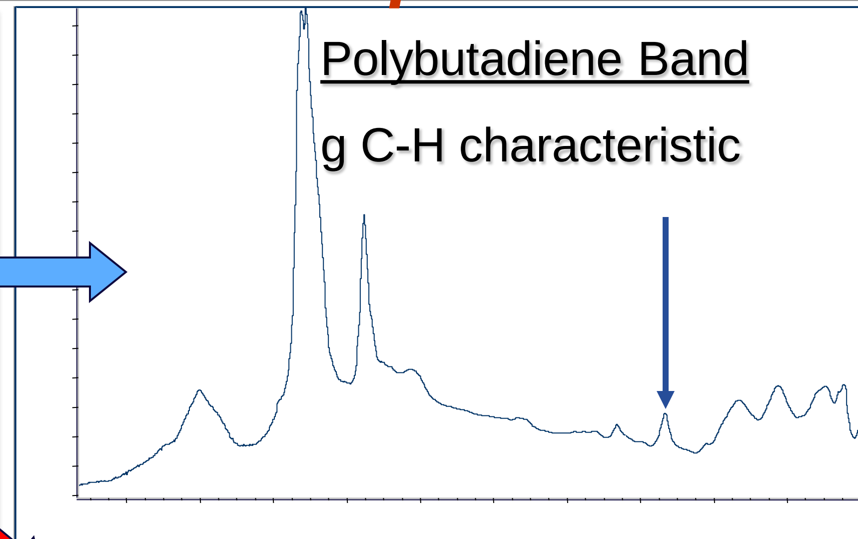
# Effect of additives on of Asphalt Structure

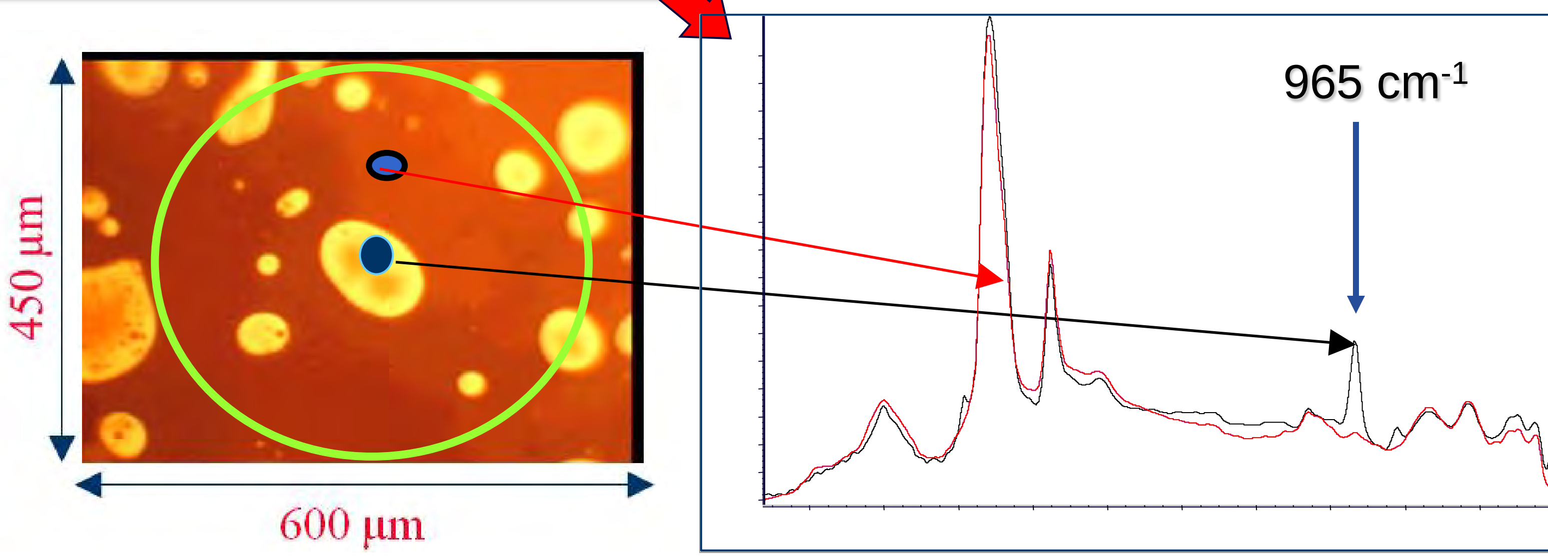



- Effect of polymer modification on microstructure & properties - UV fluorescence microscopy visualization
  - Polymer swells with light aromatic oil maltenes
  - Polymer phase inversion between 3 and 6% polymer
  - Big jump in consistency (R&B softening point, G*/sin δ…)
- *Work s: Brule – LCPC (80's) – Shell, Enichem, Elf, Kraton (90's),…*

## Effect of additives on of Asphalt Structure

- **IR Microscopy to analyze PMA structure**
  - **Spectroscopy = Global Analysis**
  - **IR Microscopy = Local Analysis**
- ***EU: LCPC-TOTAL-U Marseille in the early 2000, Mouillet et al***




EU: Mouillet et al, BLPC 2000

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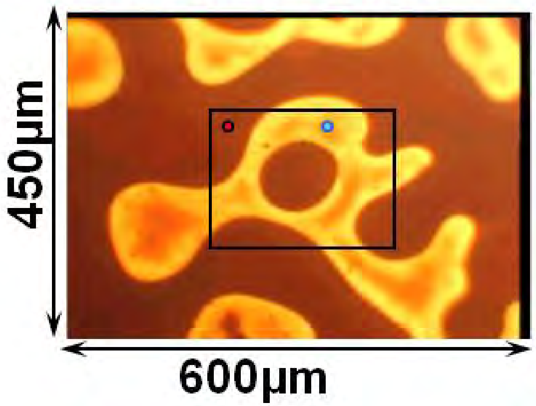
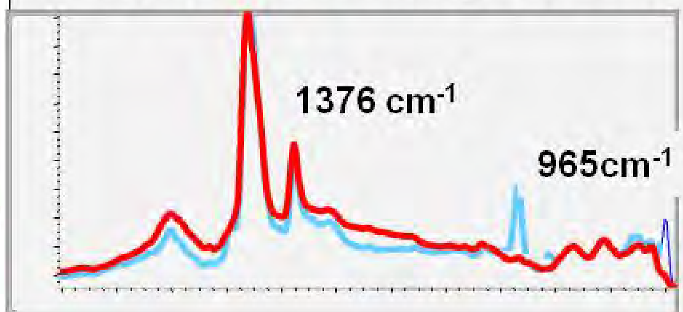
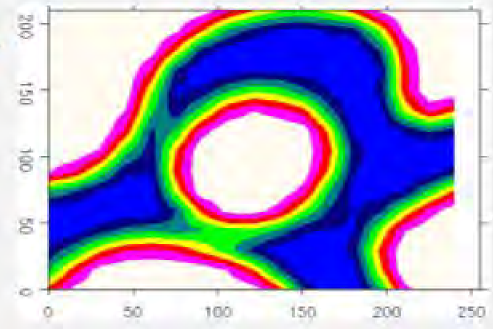
# *Effect of additives on of Asphalt Structure*

## SBS m Bitumen

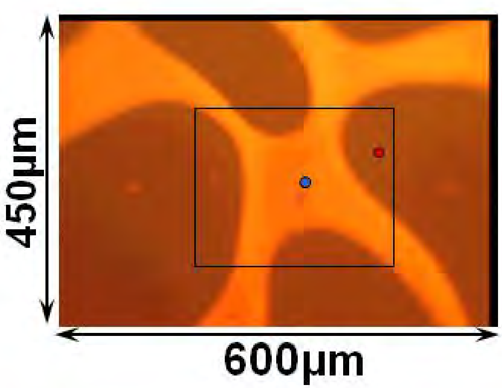



$\dfrac{\gamma CH \text{ SBS band @ } 965cm^{-1}}{\delta CH_3 \text{ bitumen band @ } 1376cm^{-1}}$

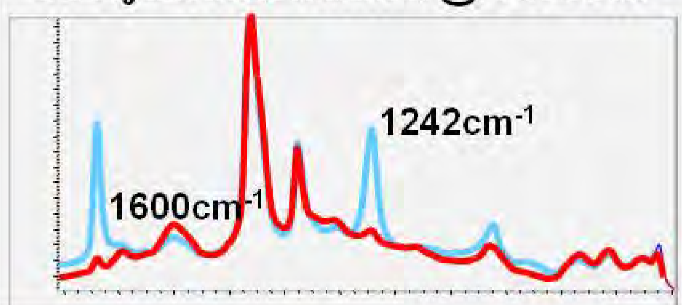


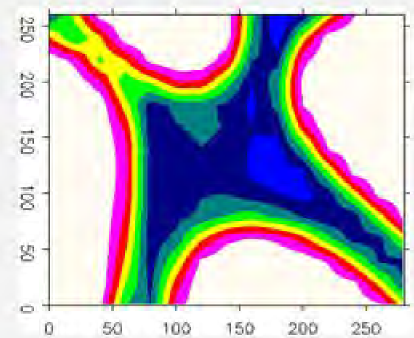




## EVA m Bitumen




$\dfrac{\nu C\text{-}O \text{ EVA band @ } 1242cm^{-1}}{\delta CH_3 \text{ bitumen band @ } 1376cm^{-1}}$




*Mouillet et al, BLPC 2000*

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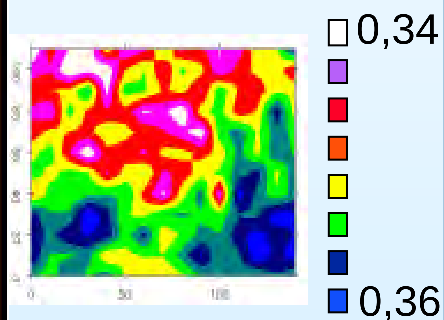
# *Effect of additives on of Asphalt Structure*

## FTIR Microscopy



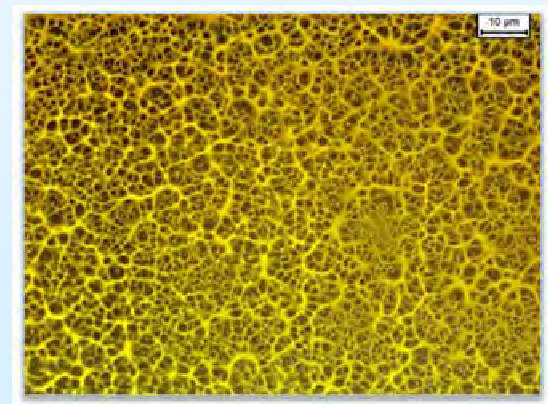

**Fine dispersion of a cross-linked PMA**

✓Storage stable

✓Does not evolve significantly during aging

✓Better overall properties

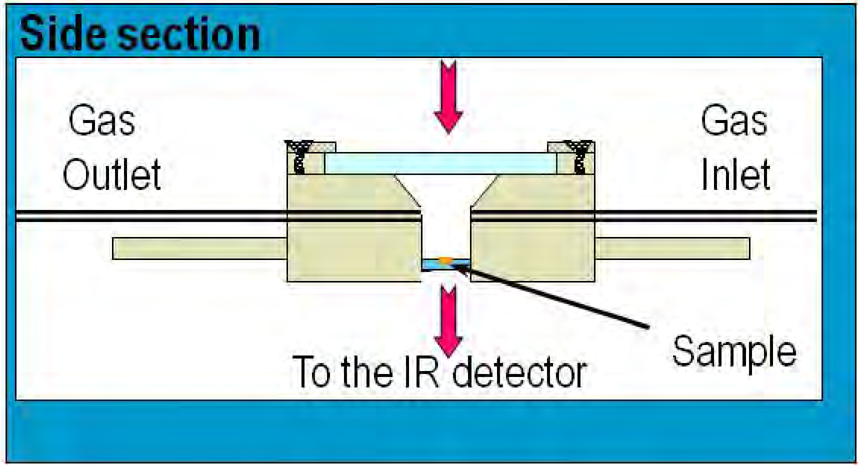
## UV epi-fluorescence Microscopy



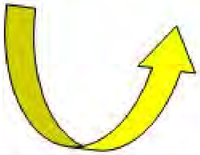
**Microstructure of a cross-linked PMA**

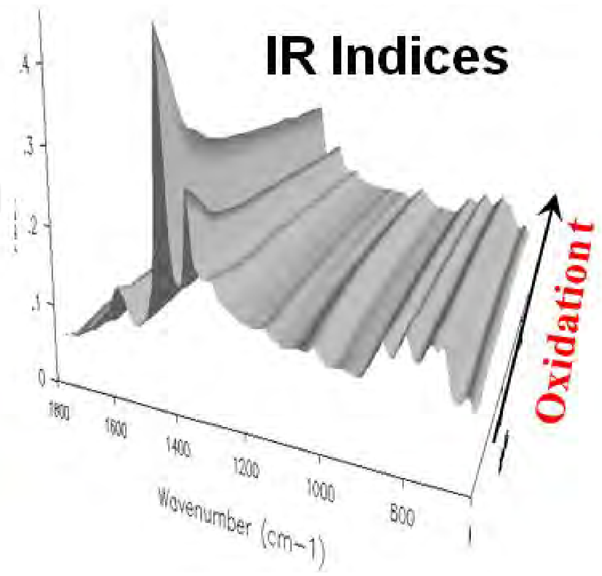
3 D Network revealed by N-hexane rinse

# Effect of additives and aging on of Asphalt Structure




**In situ Oxidation Analysis**






Oxidation cell **to analyze in situ the aging effect on PMA structure**

- Temperature sweep
- Heating rate
- Oxidant or neutral gas
- Allowing to continuously visualize and analyze the chemical evolution of phases

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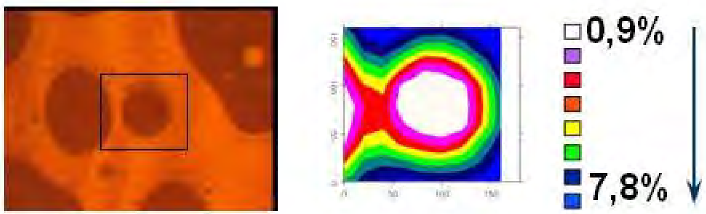
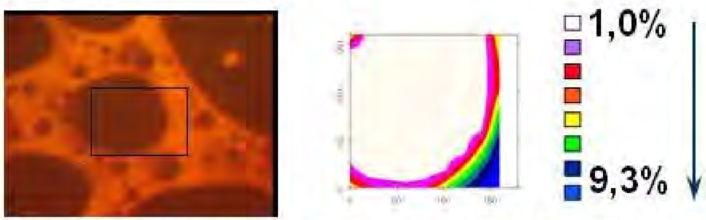
# Effect of additives and aging on of Asphalt Structure

T=0'

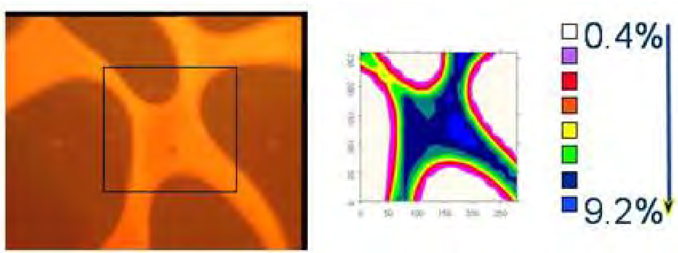



- Before aging

T=60'




- After 60 min in aging cell 130°C/air
- Same focus




- After RTFOT+PAV aging

## Aging effect on PMA structure by IR Microscopy

### Before aging

- Phase inversion at 6% EVA
- EVA swollen by slightly condensed aromatics substituted by aliphatics

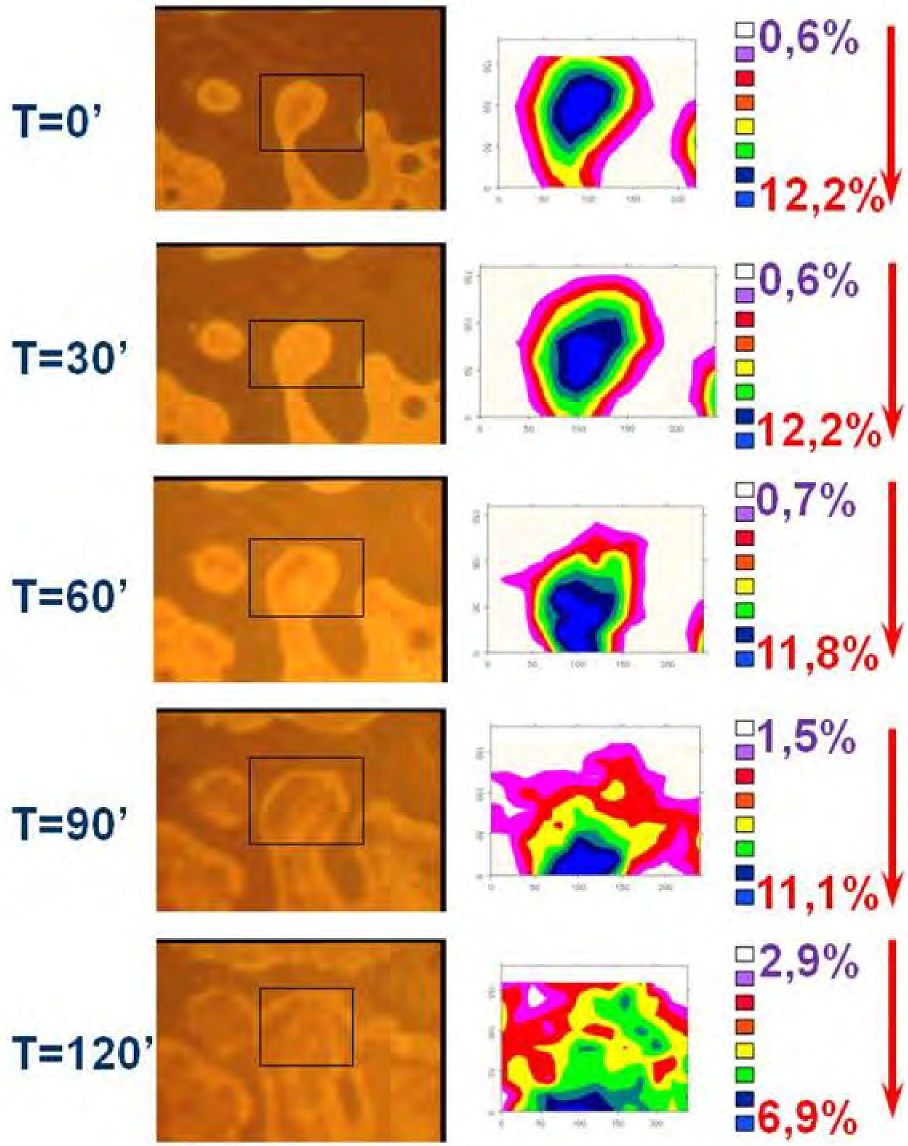
### After aging

- % EVA increase in polymer nodules
- Stability of aromatics and decrease in aliphatics & condensed aromatics

→ migration of the fraction swelling EVA to the surrounding matrix

Durrieu et al, E&E congress 2004

# Effect of additives and aging on of Asphalt Structure




**Ageing conditions : 130°C / Air**

- **PMB with 6% SBS linear**

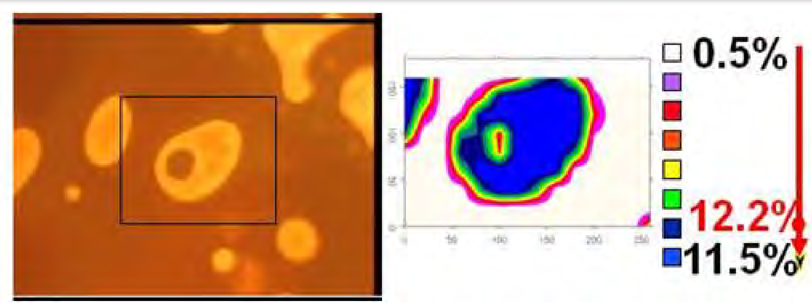
➡ **Homogenization of SBS**

➡ **Decrease in SBS content in polymer nodules**

➡ **Increase in SBS in bitumen matrix**

➡ **Lower oxidation level (oxydes)**

➡ **In line with RTFOT+PAV**



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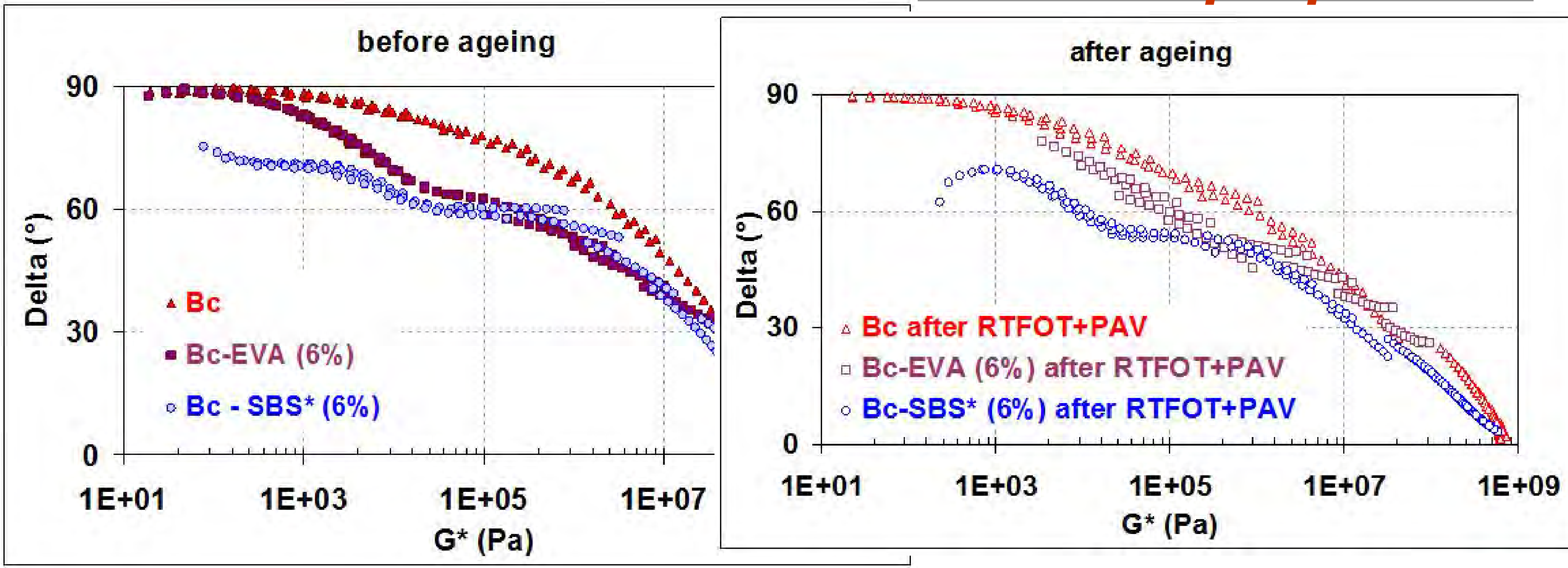
# Effect of additives on Asphalt Mechanical properties




- **Polymers impart a rubbery plateau effect – depending on polymer content, process**
  - Confirmed by MSCR results outside the linear range
- **Rubbery effect degrades upon oxidation – differently for SBS vs EVA**
  - EVA itself is not oxidized, but its compatibility with oxidized asphalt molecules decreases
  - SBS oxidizes (chain scissions) but becomes more compatible

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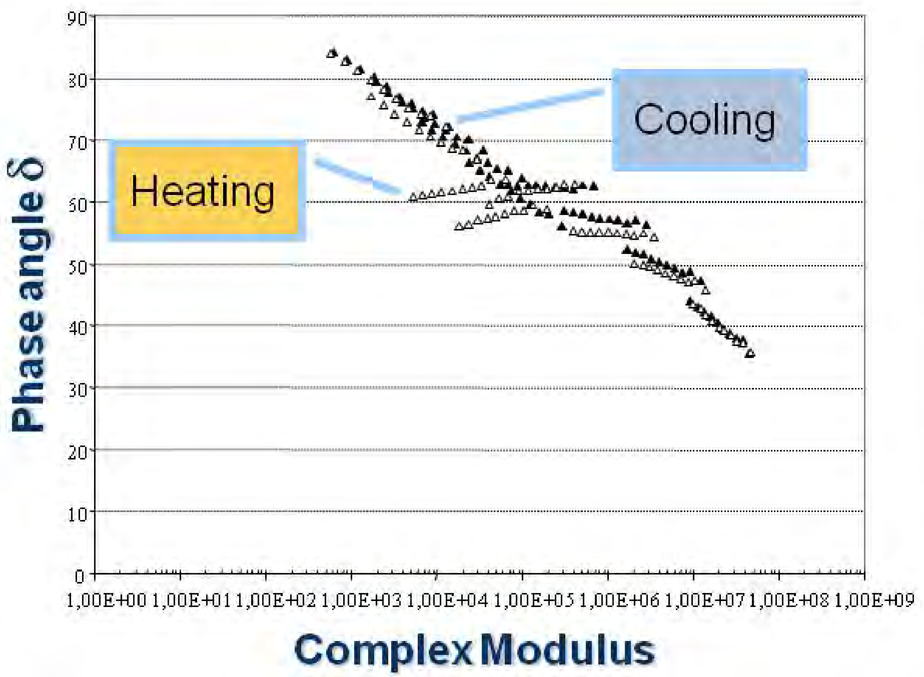
# *Effect of additives on Asphalt Mechanical properties*

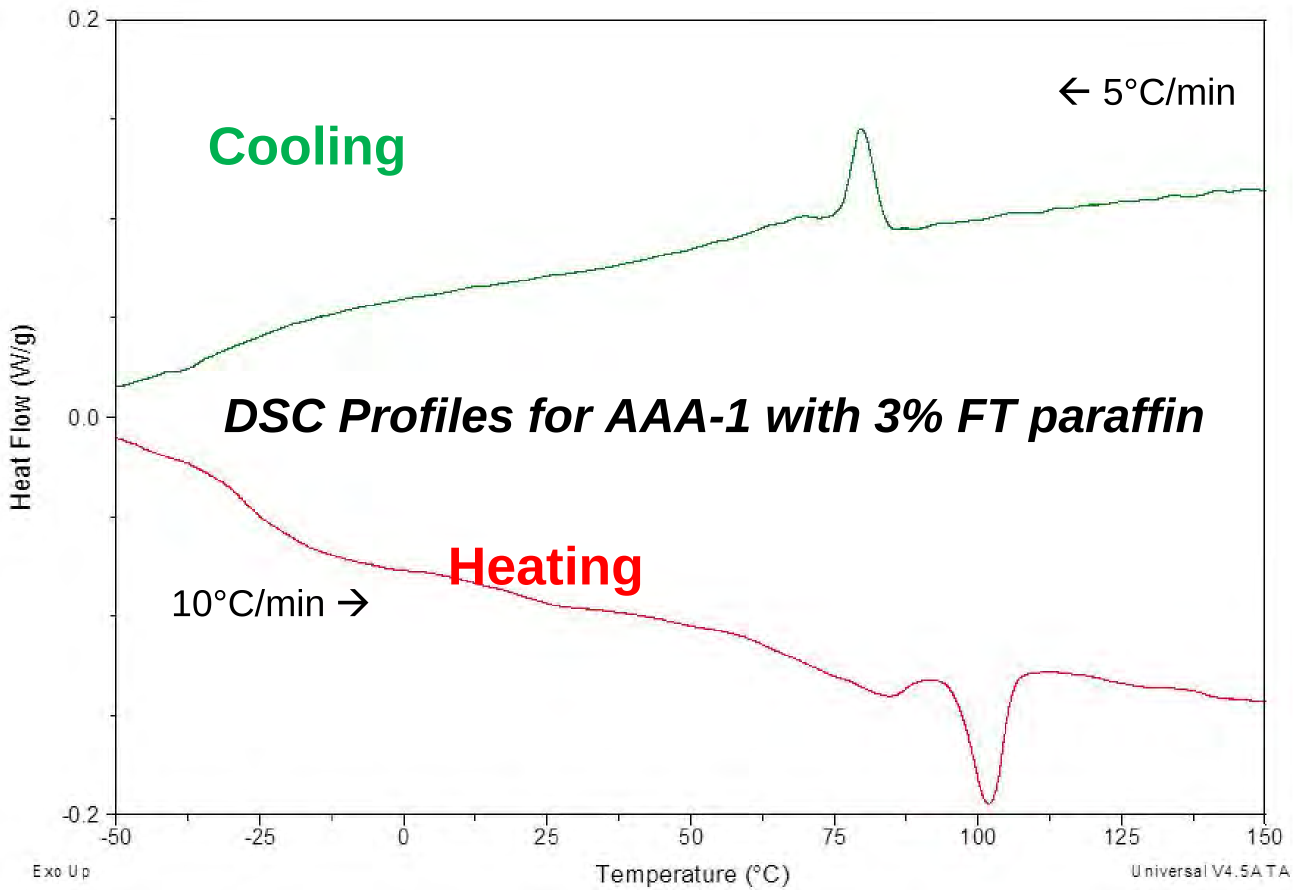



- **EVA crystallinity effect on binder properties (6% EVA):**
  - ✓No single curve in Black space – TTSP not applicable
  - ✓No rheological behavior superposition between cooling and heating

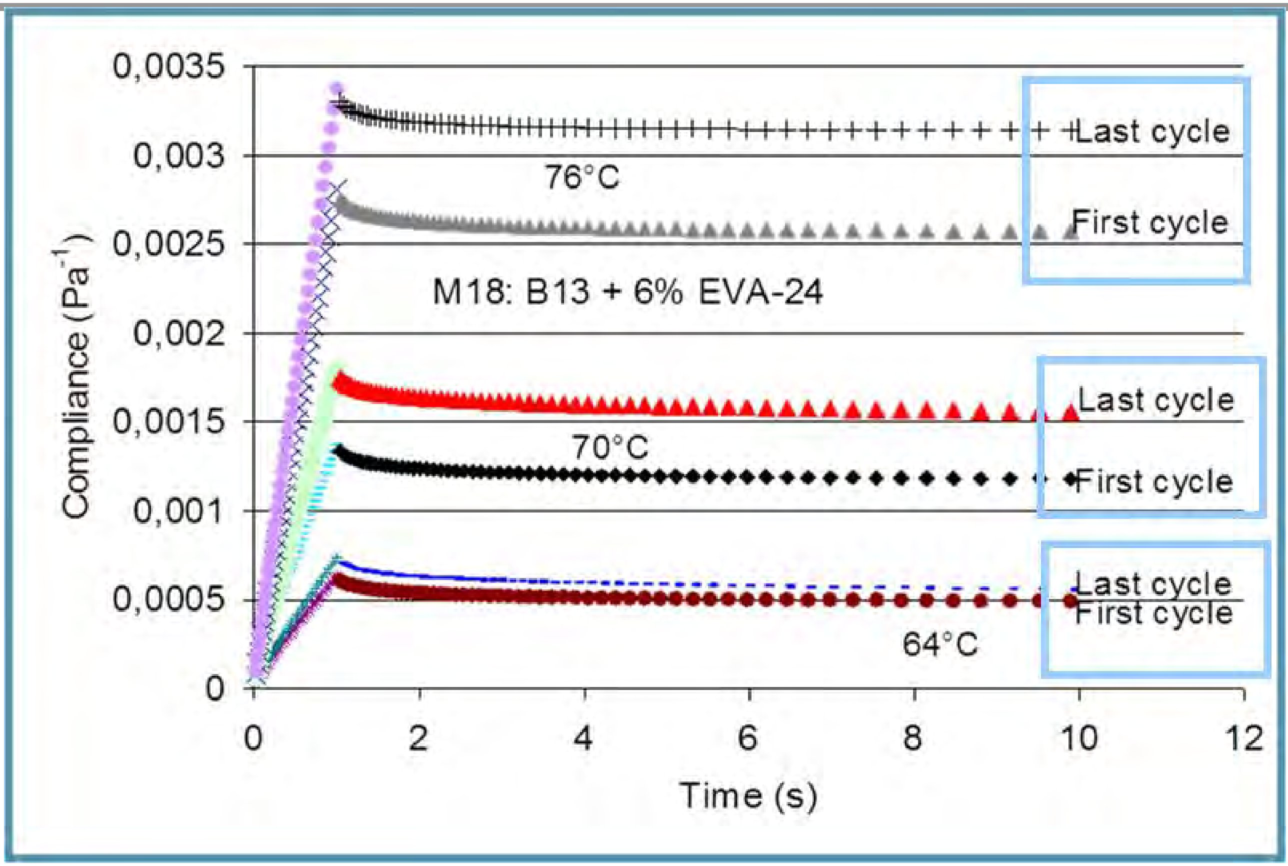
- **Dependency on crystallinity - Plastomer PMA**
  - **Influence of thermal history on crystalline properties**
  - **Crystallization vs. Melting hysteresis in DSC - Cooling vs. Heating**
  - **Occurs with FT paraffins and PE type polymers**
- ***Works: Largeaud, Brule late 90's, Mouillet 2000's, WRI 2014***

# *Effect of additives on Asphalt Mechanical properties*

**Crystalline additive dependency on thermal history by Differential Scanning Calorimetry – valid for PE, EVA, EBA, FT Paraffin, amid wax…**

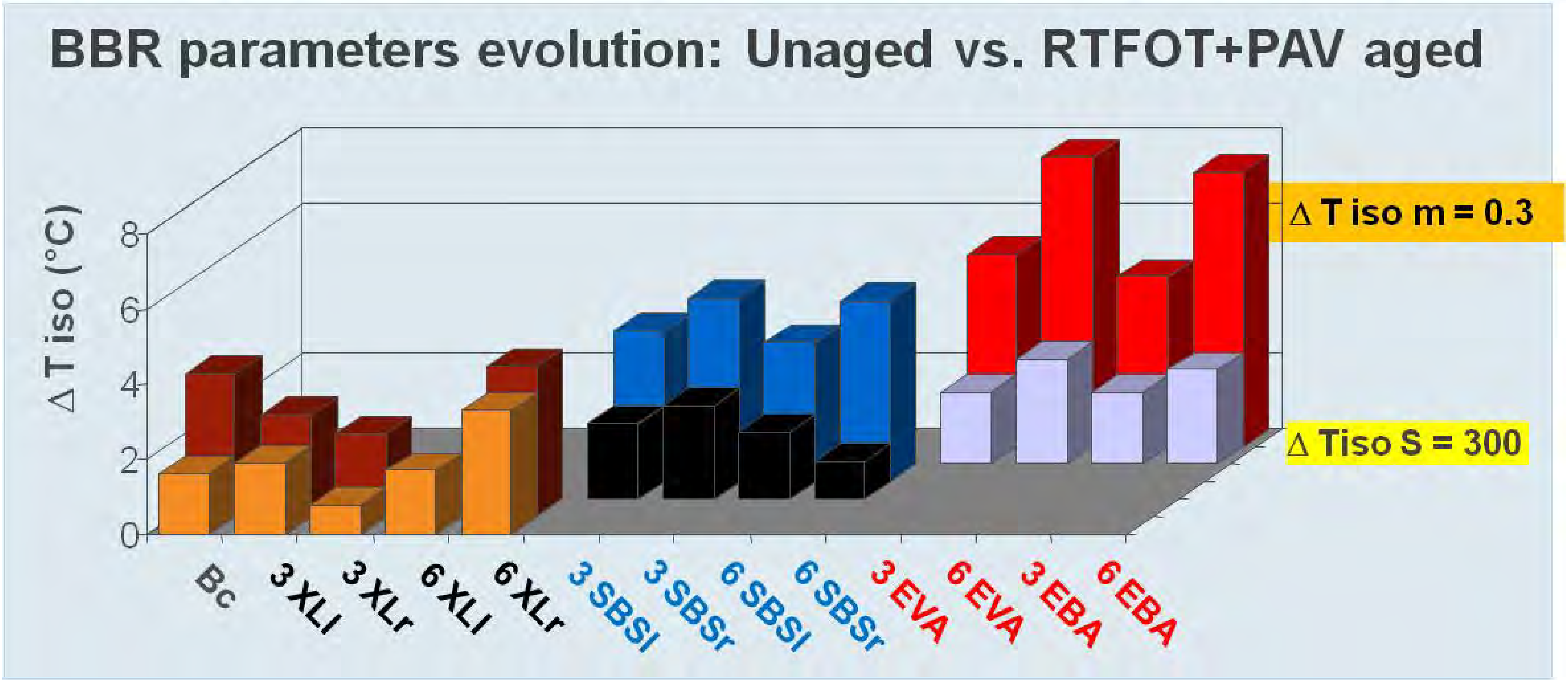


# Effect of additives on Asphalt Mechanical properties




- **Repeated creep recovery test** **for EVA PMA: softening effect**
  - **Modulus loss with time and T due to melting of PE crystalline fraction**
  - **No change in elastic recovery - ER very small for plastomers PMA**
- ***Works by Le Hir, Binard, Anderson, TRB 2001, E&E 2004***

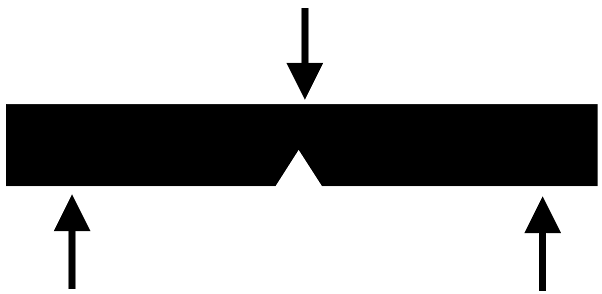
# Effect of additives on Asphalt Mechanical properties




- **PMA's low temp properties (BBR) greatly affected by aging**
  - **M-value more "severe" indicator of binder aging**
  - **EVA PMA more affected than SBS, especially crosslinked which seem to resist oxidation better than the base**
  - **M-value relates to field cracking (EPFL – LAVOC study in CH)**

# Effect of additives on Asphalt Mechanical properties

## Mode-I Fracture Test

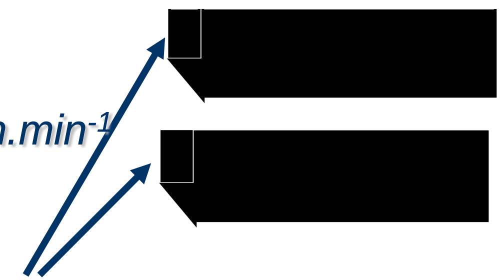


*Environmental chamber at -20°C*

*Test*

*Speed = 0.6 mm.min$^{-1}$*

***T = -20°C***



*Rupture surfaces observed by ESEM / CLSM*

- **Fracture mechanics to assess low temperature fracture properties**
  - **$K_{IC}$ = failure load × f (span, crack length, sample dimensions)**
- **Observation by ESEM/CLSM – cold transfer**

- *Works by Hesp (CA), Lapalu et al (FR) - 2000*

*Neat asphalt*

*($K_{IC}$ = 48 kPa.m$^{1/2}$)*

- No topographic contrast
- Brittle rupture ⇨ low $K_{IC}$

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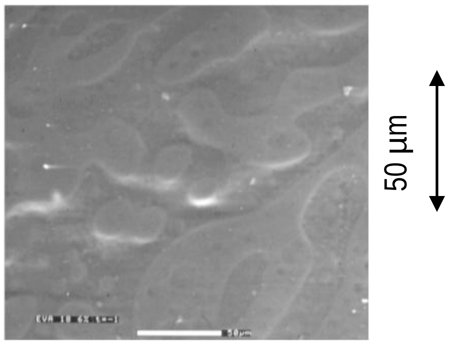
# *Effect of additives on Asphalt Mechanical properties*

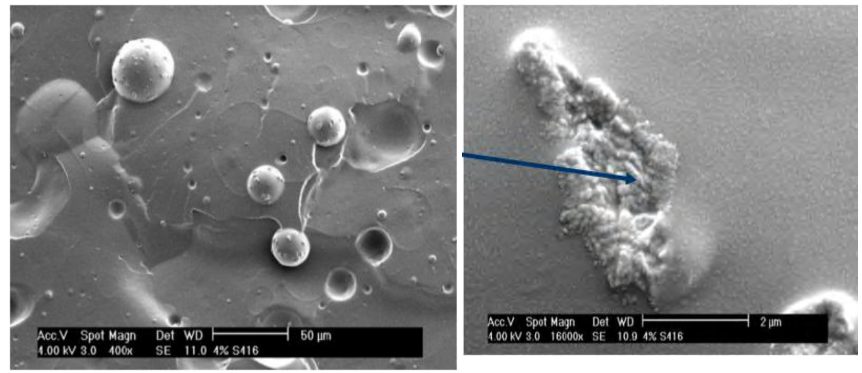
*6% EVA-28 blend* *ESEM obs.*

*($K_{IC}$ = 74 kPa.m$^{1/2}$)* *at -5°C*




*Physical blend 4% SBS** *CLSM obs.*

*($K_{IC}$ = 107 kPa.m$^{1/2}$)* *at -165°C*




- Polymer glassy at test temperature
- Polymer-rich particles pulled-out with no deformation
- Fracture mechanism governed by the (poor) adhesion between phases
- ⇨ low $K_{IC}$

- Particle pull-out (crack deflection)
- Plastic deformation of SBS nodules
- SBS in rubbery state ⇨ High $K_{IC}$

*4% Crosslinked SBS*

*($K_{IC}$ = 113 kPa.m$^{1/2}$)*


- ***Works by Lapalu et al (FR) - 2000***

# Outline

- **Background - Context**
- **Chemical-physical and structural properties of asphalt**
  - **Impact on asphalt mechanical properties**
- **Asphalt modification**
  - **Impact on structure and mechanical properties**
- **Summary**
- **Perspectives**

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# Summary

- **Asphalt binder physical properties are intimately related to their chemical composition and structure, with a very high dependency on the thermal history**
  - Associations – interactions - Wax precipitation - dissolution
  - Phases – multiple – exchanges – molecule transfer
  - Glass transition
  - Physical and chemical oxidative aging / hardening
- **Comparing binders in the same physical state to measure intrinsic properties is essential**
- **Asphalt modification incl. RAP drastically change structure, rheology, event the effect of aging**
  - Compatibility / Polymer swelling
  - Chemical reactions like binder oxidation, PMA crosslinking
- **"Real life" is impacted by those features**
  - **Binder formulation and testing**
  - **Performance in the field**

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# Perspectives

- ***Application of relevant material/chemical analyses to asphalt can make a change in understanding and designing asphalt materials***
- ***Some already did***
  - ***Rheology-Mechanics: DSR, DMA, FT***
  - ***Thermal analysis: DSC***
  - ***Chromatography: TLC, HPLC, SEC-GPC***
  - ***Microscopy techniques: IR, AFM, ESEM***
  - ***Spectroscopy: IR***
- ***New characterization techniques will have impact on product development and vice versa: PMA, WMA…***
  - ***Method coupling will become more affordable and usable***

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# Thank you !


## Questions?

jplanche@uwyo.edu