Rheological, Chemical, Mechanical Properties of Re-refined Engine Oil Bottoms (REOB) Modified Binder

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The Story!

- Background
- Objectives/Scope
- Methodology
  - Binder Experiment
    - Gel permeation Chromatography (GPC)
    - X-ray fluorescence spectroscopy (XRF)
    - Fourier transform infrared (FTIR) spectroscopy
    - Atomic Force Microscopy (AFM)
  - Mixture Experiment
    - Semi-circular bend (SCB) test
- Results
- Summary and Conclusion

Use of REOB: Concern

- **Inconsistent and conflicting conclusions**

Detrimental	Not Detrimental
Poor field performance	Equal field performance
Adverse effect on binder properties	Equal or improved binder and mixture properties

- **Limitations with current Superpave testing/specification**
  - **Need for additional aging/testing protocols**
  - **Sometimes requires other analysis approaches (e.g., GPC, FTIR, XRF etc.)**

Objectives

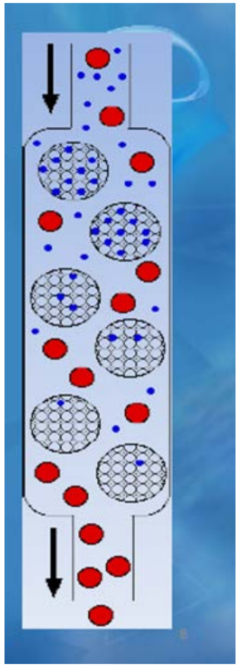
- **Evaluate rheological, chemical, micro-mechanical and mechanical properties of aged binders containing**
- **Correlate binder properties to mixture intermediate temperature cracking performance**

Scope

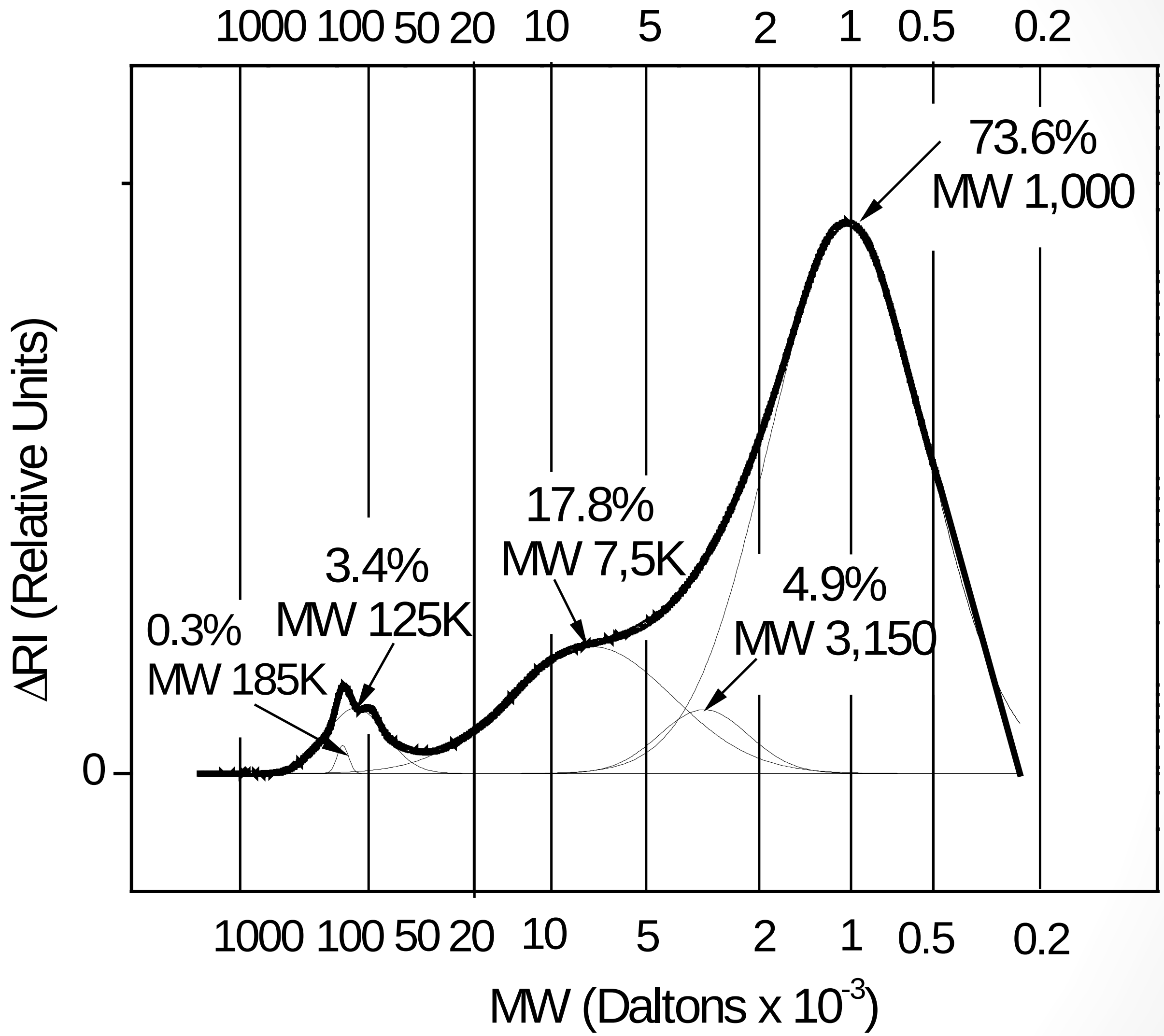
- 12.5 NMAS asphalt mixture
- Four Binders
  - PG 70-22
  - 0-, 5-, 10-, and 15% REOB
- Binder Experiment
    - Rheological tests
    - Micro-mechanical properties
      - atomic force microscopy
    - chemical properties
      - GPC, FTIR, and XRF
- Mixture Experiment
  - SCB at intermediate temperature
  - ASTM D 8044

Binder Experiment • Gel Permeation Chromatography (GPC)

PMAC



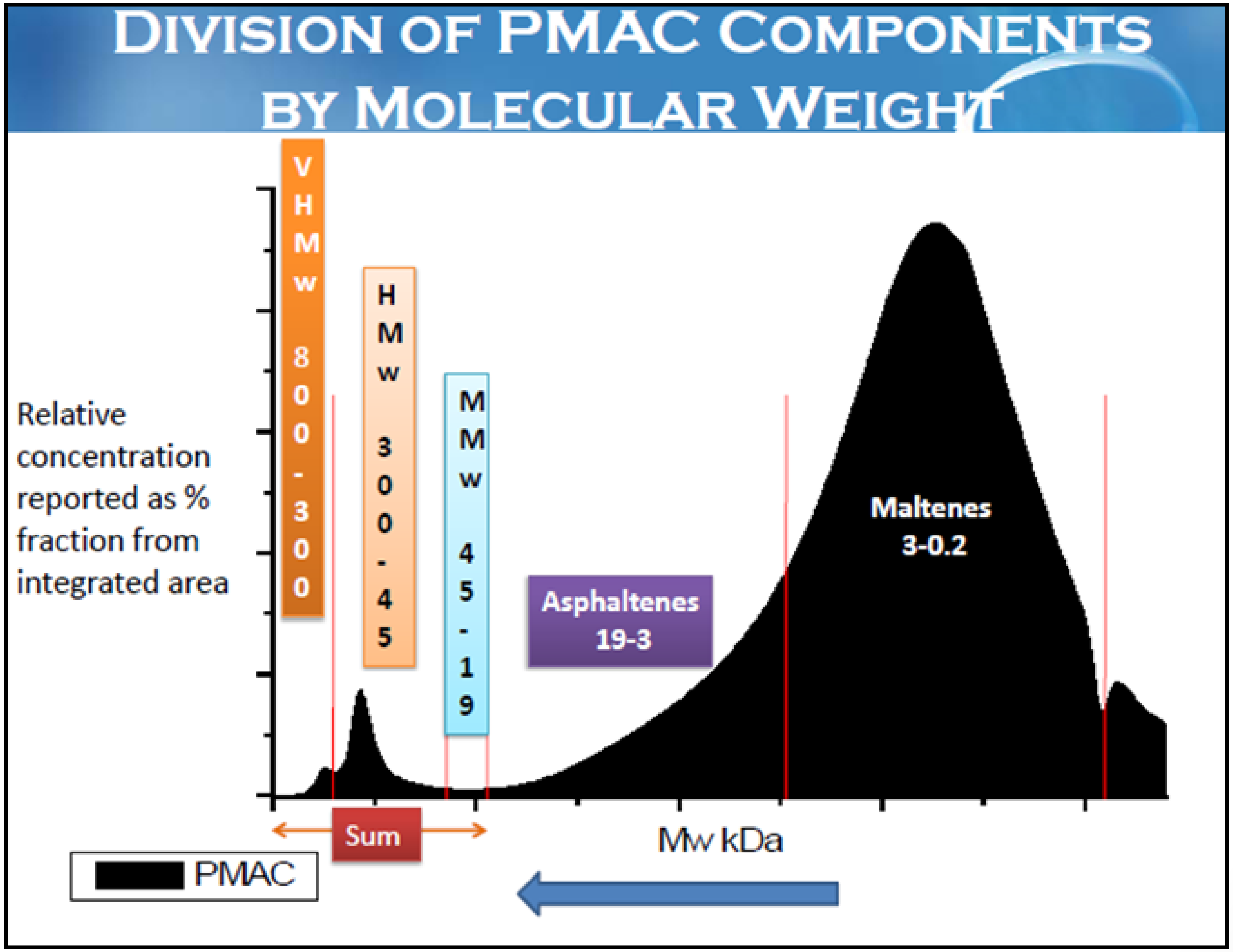
GPC
Analysis Principle



Increasing Elution Volume ⟶

Binder Experiment

- Quantification of GPC curves by integration



Binder Experiment

- X-ray Fluorescence Spectroscopy (XRF)

- To identify elemental composition of binder samples generally found in REOB
    - Calcium (Ca)
    - zinc (Zn)
    - molybdenum (Mo)
    - copper (Cu)

EDXRF PANalytical Epsilon 1Spectrometer

Binder Experiment

- Fourier Transform Infrared (FTIR) Spectroscopy

- To identify chemical functional groups
- Carbonyl Index (CI): presence of REOB and aging change

Bruker Alpha FT–IR spectrometer)

Binder Experiment

- Atomic Force Microscopy (AFM)

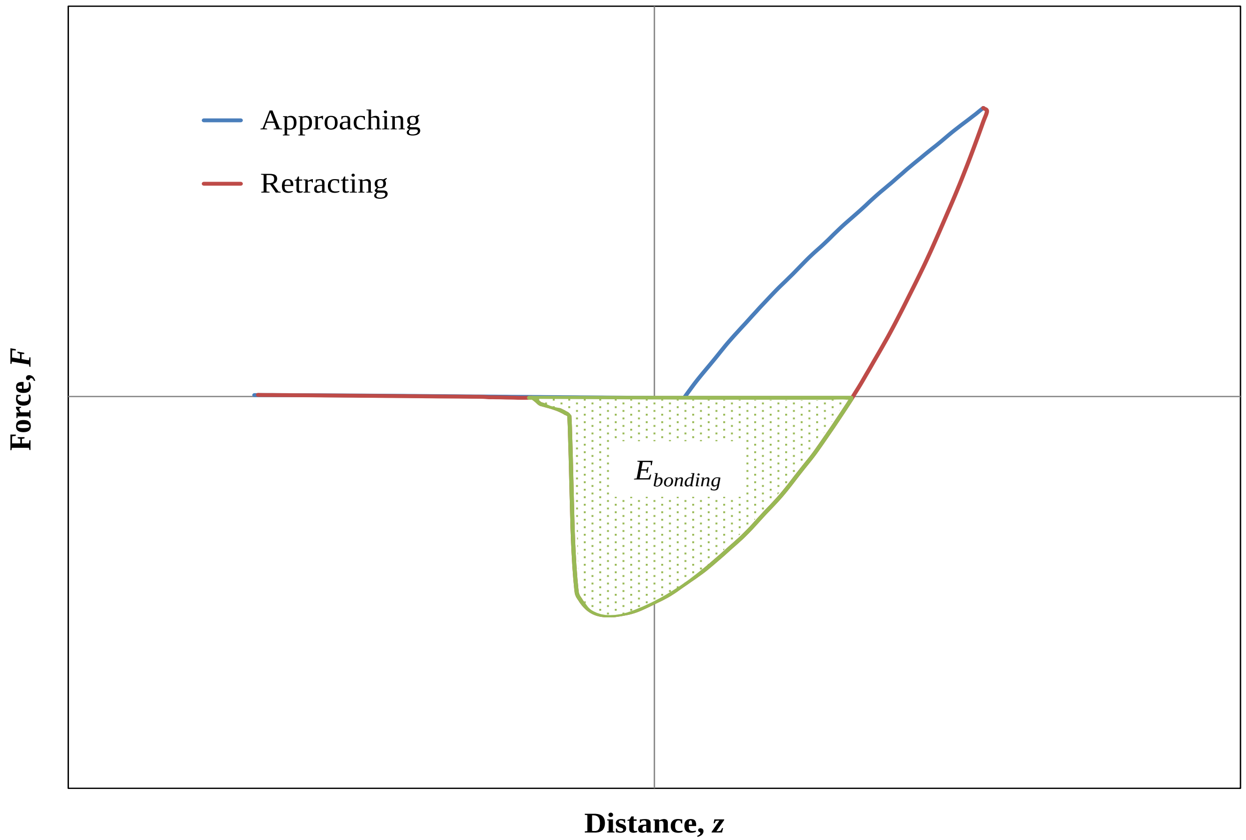
Reduced Elastic modulus

$$E_{reduced} = \frac{\pi}{2} \frac{F}{\delta^2 \tan(\alpha)}$$

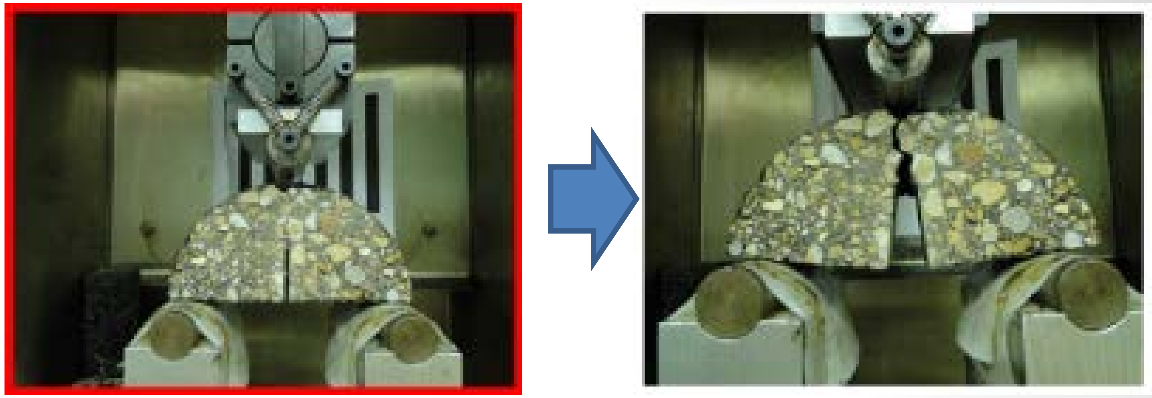
Total energy needed to separate AFM tip from a sample

$$E_{bonding} = \int_{z_o}^{z_1} F dz \approx \frac{\Delta z}{2N} \sum_{i=1}^{N} [F(z_{i+1}) + F(z_i)]$$

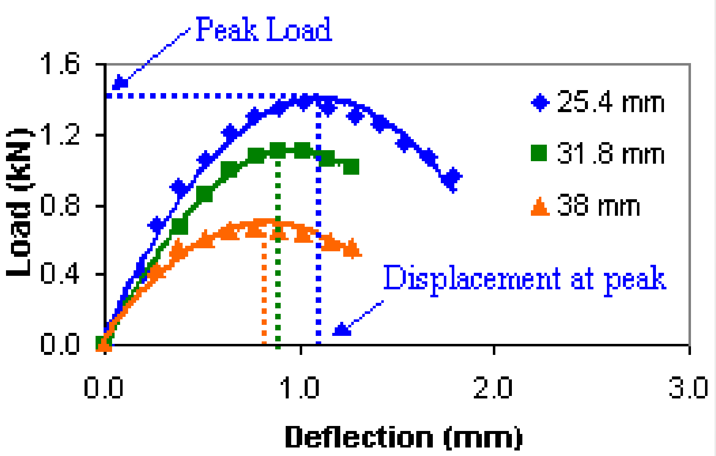
F: measured force
δ: indentation depth
α: half-opening angle of the AFM tip
d: cantilever deflection
z: piezo-driver displacement

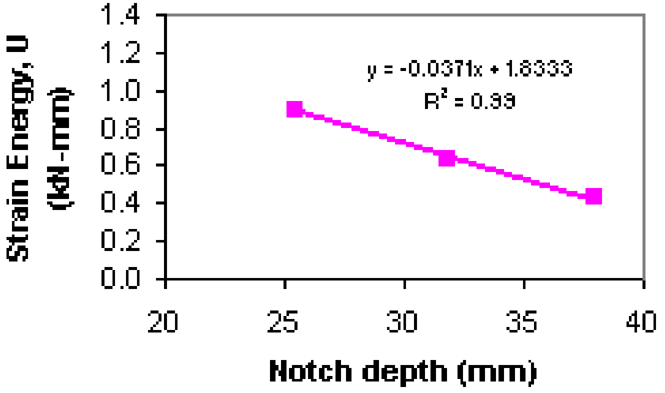


Mixture Experiment



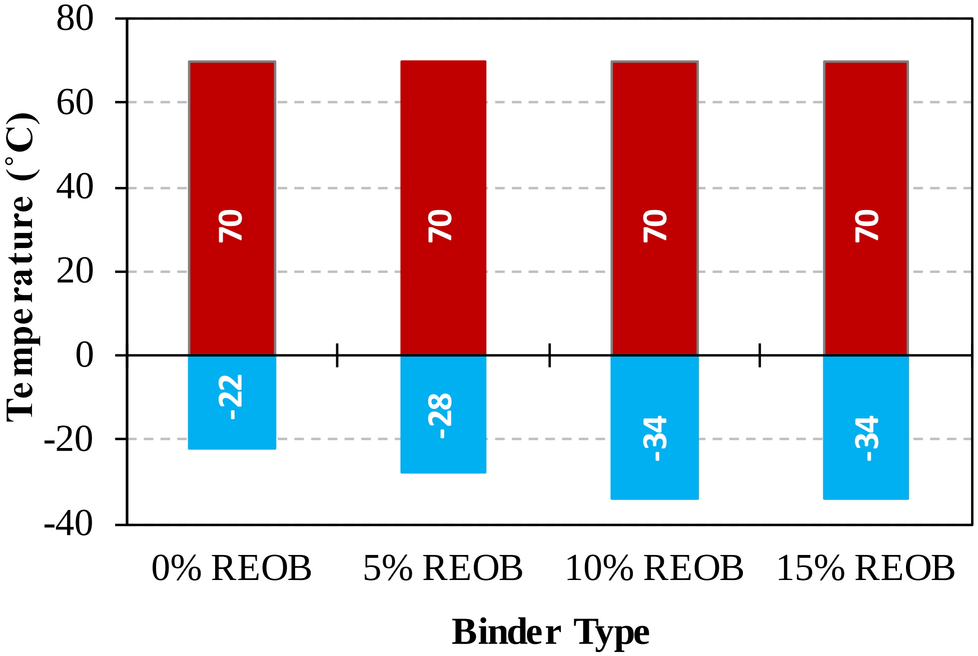
- Semi-Circular Bend Test
- ASTM D8044
- Temperature: 25°C
- Half-circular Specimen
  - Laboratory prepared
  - 150mm diameter X 57mm thickness
  - simply-supported and loaded at mid-point
- Notch controls path of crack propagation
  - 25.4-, 31.8-, and 38.0-mm
- Aging: 5 days, 85°C
- Loading type
  - Monotonic
  - 0.5 mm/min
  - To failure
- Record Load and Vertical Deformation
- Compute Critical Strain Energy: J_c

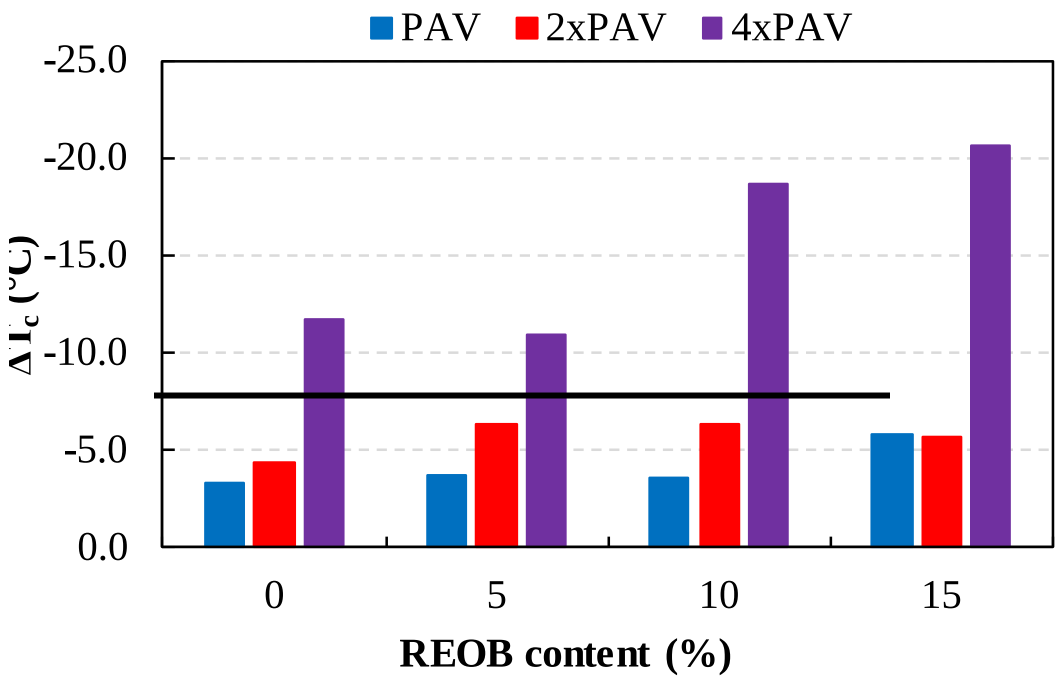




Results

- PG test results

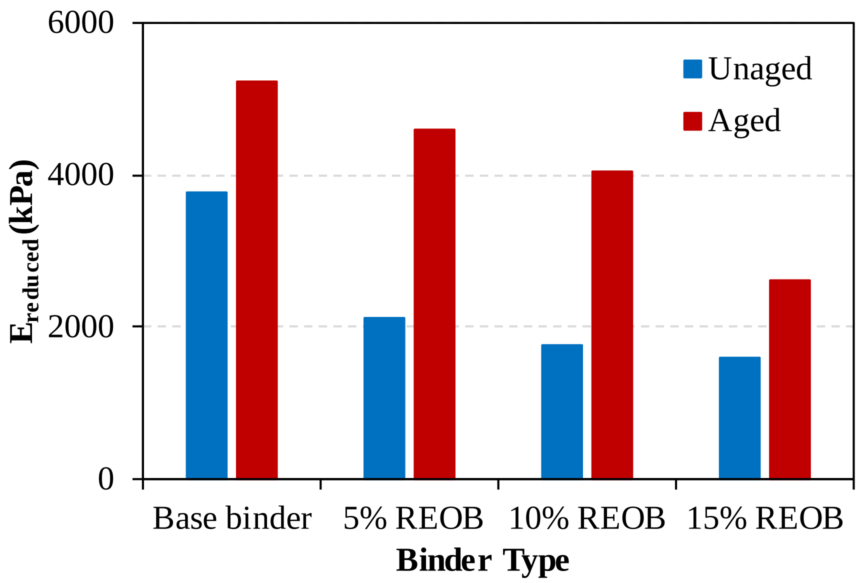




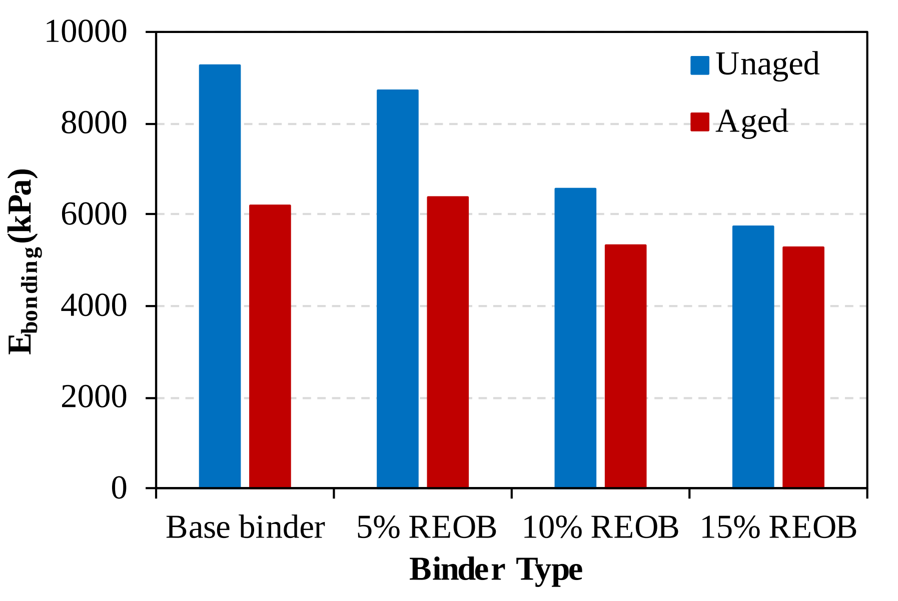
Results

- Atomic Force Microscopy

Reduced Elastic modulus

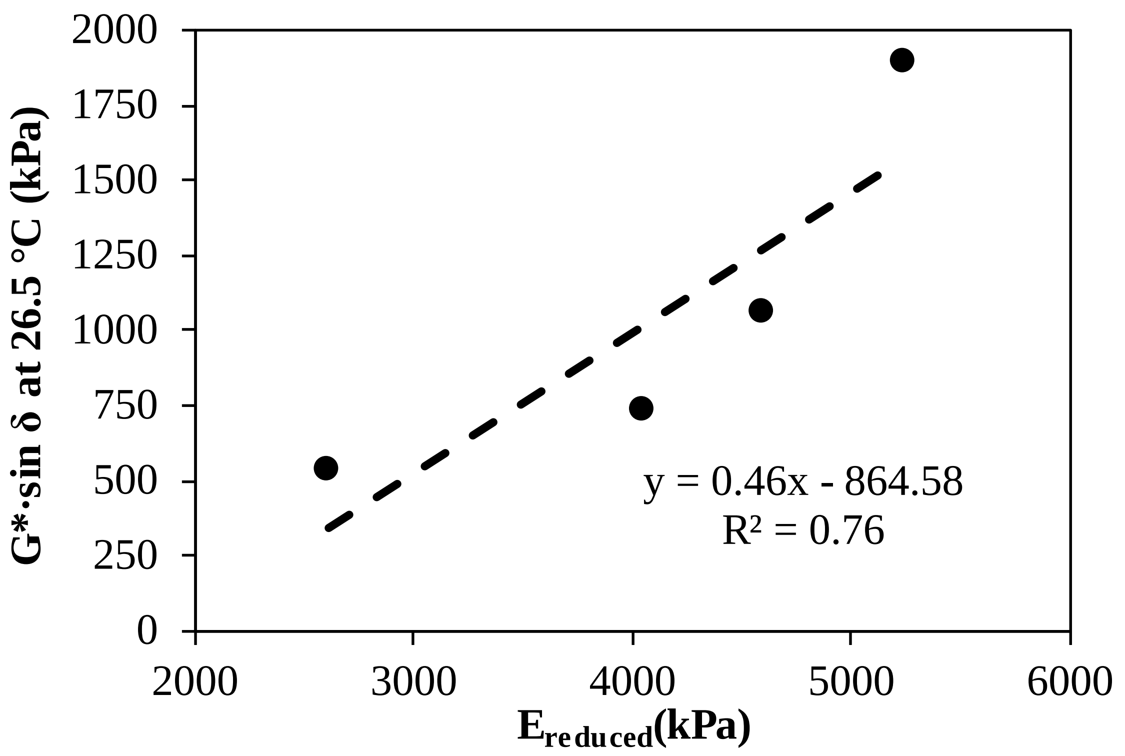


Total energy needed to separate AFM tip from a sample



Results -- AFM

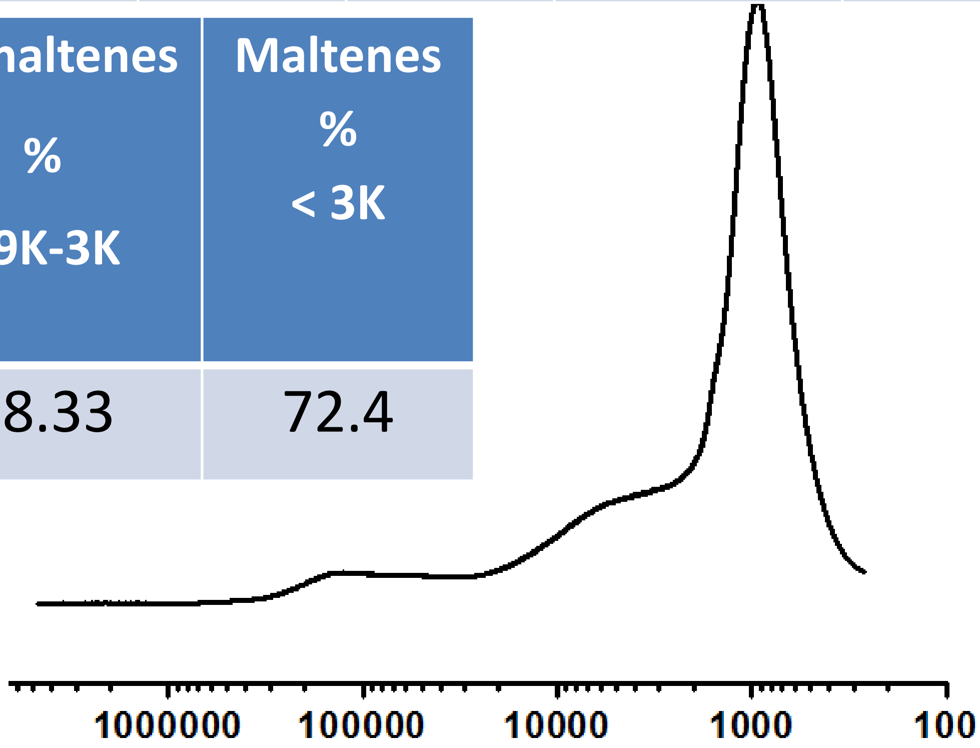
- Relationship between $E_{reduced}$ and $G^*sin\delta$



SARA data of original and aged REOB

	Asphaltenes %	Resins %	Cyclic %	Saturates %	Total %
Original REOB sample	15	34.7	0.8	63	100
RTFO	3.7	21.3	0.9	74.1	100
PAV	2.1	25.5	1.2	71.2	100

Sample Name	1000-300K (%)	300-45K (%)	45-19K (%)	Asphaltenes % 19K-3K	Maltenes % < 3K
REOB	0.36	5.54	3.37	18.33	72.4



Determination of maltenes, asphaltenes and polymer content based on the molecular weight regions

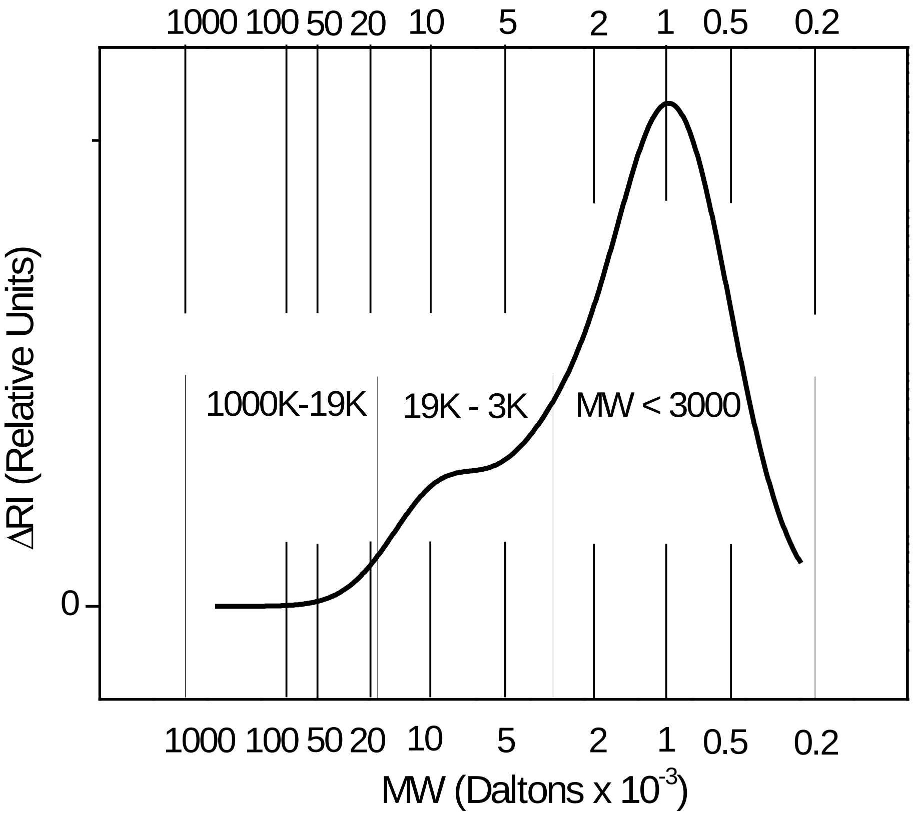
Compositional analysis

- Gel Permeation Chromatography

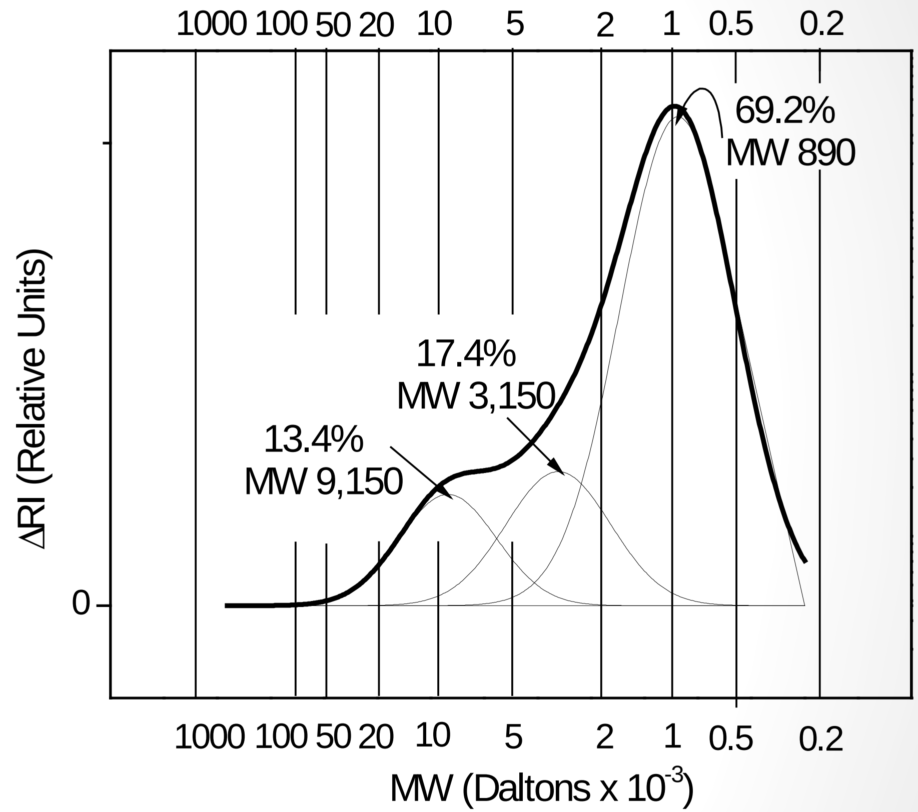
Sample	HMW* Polymer 300-45K, %	Associated Asphaltenes 45-19K, %	Asphaltenes 19-3K, %	Maltenes < 3K, %
REOB	5.9	3.37	18.33	72.4
Unaged base binder	3.96	1.63	21.33	73.08
Aged base binder	3.16	3.76	24.87	68.27
Aged 5% REOB modified binder	2.8	3.59	23.66	69.95
Aged 10% REOB modified binder	4.57	3.95	24.69	66.79
Aged 15% REOB modified binder	5.1	3.71	23.96	67.23

Results – Compositional analysis

- Gel Permeation Chromatography



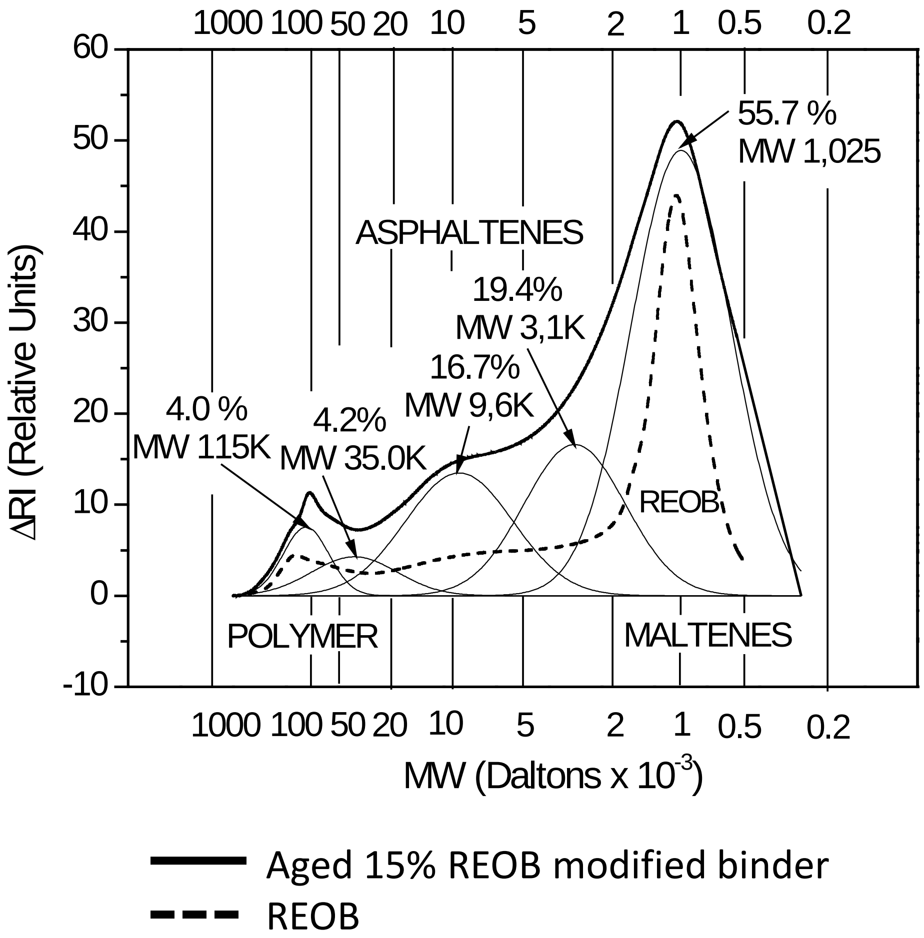
Determination of maltenes and asphaltenes content of 64-CO binder based on the molecular weight regions

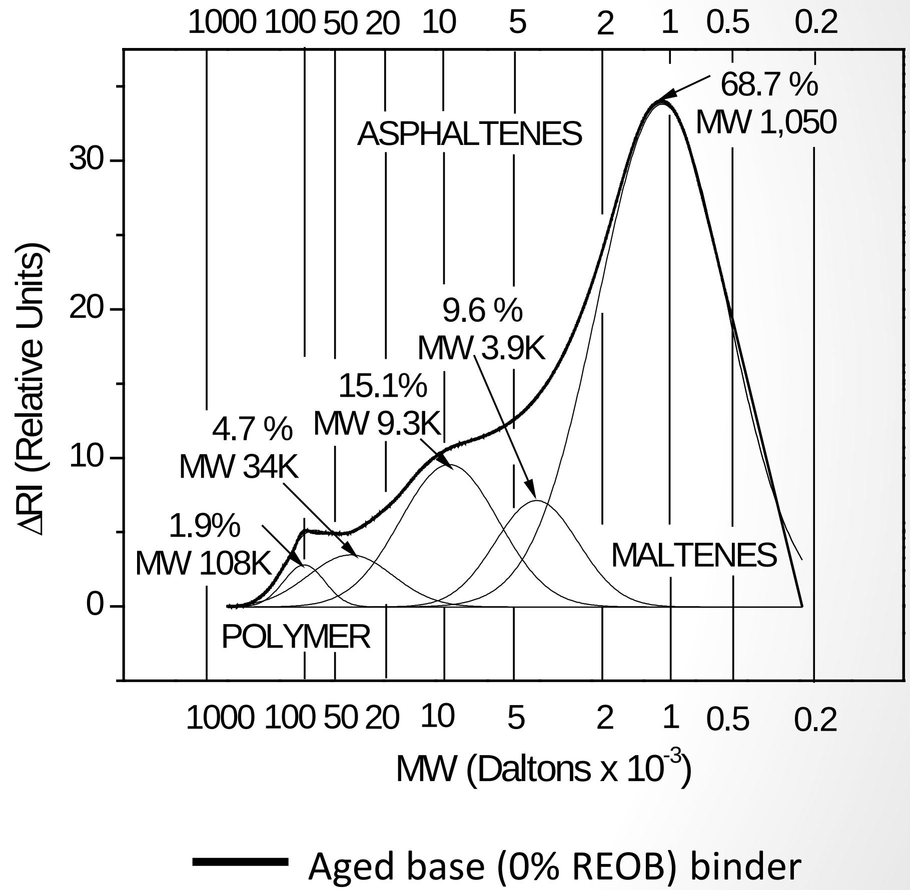


Determination of maltenes and asphaltenes content of 64-CO binder by deconvolution of the GPC curve

Results -- Compositional analysis

- Gel Permeation Chromatography





Compositional analysis

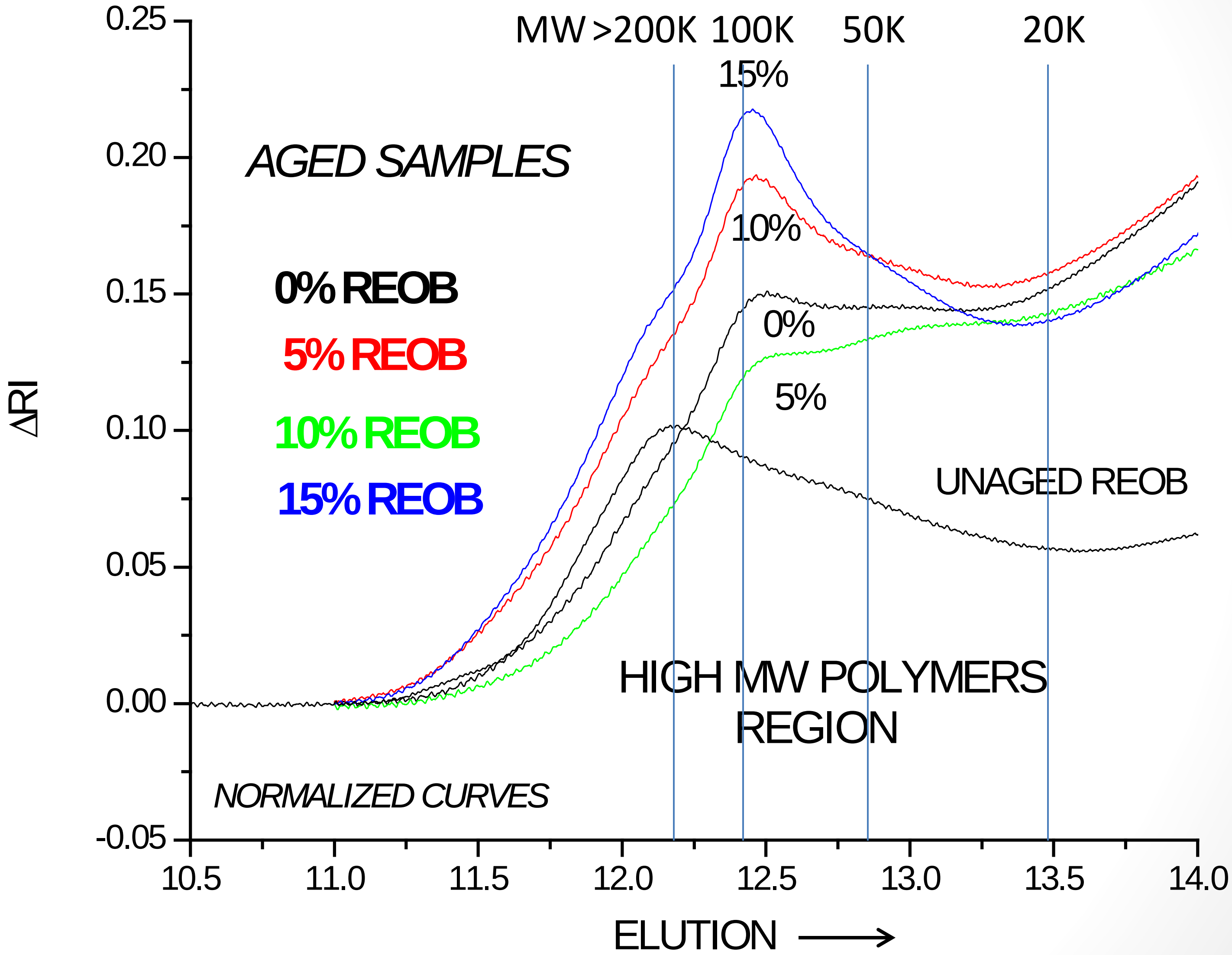
- Gel Permeation Chromatography

 - Distribution of molecular species showing peak molecular weights

Sample	HMW* Species %/MW	Associated Asphaltene Species %/MW	Asphaltenes 2 %/MW	Asphaltenes 1 %/MW	Maltenes %/MW
Aged base binder	1.9 /109K	4.7 /34K	15.1 /9.3K	9.6 /3.9K	68.8 /1,050
Aged 5% REOB modified binder	1.5 /90.5K	4.4 /39K	17.8 /8.5K	7.6 /3.5K	68.7 /1,050
Aged 10% REOB modified binder	4.1 /110K	3.7 /32K	14.6 /10.8K	14.8 /3.8K	62.8 /1,050
Aged 15% REOB modified binder	4.0 /115K	4.2 /35K	16.7 /9.6K	19.4 /3.9K	55.7 /1,025

Compositional analysis

- Gel Permeation Chromatography



Compositional analysis

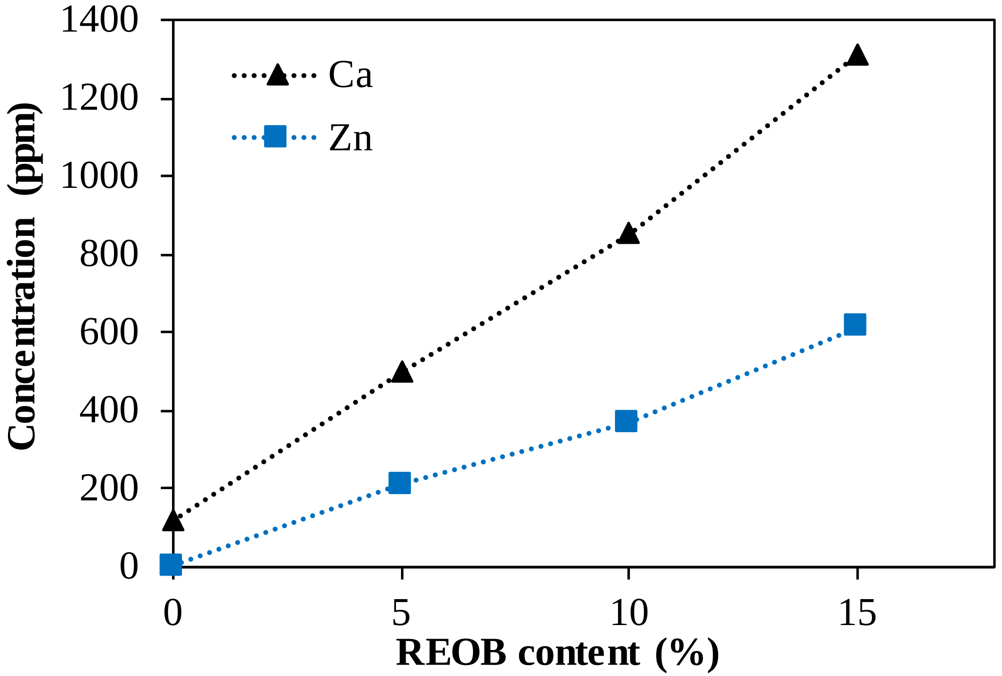
- Gel Permeation Chromatography

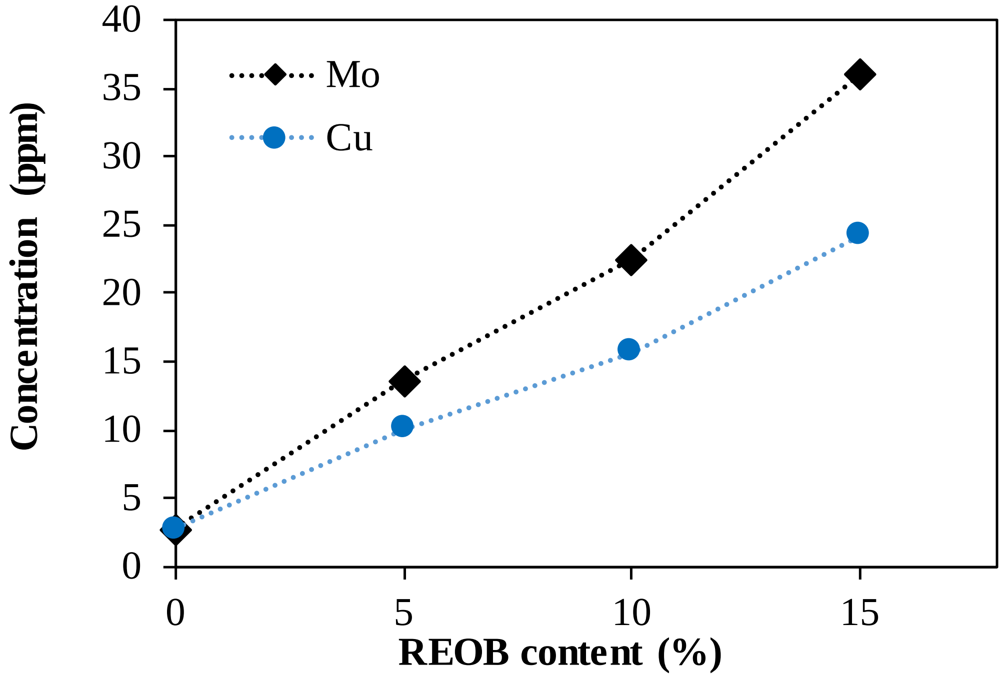
 - Comparison of theoretical data calculated according to percentage of REOB content with experimental results

Sample	>45K, %	Asphaltenes, %	Maltenes, %
5% REOB modified binder			
Calculated	3.3	28.22	68.48
Integrated	2.8	27.25	69.95
De-convoluted	1.5/90.5K	29.75	68.75
10% REOB modified binder			
Calculated	3.4	27.89	68.68
Integrated	4.6	28.64	66.79
De-convoluted	4.1/110K	33.10	62.80
15% REOB modified binder			
Calculated	3.6	27.51	68.89
Integrated	5.1	27.67	67.33
De-convoluted	4.0/115K	40.30	55.70

Compositional analysis

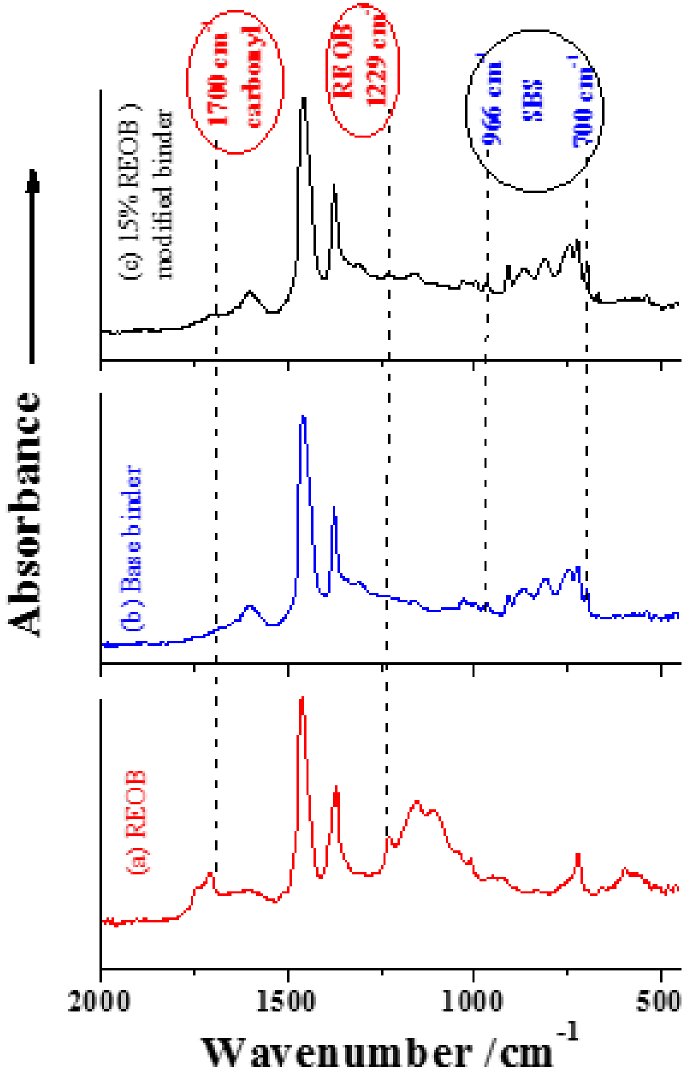
- X-ray fluorescence spectroscopy

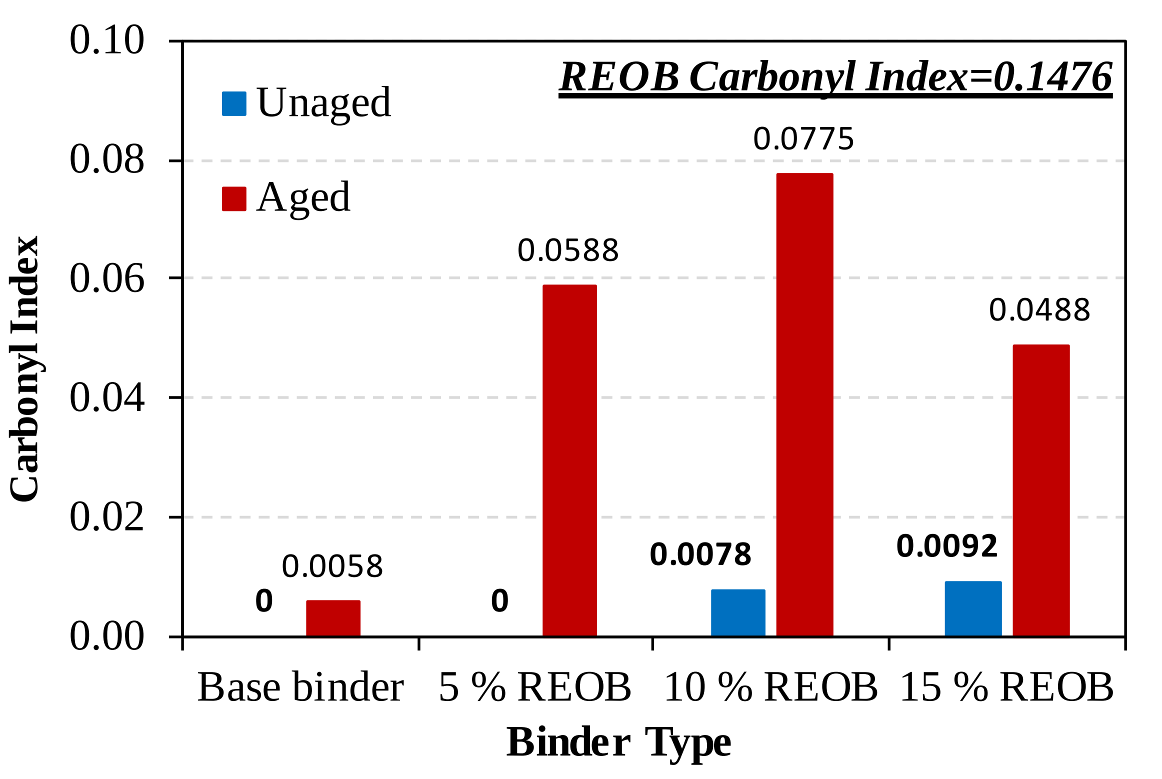




Compositional analysis

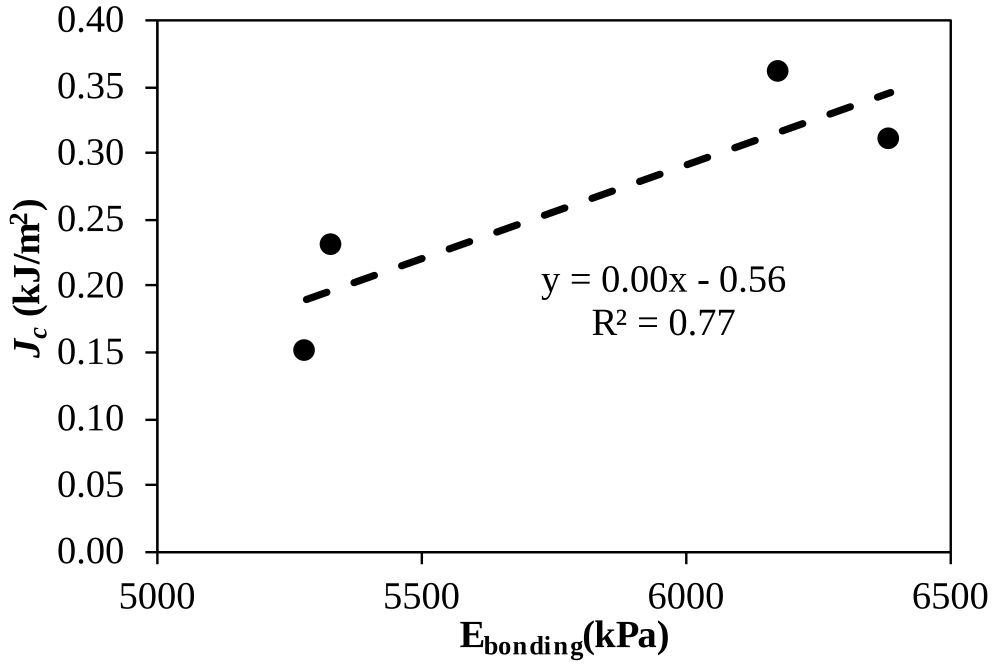
- Fourier transform infrared spectroscopy

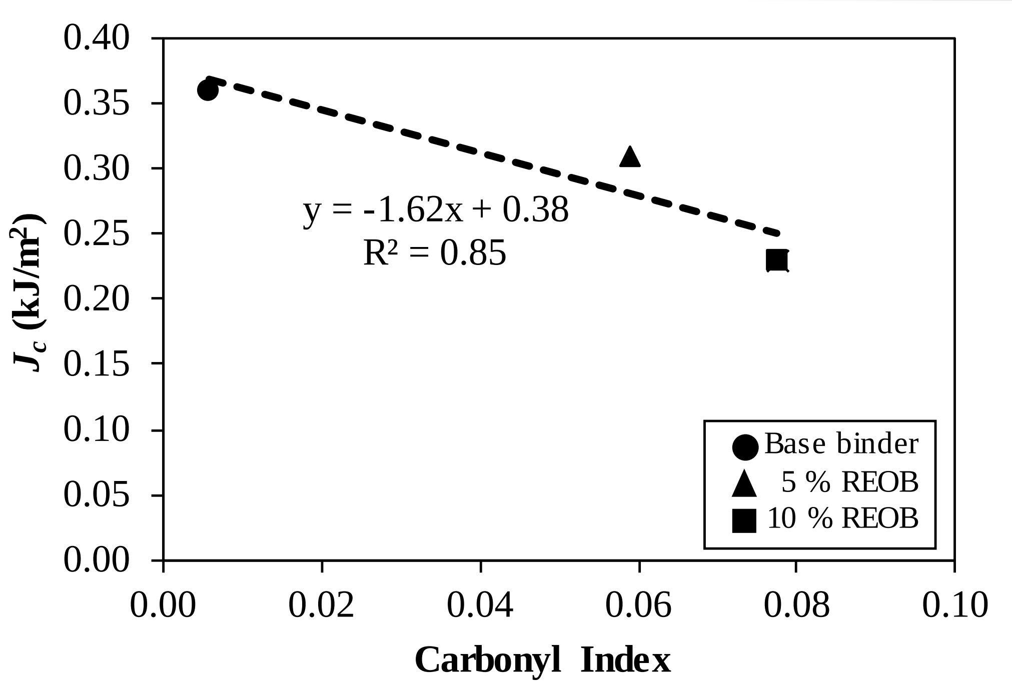




Results

- Relationship between mixture cracking performance and binder properties





Summary and Conclusion

- Evaluated rheological, chemical, micro-mechanical and macro-mechanical properties of aged binders containing
  - REOB contents (0-, 5-, 10-, and 15 %)
- In general, binders containing 5% REOB did not adversely affect binder and mixture performance
- ΔTc increased (-) with an increase in REOB content
  - More pronounced for 2 PAV and 4 PAV aged binders
- Addition of REOB softened the binder
  - low PG decreased with increased REOB content.
- Microscale AFM test results exhibited a decrease in stiffness and bonding energy with an increase in REOB content
- XRF and FTIR spectroscopy successfully identified REOB in binders

Summary and Conclusion

- Residual polymer content in REOB influenced the distribution of maltenes and asphaltenes when REOB concentrations were greater than 5%

- Good correlation was observed between microscale AFM stiffness and PG parameter, G*sinδ as well as between AFM bonding energy of binders and SCB J_c mixture cracking performance

- Good correlation between FTIR CI of binders and SCB J_c mixture cracking performance was found up to REOB content 10%


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Photo: Jim Zietz, Office of Public Affairs

THANK YOU

Sample Name	Total High MW %	Asphaltenes %	Maltenes %
REOB	**16.00**	**20.97**	**63.03**
REOB-RTFO	**16.66**	**21.7**	**61.64**
REOB-PAV	**18.84**	**21.61**	**59.55**