Louisiana Perspective on Adhesion and Cohesion Determination

Presenter:

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PAVEMENT PERFORMANCE PREDICTION, P_3 SYMPOSIUM
22 June 2005, Cheyenne, Wyoming

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Adhesion

Cohesive Forces + Adhesive Forces

Cohesive Forces

- Responsible for binder failure
- Dependent upon temperature
- Become evident at lower temperatures, particularly around Tg
- Reduced by phase separation (e.g., paraffin crystallization of asphalts, decreasing incompatibility of modifying polymers as temperature decreases, etc.)

Cohesive Forces

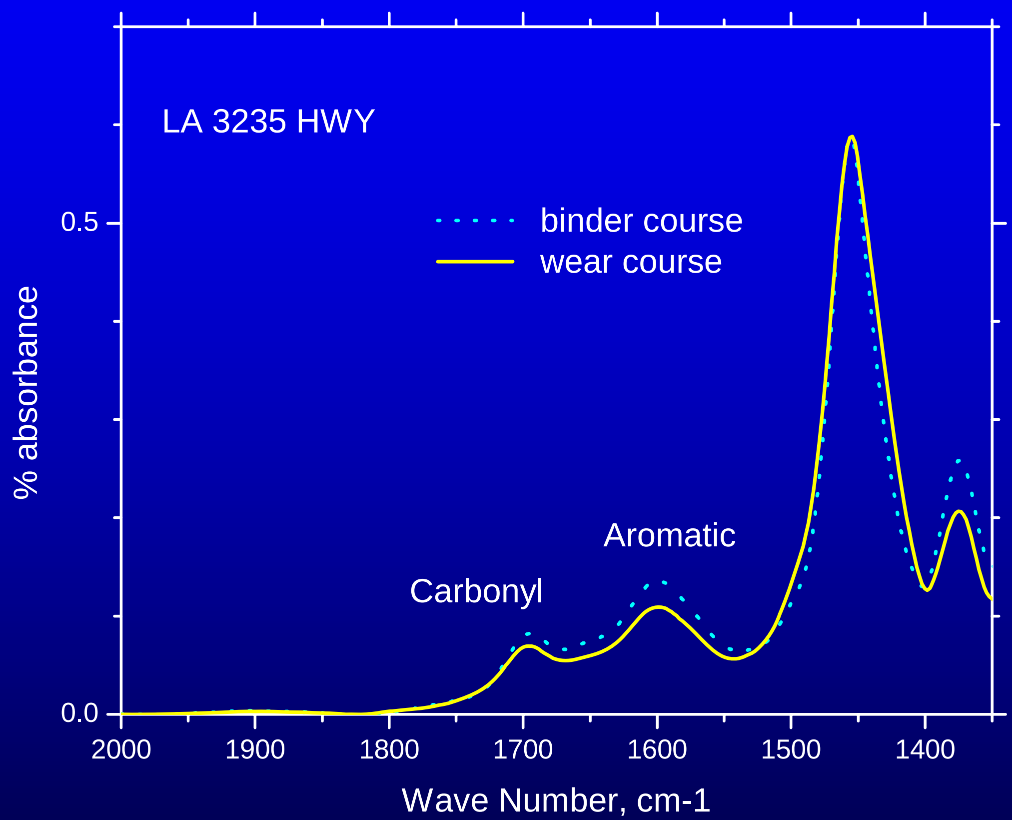
- Additives, such as polymers, increase the cohesiveness of asphalts
- Degradation of polymers by oxidation is prone to mechanical failure of the pavement

Cohesive Forces

- **Responsible for binder failure (cracking):**

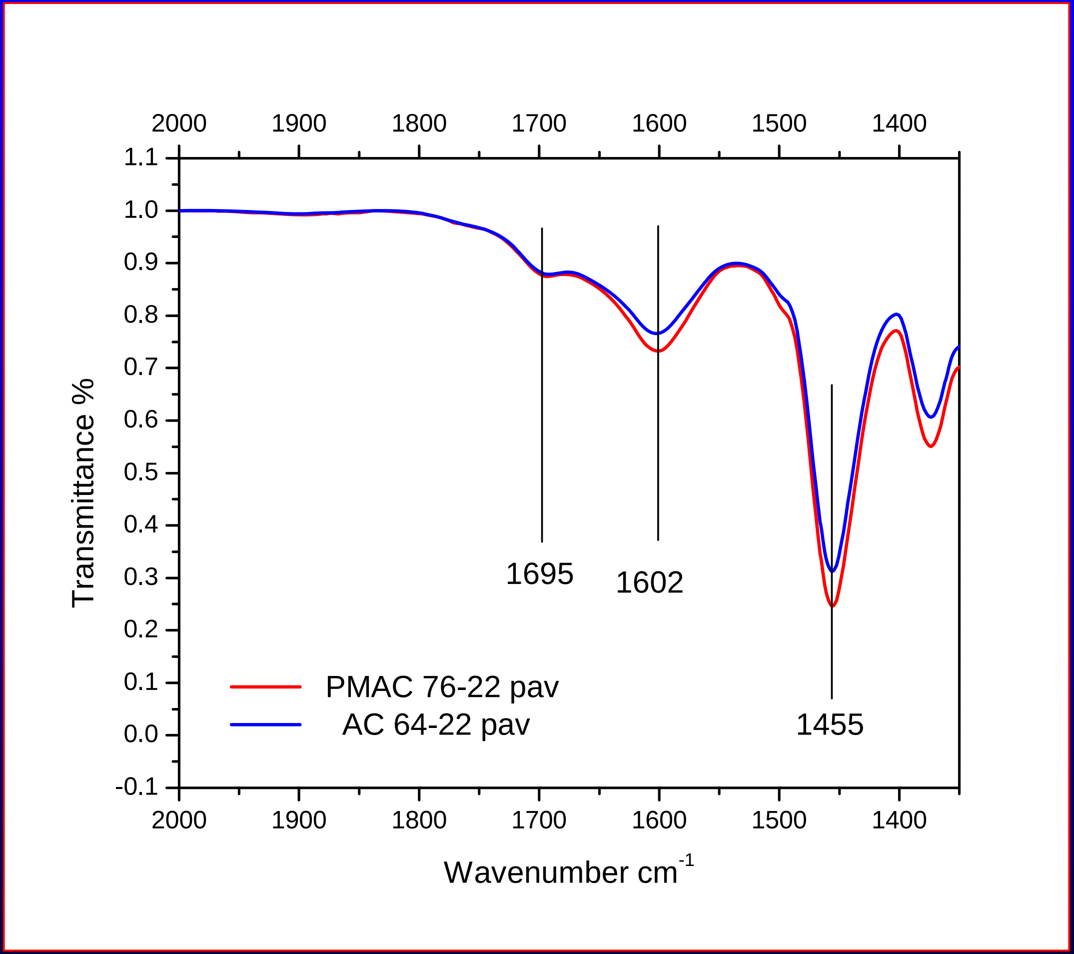
Case Analysis: Failure of LA 3234 HWY A 3 yrs old road

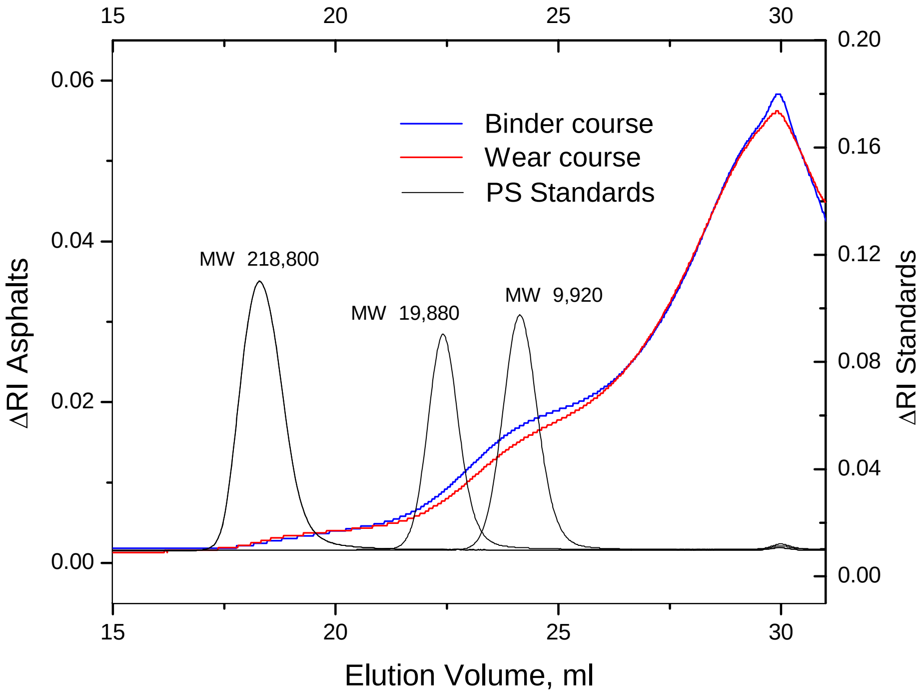
FTIR data



LA 3235 HWY
binder course
wear course
Aromatic
Carbonyl
0.5
0.0
% absorbance
2000
1900
1800
1700
1600
1500
1400
Wave Number, cm-1

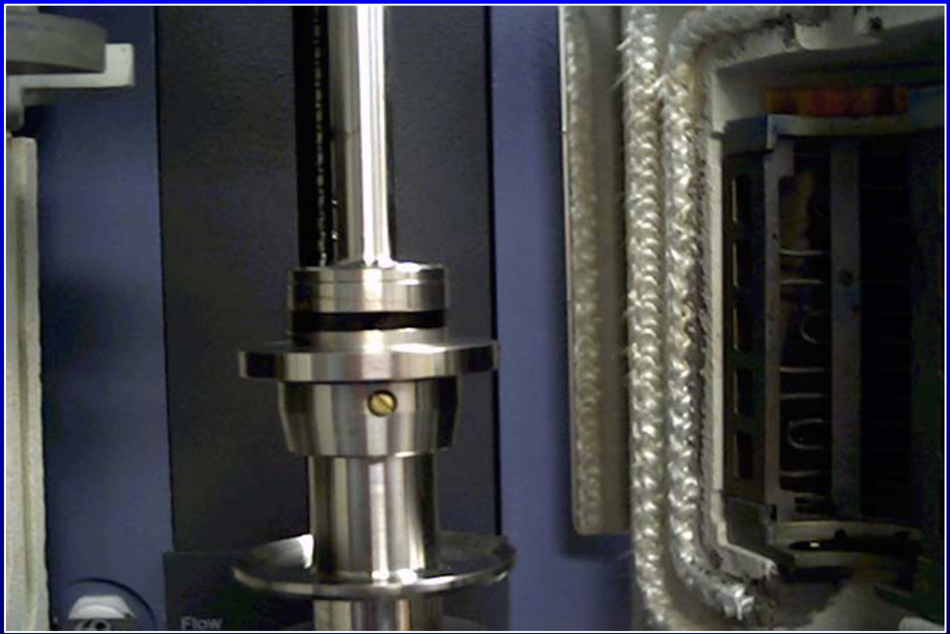
FTIR Spectra of a binder with and without 3% of SBS copolymer after PAV aging

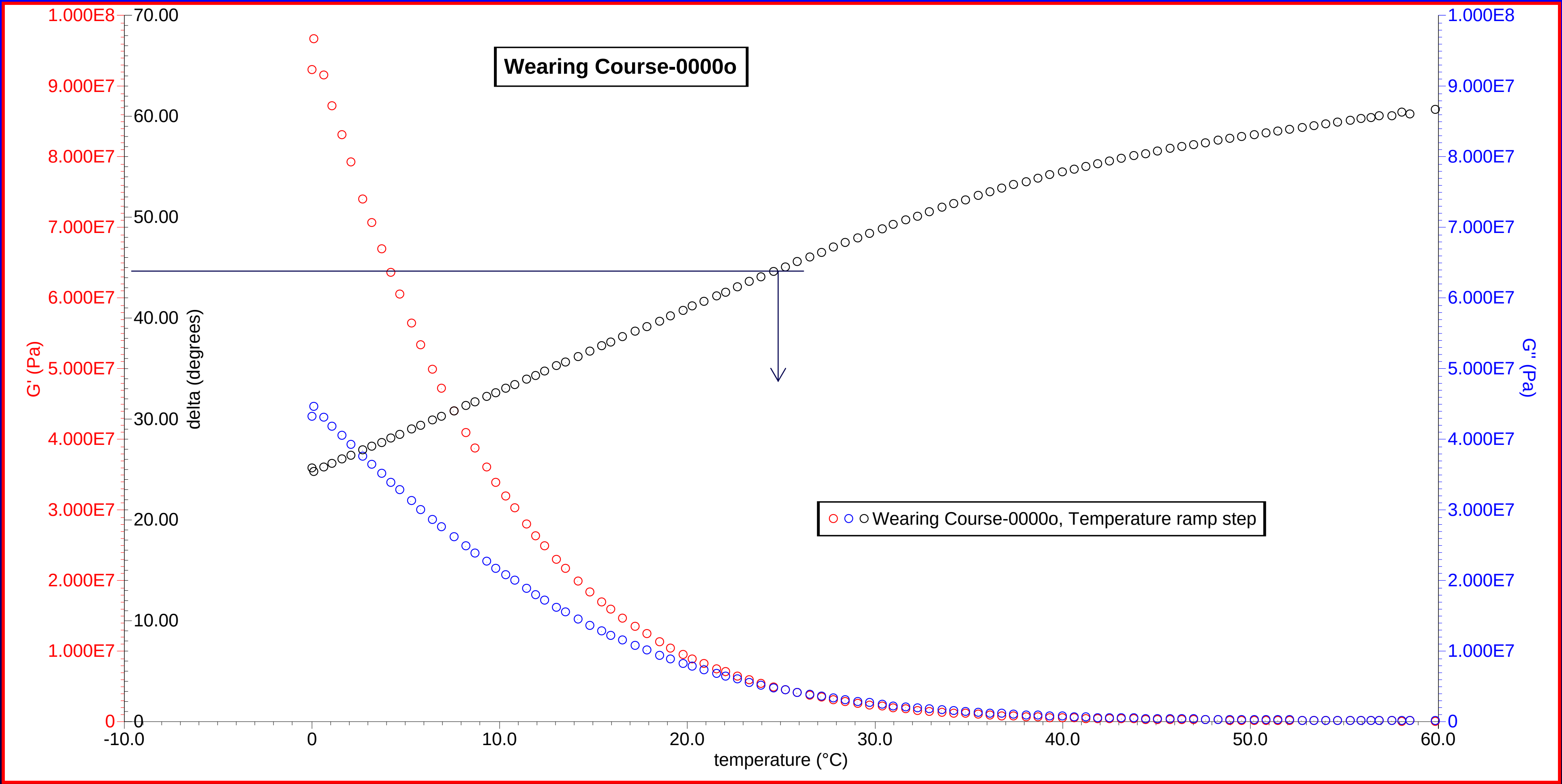




15
20
25
30
0.20
0.16
0.12
0.08
0.04
0.00
0.06
0.04
0.02
0.00
Binder course
Wear course
PS Standards
MW 218,800
MW 19,880
MW 9,920
ΔRI Asphalts
ΔRI Standards
Elution Volume, ml

DSR Measurements





Wearing Course-0000o
Wearing Course-0000o, Temperature ramp step
G' (Pa)
delta (degrees)
G'' (Pa)
temperature (°C)
1.000E8
9.000E7
8.000E7
7.000E7
6.000E7
5.000E7
4.000E7
3.000E7
2.000E7
1.000E7
0
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0
-10.0
0
10.0
20.0
30.0
40.0
50.0
60.0

DSR Data (10 rad/sec)

Asphalt	*Aging Time*	*T* (°C) @ G′=G″	*η** Pa.s
PMAC 76-22	Un-aged	9.5	
0.5 PAV Dry/Wet	Equiv. 3-4 yrs	23.8 / 20.3	
1.0 PAV Dry/Wet	Equiv. 7-8 yrs	30.6/22.1	
1.5 PAV Dry/Wet	Equiv >10 yrs	42/36	
I-55 Extract	3 yrs	21.0	
I-55 Extract	5 yrs	27.3	
I-55 Extract	7 yrs	29.4	
LA 3235 Wear	3yrs	25.2	6.2 E5
LA 3235 Binder	3yrs	26.4	6.8 E5

Differences

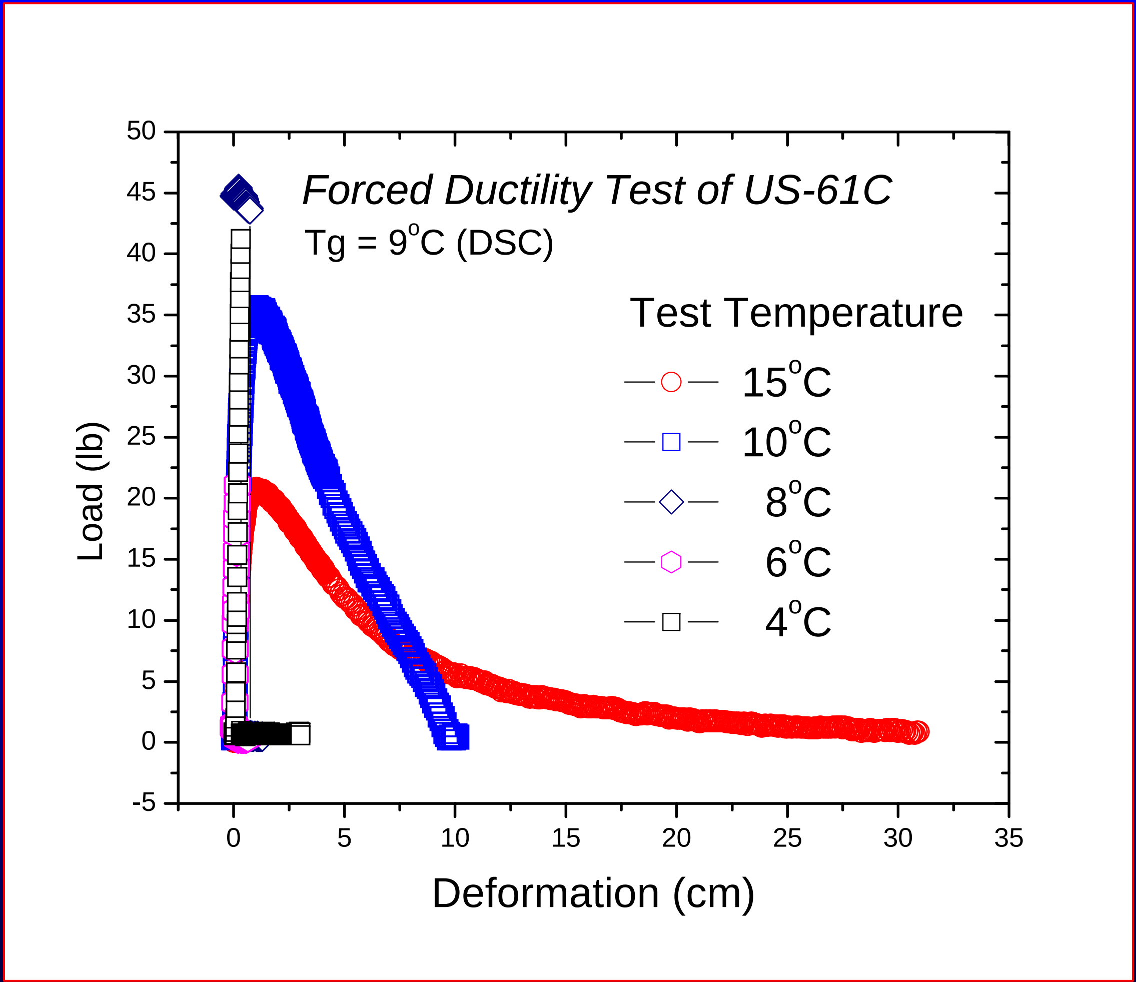
- Difference in oxidation rate for the same aging time (3 years). The binder course looks more like a 5 year old asphalt. Higher viscosity recorded.
- A higher concentration in asphaltene region both in FTIR and GPC traces support this observation.
- Why? 

Cohesive Forces

Indirectly determined by tension measurements:

- **Forced Ductility**
- **BBR**
- **Direct Tensile Test**

Forced Ductility Test



Adhesive Forces

Evident on road distress, e.g., stripping

Stripping

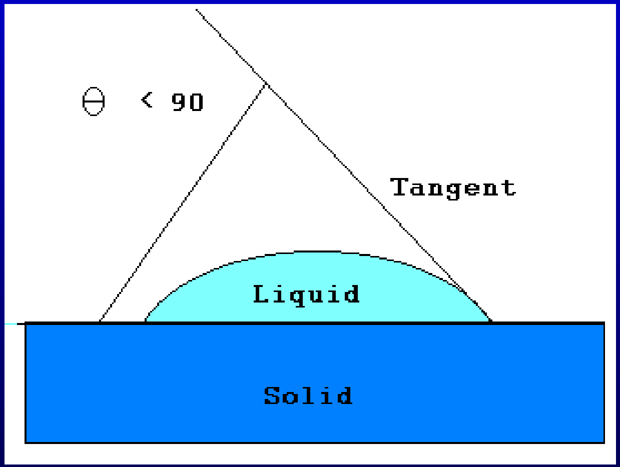
- Anti-stripping agents added to binders
- They increase the surface energy of the asphalt
- Surface energy of asphalts can be determined by contact angle measurements

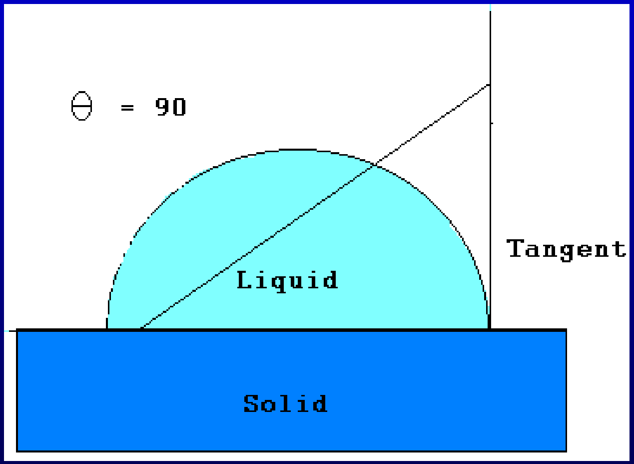
Contact Angle

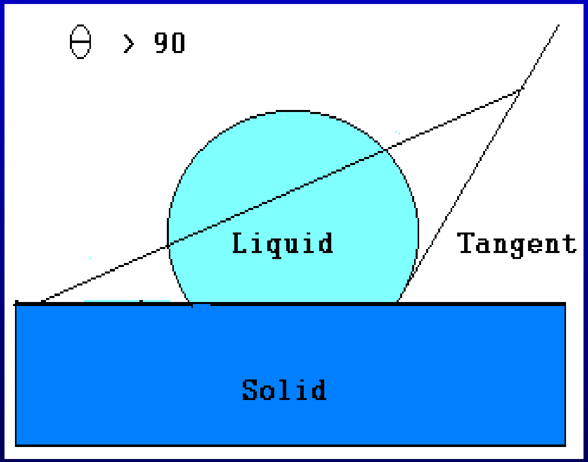
- **Measurement of contact angles yield data which reflect the thermodynamics of a liquid/solid interaction**
- **The solid is tested against a series of liquids and contact angles are measured**
- **Calculations based on these measurements produce a parameter (critical surface tension, surface free energy, etc) which quantifies a characteristic of the solid which mediates wetting**

Contact Angle Measurements

Contact angle, θ , is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, gas (air) and solid intersect as shown below:







Contact Angle Measurements

Contact angle easily measured by Wilhelmy plate method.

Wetting force = $\gamma_{LV} P \cos\theta$ Eq. 1

where γ_{LV} is the liquid surface tension (liquid/vapors i.e., liquid/air) tension, P is the perimeter of the probe and θ is the contact angle.

Case Analysis: Contact angle measurement of an asphalts with and without stripping agent added

- **Both a polar block copolymer and a regular stripping agent were added to an AC 30 binder as stripping agents**
- **Two reference liquids, whose surface energy components are known, were used in these experiments, viz., distilled water (very polar) and formamide (moderately polar).**

Table 1. Contact angle θ data measured in water and formamide

SAMPLE	θ_{water} (°)	$\theta_{formamide}$ (°)
AC-30	103.9	79.5
AC-30 + Copolymer	96.3	86.2
AC-30 + Stripping Agent	80.6	76.0

Disperse and polar components of the surface tension, γ

- **Taking into account both the polar and the disperse (non-polar) components, the surface tension γ_l of a liquid can be described by the following equation (Fowkes):**

$$\gamma_l = \gamma_{ld} + \gamma_{lp} \qquad \text{Eq. 2}$$

where γ_{ld} is the disperse component and γ_{lp} is the polar component of the surface tension.

Disperse and polar components of the free energy of a solid

- A set of equations allows the calculation of the dispersive component γ_{sd} and polar component γ_{sp} of the free energy of the solid:

$(1+ \cos \theta_w) \gamma_w = 4[(\gamma_{fp} \gamma_{sp})/ (\gamma_{fp} + \gamma_{sp}) + (\gamma_{fd} \gamma_{sd})/ (\gamma_{fd} + \gamma_{sd})]$
Eq. 3

$(1+ \cos q\ f) \gamma_f = 4[(\gamma_{fp} \gamma_{sp})/ (\gamma_{fp} + \gamma_{sp}) + (\gamma_{fd} \gamma_{sd})/ (\gamma_{fd} + \gamma_{sd})]$
Eq. 4

Free Energy of a Solid, γ_s

- **The total free surface energy γ_s is merely the sum of its two component forces:**

$$\gamma_s = \gamma_{sp} + \gamma_{sd} \qquad \text{Eq. 5}$$

Calculations

The free energy of asphalt samples were calculated using:

- the surface tension components (dyne/cm), of the liquids

Water:

$\gamma_w = 72.18$ $\gamma_{wp} = 50.56$ and $\gamma_{wd} = 21.62$

Formamide:

$\gamma_f = 52.50$ $\gamma_{fp} = 17.20$ and $\gamma_{fd} = 35.30$

- the values of contact angles determined for each asphalt sample (Table 1)

Table 2. Free Energy γ_s of Asphalts

Asphalt Sample	Disperse γ_{sd}	Polar γ_{sp}	Total γ_s
AC-30 Base asphalt	14.31	5.59	19.90
AC + 20% Rubber (Literature Data)	6.51	7.56	14.07
AC-30 + 1% Block copolymer	6.35	26.33	32.68
AC-30 + 1% Anti-Stripping Agent	8.44	18.20	26.64

Case Analysis Results:

- **Increased polarity of asphalt is reflected by increased surface energy. A better adhesion to mineral surfaces is expected.**
- **Perhaps a simple contact angle measurement vs. water will give a glimpse: the lower the angle, the more polar the asphalt. Polarity might be increased by acid additives, such as PPA.**
- **Antistripping tests (boiling) supported this conclusion in the case of the block copolymer.**

ADHESION

- **Standard tests**
  - **Evaluate**
    - » **Ultimate strength, elastic modulus**
    - » **Homogeneous material with no inherent defects**
    - » **Heterogeneous materials such as asphalt pavement do not fit this description**

For Asphalt Pavements:

- Produce a standardized method by which a material parameter can be used to rank the static fracture resistance of asphalt mixtures

Determination of the critical value of J-integral might be the answer

- **Also refer to the critical strain energy release rate, or J_c**

The J_c characterization

- **Test:**
  - **Three point bend beam specimens of substantial span length.**
  - **Difficulties:**
    - » **Sample preparation**
    - » **Sagging of the beam under its own weight**
    - » **Sagging intensifies at elevated temperatures**

Alternatively:

- A semi-circular core specimen is used for the evaluation of the fracture resistance, J_c of various asphalt mixtures.
- Advantages
  - compact and stable so that there is minimal deformation due to its own weight.
  - can be obtained from SGC or taken from the field.
  - multiple specimens can be obtained from one core
  - reducing the error caused by heterogeneities among samples

Fracture Resistance, J_c

- **Fracture resistance characterization is a more relevant approach since it**
  - **accounts for the flaws as represented by a notch**
  - **gives the resistance of the material to crack propagation**

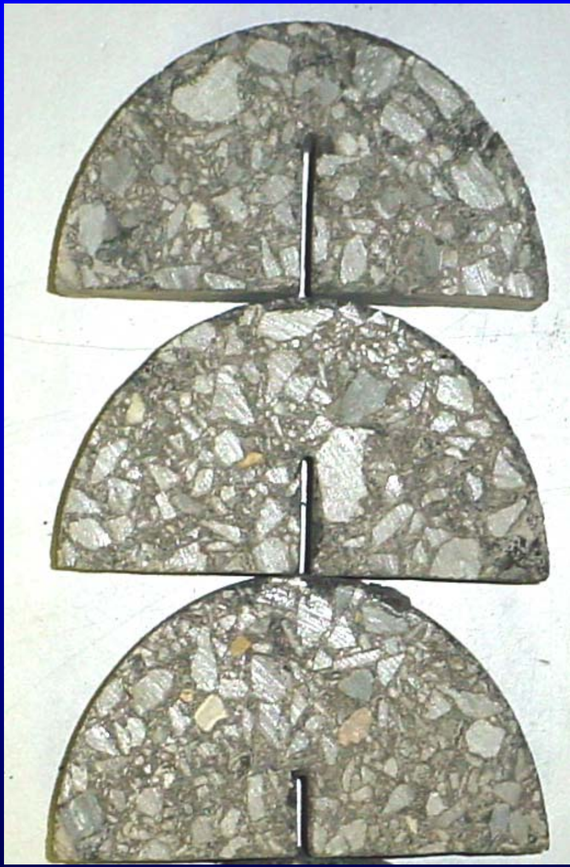
Fracture Resistance Characterization

- Originally used by Chong et al. (Int J. of Fracture, 1984)
  - evaluated the critical value of the J-integral of rock and cementous materials

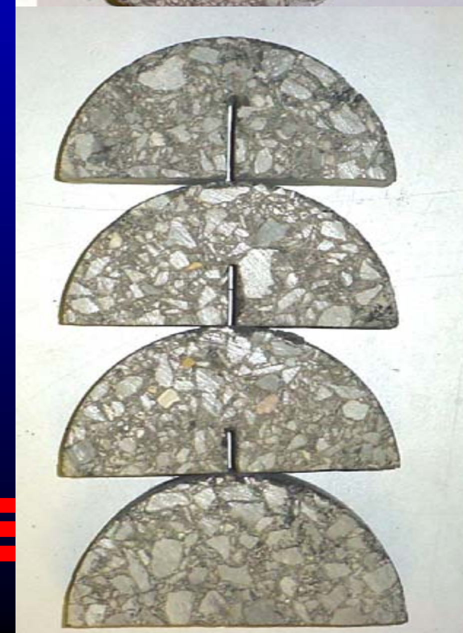
- Dongre et al. (TRB, 1989)
  - Characterized the fracture resistance of asphalt mixture at low temperatures and showed that
  - J_c is sensitive to asphalt mix properties and concluded that its use warranted further study.
- Bhurke (TRB, 1997)
  - Studied polymer modified asphalt concrete using the J_c fracture resistance approach
  - Evaluated the effect of four different polymer additives on the fracture behavior
  - Concluded that the tests were repeatable and were sensitive to material differences due to polymer modification.

Semi-Circular Bend (SCB) Test

- **Sample Geometry:**
  150mm X 57mm
  Four specimens
- **Three notch depths:**
  25.4 mm
  31.8 mm
  38 mm

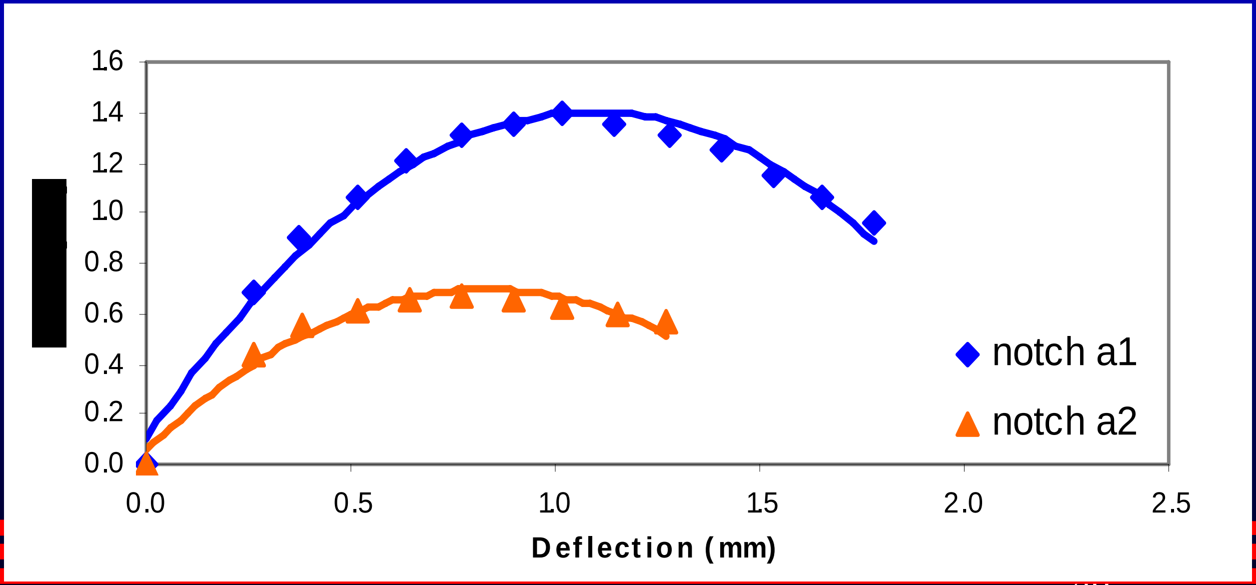



SCB Sample Preparation

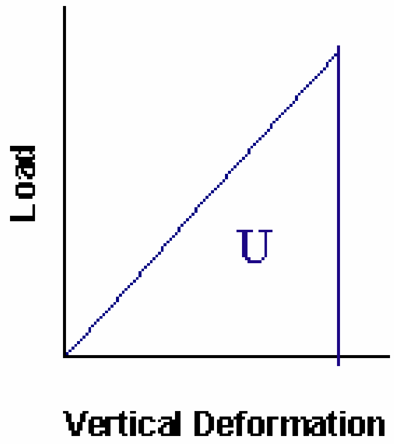


SCB Test Conditions

- Loading rate: 0.5 mm/min
- Load and deformation are recorded
- Test temperature: 25 ºC
- Triplicate testing



Strain Energy Release Rate, G



$$G = -\left(\frac{1}{b}\right)\frac{dU}{da}$$

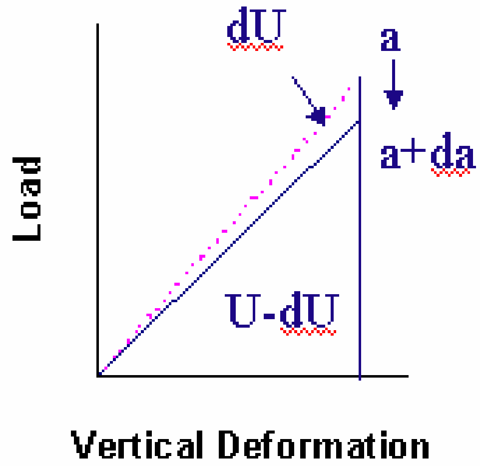
$$= K^2/E'$$

Where,

K-stress intensity factor

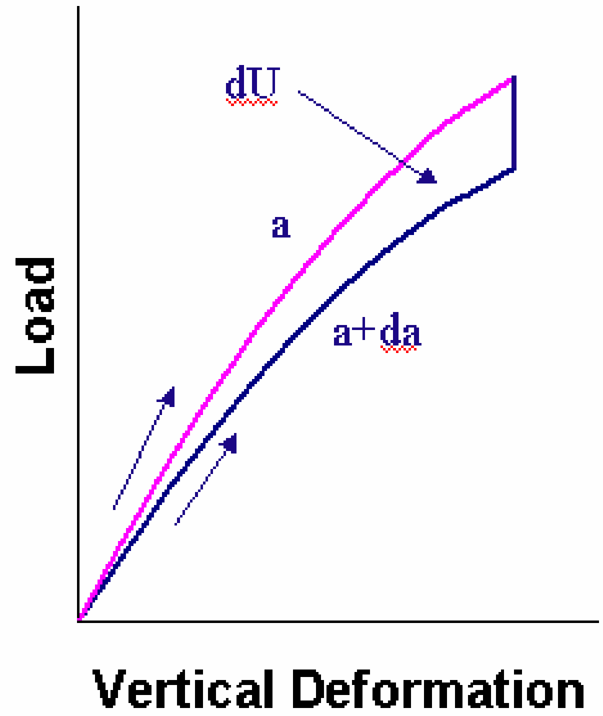
E' = E (plane stress)

E' = E/(1-ν^2) (plane strain)

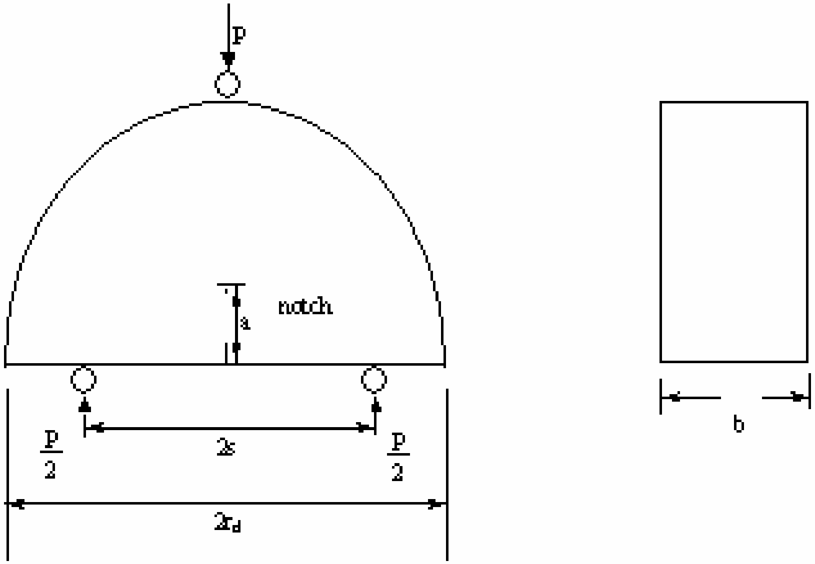


linear-elastic fracture mechanics (LEFM)

J-Integral

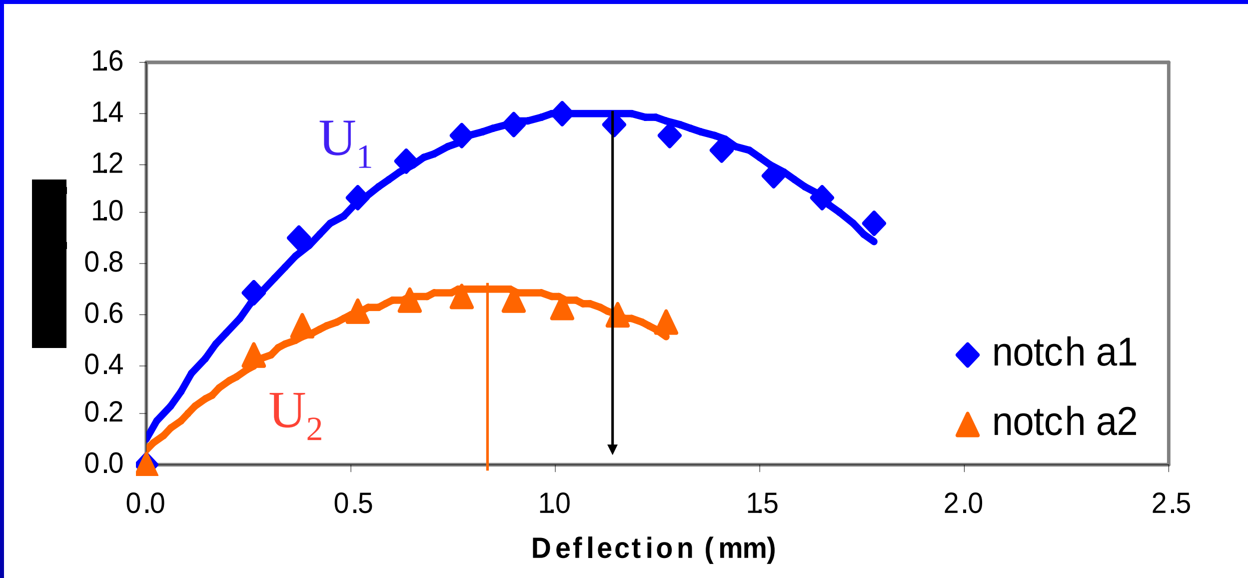


$$J_c = -\left(\frac{1}{b}\right)\frac{dU}{da}$$



Elastic-Plastic Behavior

Determination of J_c

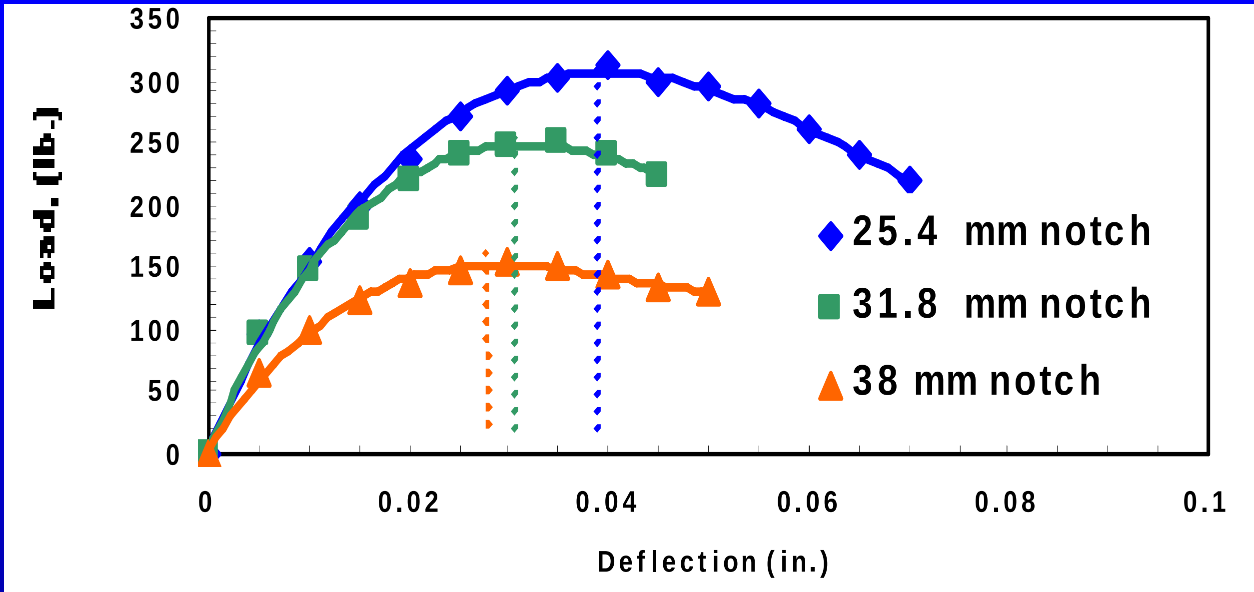


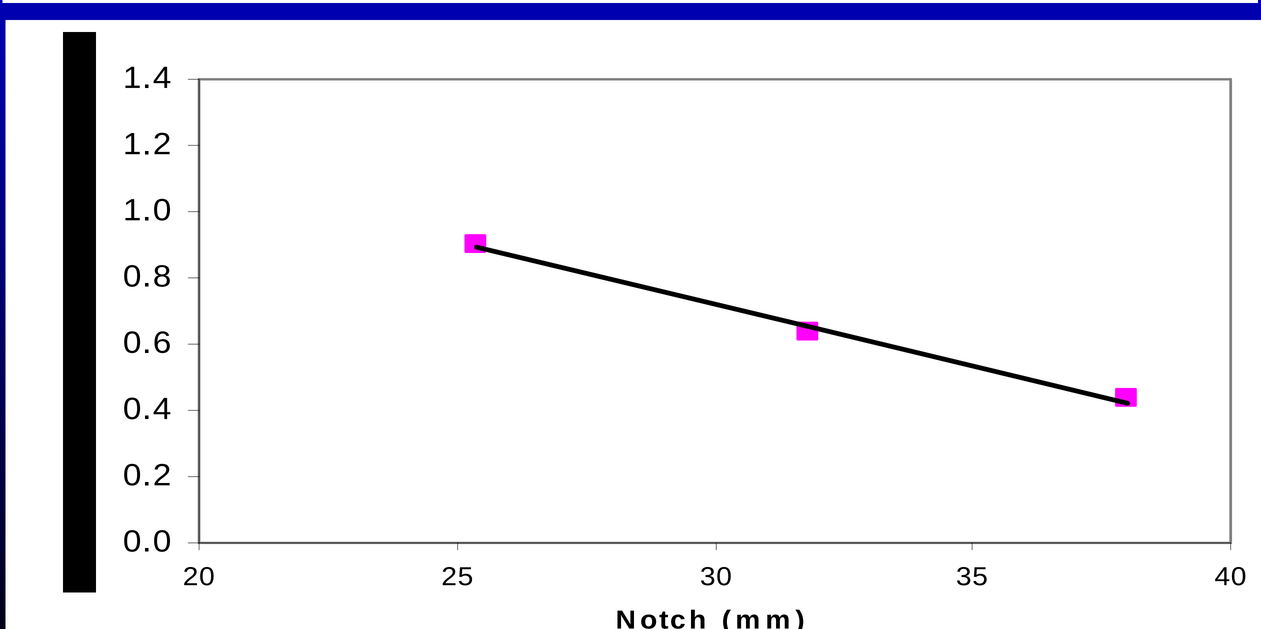
$$J_c = \left(\frac{U_1}{b_1} - \frac{U_2}{b_2} \right) \frac{1}{a_2 - a_1}$$

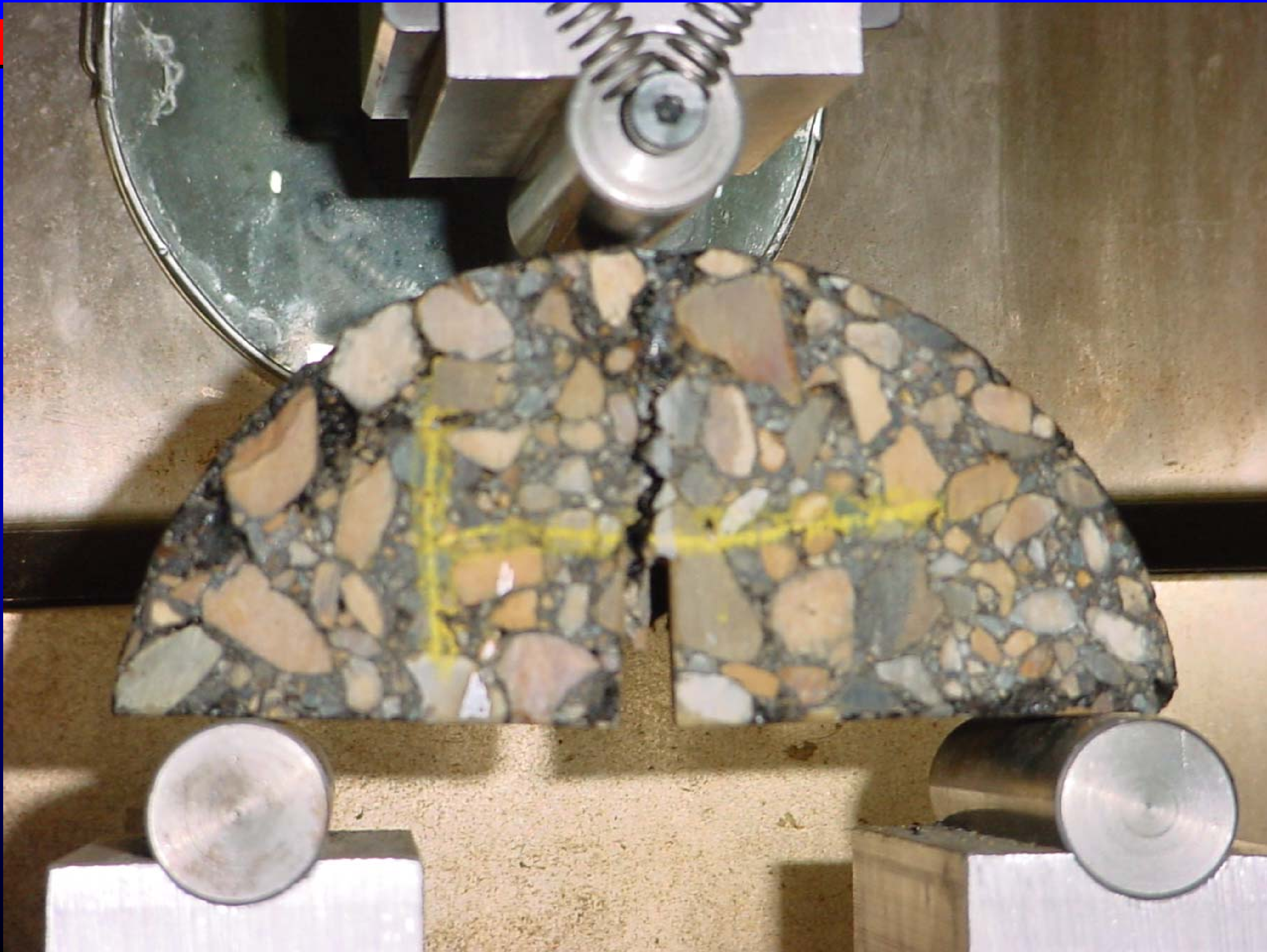
U is the total strain energy to failure

Jc: the critical strain energy release rate

Determination of J_c







Crack Inspection

Recent Applications:

- **Mull et al. (J. Mat Sc, 2001)**
  - concluded that the J-integral approach, employing the semi-circular bend specimen was able to discriminate the effect of different polymer modifiers on the fracture resistance of the asphalt pavement.

- **Molenaar et al. (AAPT 2002)**
  - be preferable to the indirect tensile test that is commonly used since tension appears to be the dominant failure mode even at higher temperatures.

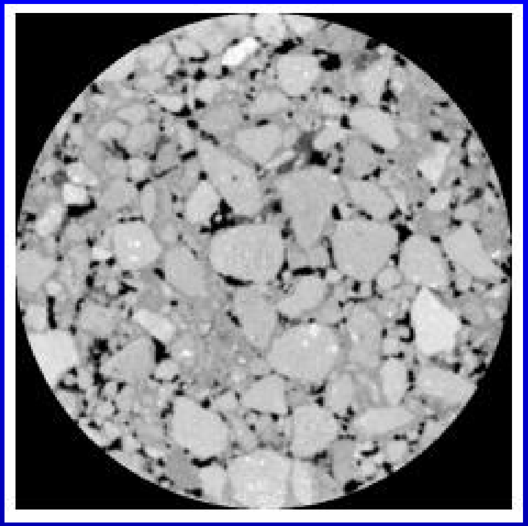
Applications (Contd.)

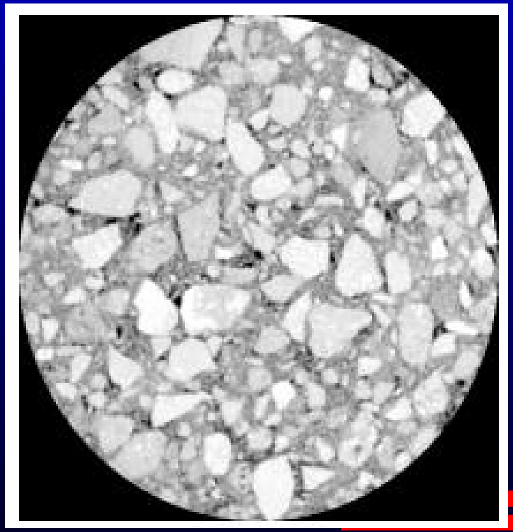
- **Smit et al. (TRB, 2003)**
  - **Suitable alternative to the ITS for evaluating the tensile strength characteristics of asphalt mixture.**
  - **Moisture damage of asphalt mixtures**

Recommendation

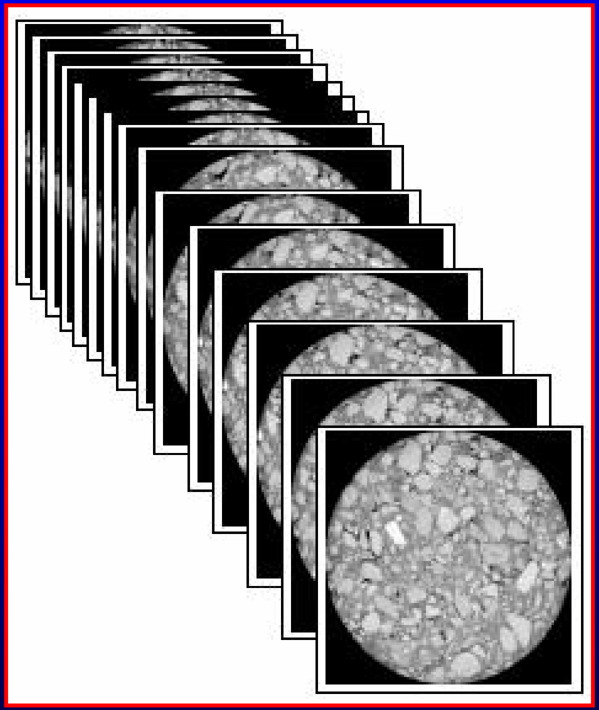
- Perform an extensive testing program
  - specimen geometry
  - environmental conditions
  - on the values of J_c obtained using the semi-circular bend specimen
- Produce a standardized method by which J_c can be used as a material parameter to rank the static fracture resistance of asphalt mixtures

X-Ray Tomography

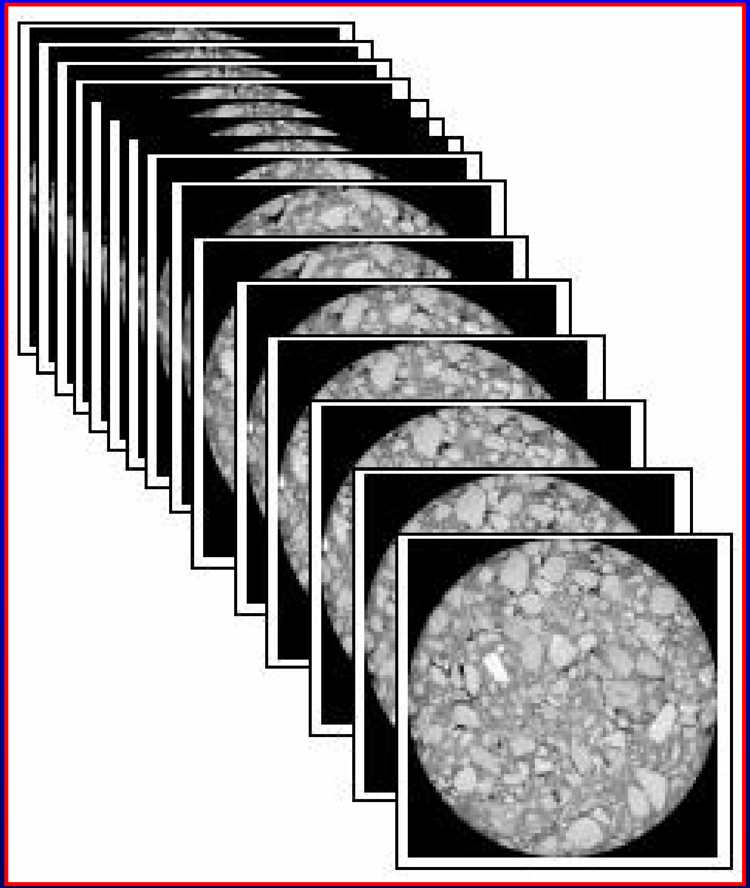




Aggregate Structure Properties from X-Ray Tomography Image Analysis

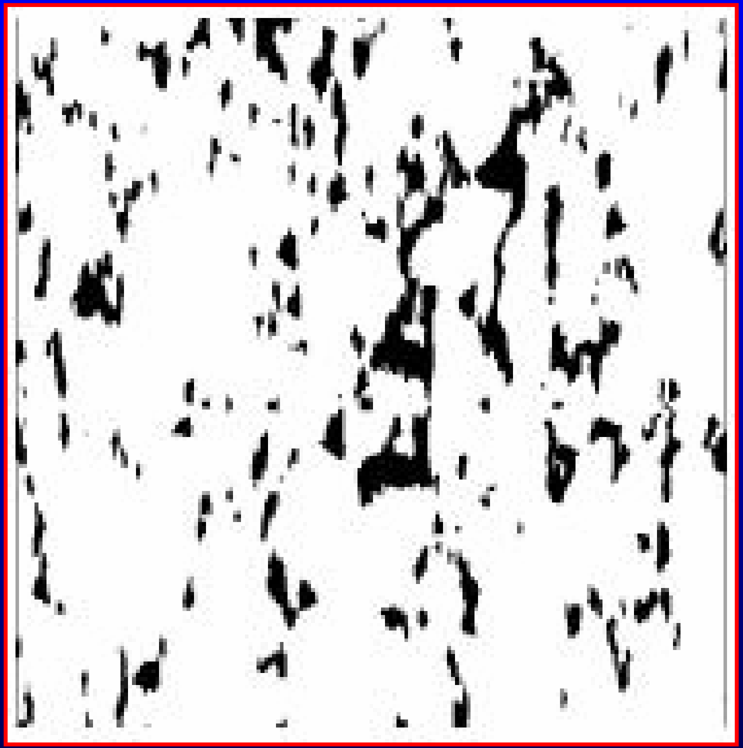


A Virtual Cut



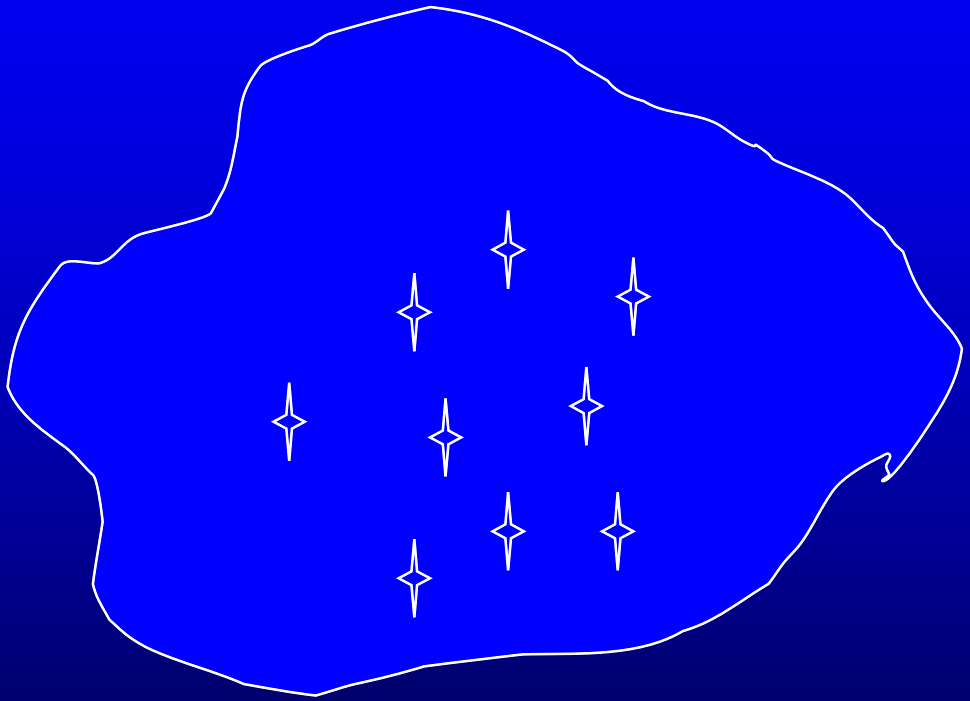
(a) A Stack of Tomography Images

(b) Void System on a Virtual Cut through the Reconstructed 3D Void System of a Coarse Mix Specimen



RHEOLOGICAL BEHAVIOR OF STRUCTURED VISCOELASTIC MATERIALS

Daniel De Kee, Tulane University, New Orleans, LA



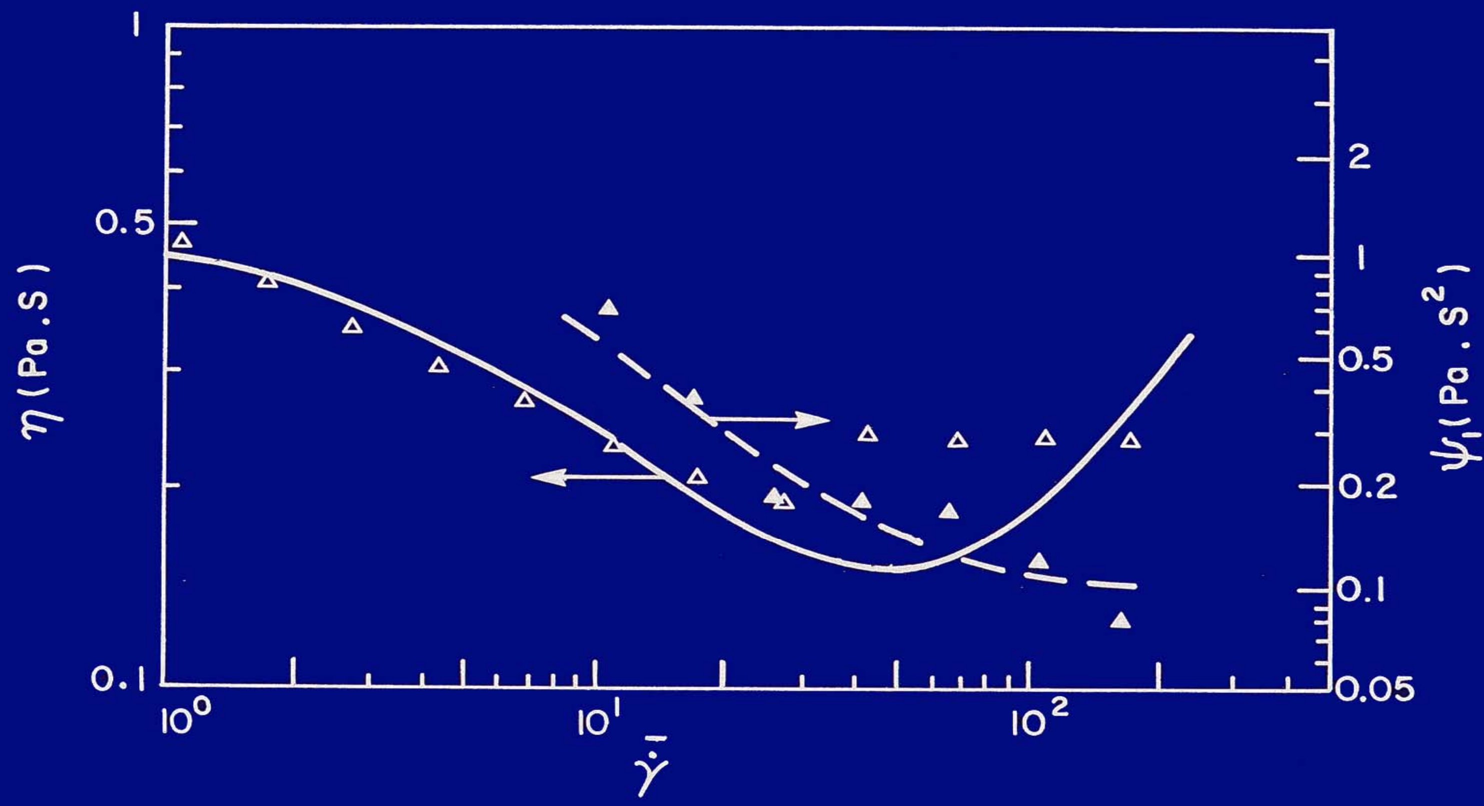
$$\frac{dn_\ell}{dt} = k_\ell \, f_1(\lambda\dot{\gamma})n$$

$$\frac{dn_c}{dt} = k_c(n_o - n) + k_1 f_2(\lambda\dot{\gamma})\, n$$

YIELD STRESS

$$\frac{dn_\ell}{dt} = k_y \, n \, \tau_1$$

$$\frac{dn_c}{dt} = k_c \, (n_p - n)$$


1
0.5
0.1
η (Pa.S)
10^0
10^1
10^2
$\dot{\bar{\gamma}}$
2
1
0.5
0.2
0.1
0.05
ψ_1 (Pa.S^2)

CONCLUSIONS

WHAT CONCLUSIONS

Instead of Conclusions!

This presentation aimed just to wet the appetite for discussing the many facets adhesion can have in considering the P_3 concept. I am looking forward learning more from this Symposium!