The Mechanical Behavior of Asphalt

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Outline

1. Early Investigations on Asphalt
2. Early Constitutive Models
3. Issues in Modeling Asphalt
4. A Thermodynamic Framework for Modeling Asphalt

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Maxwell's Observation

- *"What is required to alter the form of a soft solid is a sufficient force, and, this when applied produces its effect at once. In the case of viscous fluid it is time which is required, and if enough time is given, the very smallest force will produce a sensible effect, such as would require a very large force if suddenly applied. Thus a block of pitch may be so hard that you cannot make a dent in it by striking it with your knuckles; and yet it will in course of time, flatten itself by its own weight, and glide down hill like a stream of water."*

J. C. Maxwell, Theory of Heat, Ninth Edition, 1888

Pitch Drop Experiment

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Pitch Drop Experiment

Year	Event
1930	The stem was cut
1938 (December)	1st drop fell
1947 (February)	2nd drop fell
1954 (April)	3rd drop fell
1962 (May)	4th drop fell
1970 (August)	5th drop fell
1979 (April)	6th drop fell
1988 (July)	7th drop fell
2000 (November)	8th drop fell

Some Early Experiments on Asphalt

- Trouton conducted one of the earliest experiments on torsion and uniaxial compression on cylinders of pitch etc.
- "...the rate of flow of the material under shearing stress cannot be in simple proportion to stress ..."

Trouton(1906), Proc. R. Soc. London, Series A 57(519), 426-440.

Fig. 1.

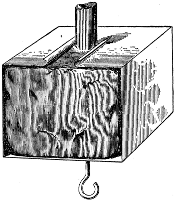

Table II.

Force.	70.	140.	240.	340.	440.
Rate of elongation ...	2·0	6·4	14	20	26

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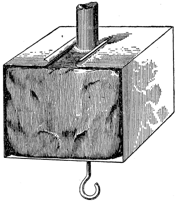

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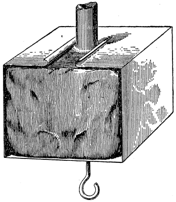

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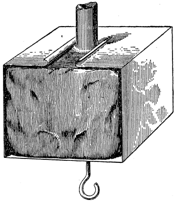

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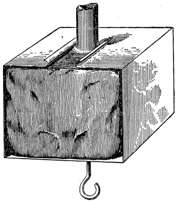

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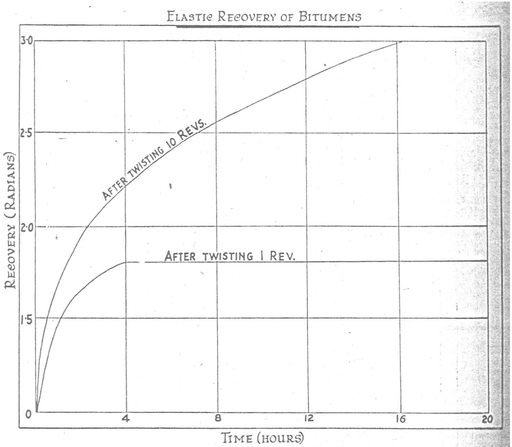

FIG. 7.

- 'Elastic recovery' in a concentric cylinder viscometer

Broome (1939), Journal of Institute of Petroleum, 25, 509-530.

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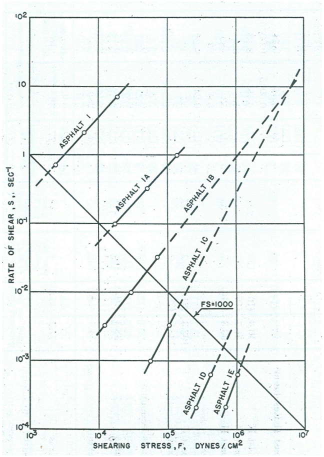

- Air-blown Gulf Coast II Asphalts of 6 different types

Romberg and Traxler(1947), Journal of Colloid Science, 2, 33-47.

Some Early Experiments on Asphalt

- *'Plastic' Bitumen: ...its viscosity is not constant, but fluctuates with the shear stress...*
- *Maltenes themselves are not plastic; not until asphaltenes are present can there be any plasticity.*
- *The influence of pressure is far greater upon asphaltic bitumens than upon lubricating oils. For instance, under 100 atmospheres, the viscosity of a non-plastic, soft asphaltic bitumen at 35°C, increased to $2\frac{1}{2}$ times its original figure.*

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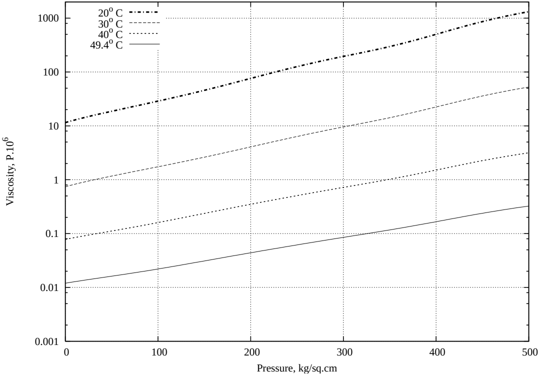
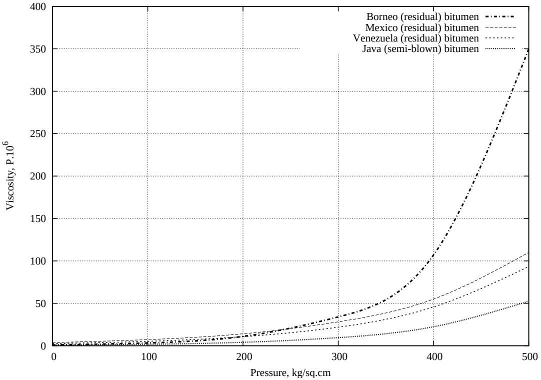
Pressure Dependence on Viscosity of Bitumen - 1950



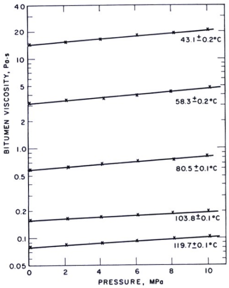
- Viscosity of California (residual) bitumen at different temperatures and pressures.

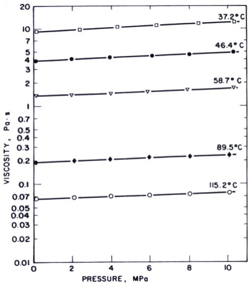
Pressure Dependence on Viscosity of Bitumen - 1950



- Viscosity of bitumens at 30°C and at different pressures

Pressure Dependence on Viscosity of Canada Oil Sand Bitumen





- Viscosity - temperature - pressure data for compressed, gas free Athabasca bitumen, 1986
- Viscosity - temperature - pressure data for compressed, cold lake bitumen, 1987

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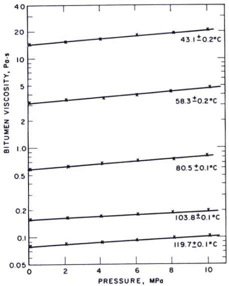

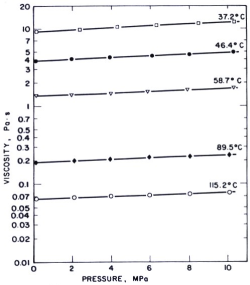

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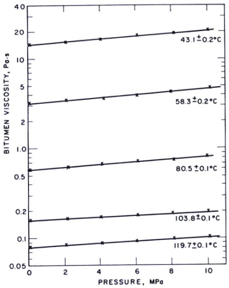

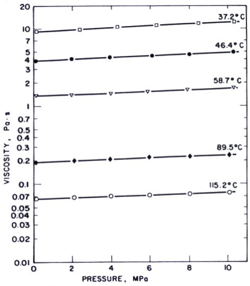

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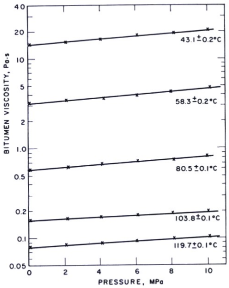

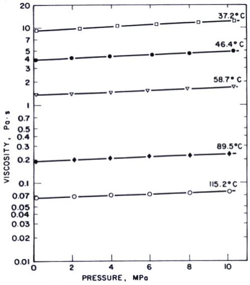

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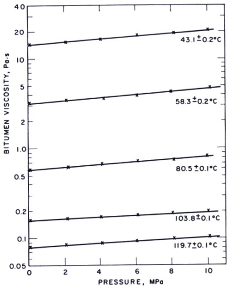

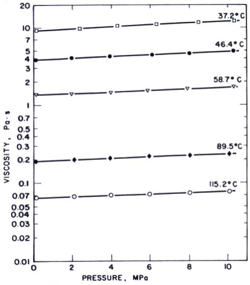

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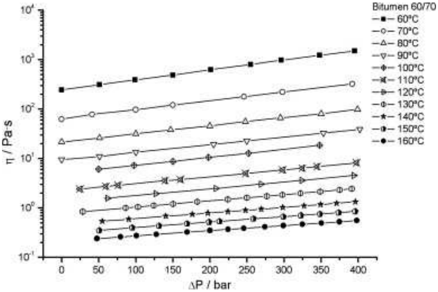

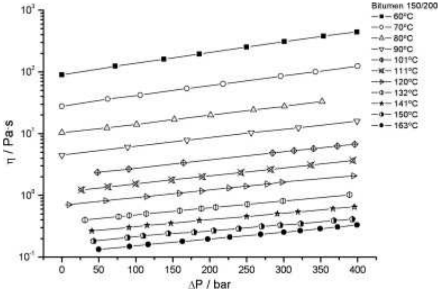

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Alfonso et al. (2006), Fuel, Manuscript in Press

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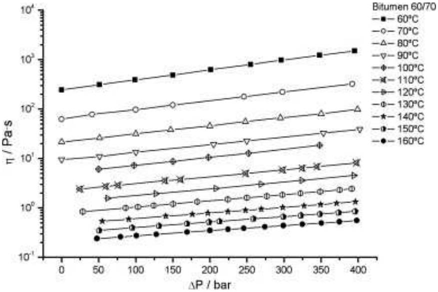

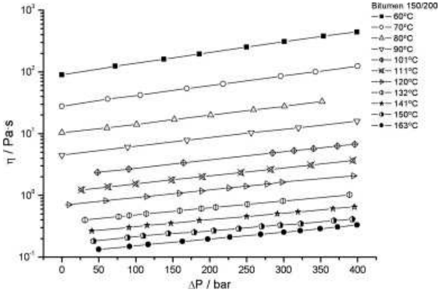

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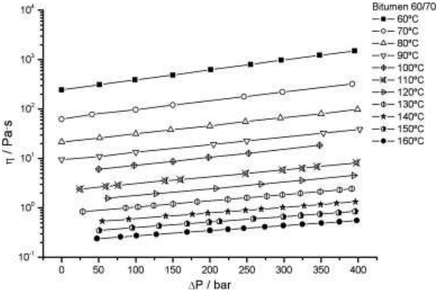

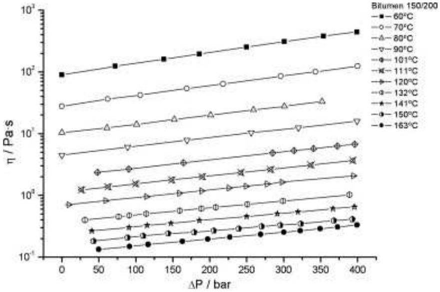

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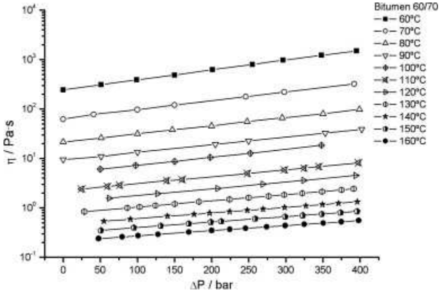

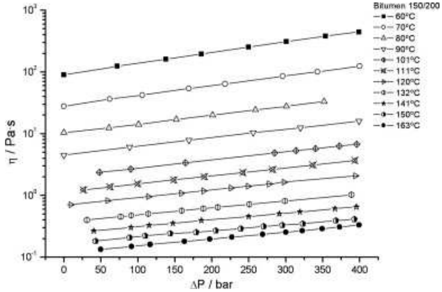

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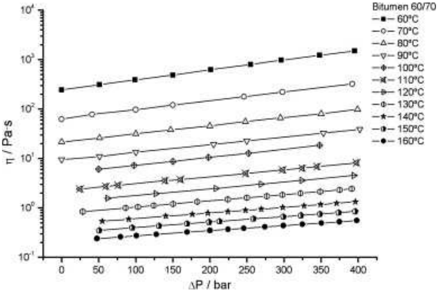

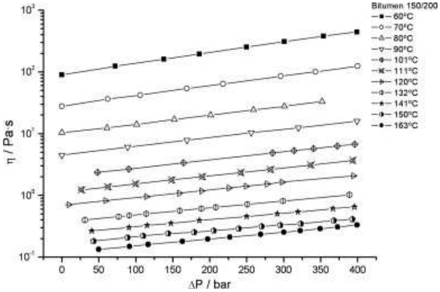

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Significance of Pressure on Viscosity of Bitumen

- Compaction Mechanics
- What is the mechanical behavior of a thin film of asphalt holding the aggregate particles during aircraft landing?
- Current state of art: Time - Temperature - Pressure Superposition (?)
- $$\log \frac{\eta}{\eta_{ref}} = -\frac{C_1\left(T - T_{ref} - \theta(P)\right)}{C_2(P) + \left(T - T_{ref} - \theta(P)\right)} \quad (1)$$

$$\theta(P) = C_3(P) \ln\left(\frac{1 + C_4 P}{1 + C_4 P_{ref}}\right) - C_5(P) \ln\left(\frac{1 + C_6 P}{1 + C_6 P_{ref}}\right) \quad (2)$$

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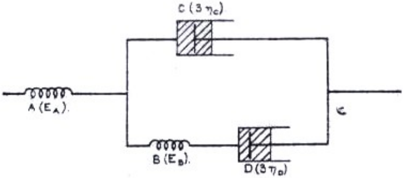
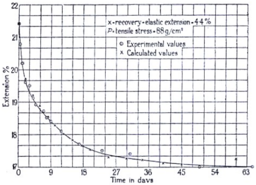
Burgers' Model - Lethersich's Experiments





- Bitumen is assumed to possess a colloidal structure consisting of asphaltenes (disperse phase, solid-like) and petrolenes (dispersion medium, viscous fluid) - 'elastic elements buried in a viscous fluid'

Lethersich (1942), Journal of the Society of Chemical Industry, 61, 101-108.

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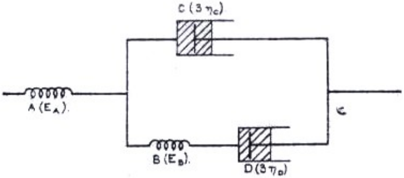

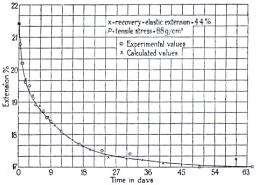

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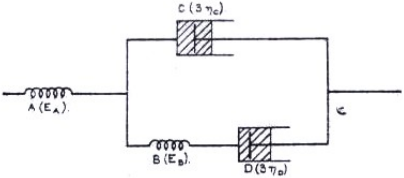

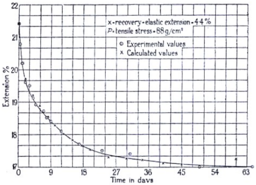

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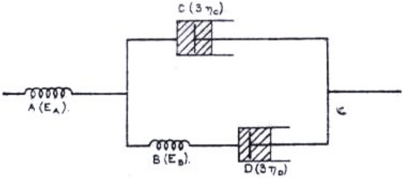

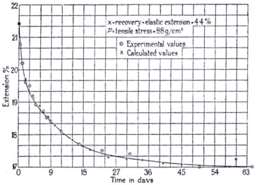

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Frohlich and Sack, 1946

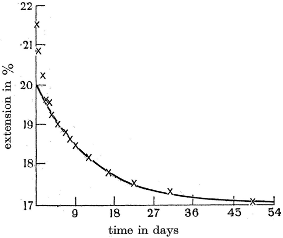
$$\mathbf{S} + \lambda\dot{\mathbf{S}} = \mu_1 \mathbf{D}_1 + \mu_2 \mathbf{D}_2, \tag{3}$$

$$\mathbf{D}_1 = \frac{1}{2}\left(\frac{\partial \mathbf{v}}{\partial \mathbf{x}} + \left(\frac{\partial \mathbf{v}}{\partial \mathbf{x}}\right)^{\mathrm{T}}\right), \tag{4}$$

$$\mathbf{D}_2 = \frac{1}{2}\left(\frac{\partial \mathbf{a}}{\partial \mathbf{x}} + \left(\frac{\partial \mathbf{a}}{\partial \mathbf{x}}\right)^{\mathrm{T}}\right), \tag{5}$$

Frohlich and Sack (1946), Proceedings of the Royal Society of London, Series A, Mathematical and Physical Sciences, 185, 415-430.

Frohlich and Sack, 1946



according to which it should be an exponential function of time. Figure 3 shows that this is the case for most of the recovery curve, but for (relatively) short times there is an additional recovery. It seems evident that the structure of bitumens is more complicated than was assumed in our model, and there are a number of suggestions one can make to account for the additional recovery (e.g. an interaction between the elastic spheres, or an elasticity of the fluid in which they are dispersed). It is not the

- Interestingly, Oldroyd (1950) developed models for emulsions which was inspired by the work of Frohlick and Sack.

Current Attempts in Modeling Asphalt

- Linear viscoelasticity - Time temperature superposition - Master curves - Complex Modulus (SHRP, USA)
- Lesueur *et al.*(1996) - failure of time temperature superposition - A bimodal model assuming asphalt as a dispersion of asphaltene particles peptized by resins
- Cheung and Cebon (1997) - ‘Eyring plasticity model’ at temperatures below glass transition with a temperature dependence of the Arrhenius type at temperatures above glass transition - Assumed that asphalt obeyed time-temperature superposition at high temperatures.

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- Lesueur *et al.*(1996) - failure of time temperature superposition - A bimodal model assuming asphalt as a dispersion of asphaltene particles peptized by resins
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- Multi-constituent nature of asphalt
  - asphalt is a mixture of different reacting and diffusing components,
  - asphalt from different sources of crude have different amounts of constituents and possibly different ability for reactions and
  - each and every manifestation of change in the behavior of asphalt (such as aging etc.,) is due to the inter-conversion of one type of constituent to the other type.
- Asphalt Transitions
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Asphalt Transitions

- Starting from a low temperature of approximately -40°C and heating asphalt at a uniform temperature rate to a temperature of +100°C, the following transitions are observed:
glassy solid $\Rightarrow$ viscoelastic solid $\Rightarrow$ viscoelastic fluid $\Rightarrow$ Newtonian fluid
- Schweyer (1973)
high temperature ($>$ 60 $^\circ$C) - Newtonian fluid,
near-transition region (between 0 and 60 $^\circ$C) - viscoelastic and
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in the temperature range of 65 - 150 $^\circ$C, asphalts behaved as Newtonian fluids and in the temperature range between 25 - 65 $^\circ$C, the behavior was essentially viscoelastic

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Asphalt Transitions

- What causes these transitions?
  - Solvation of the asphaltene shells becomes larger during temperature transition imparting a new microstructure to asphalt
  - crystallization
- One can view asphalt as a mixture of amorphous and crystalline phases and that the influence of temperature is in the melting of crystalline phases as the temperature is increased or in the formation of crystalline phases as the temperature is decreased.
- Claudy *et al.*,(1991):
  at temperatures below 0 $^{\circ}$C - glass transition
  at temperatures between 0 and 90 $^{\circ}$C - gradual dissolution of crystallized fractions and
  at temperatures roughly above 100 $^{\circ}$C - asphalt behaving as a 'homogeneous solution'

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Asphalt Transitions - Noel and Corbett (1970)

- One of the significant investigation on the crystalline phases in asphalts
- Used Differential Scanning Calorimetry (DSC) and tested 6 different types of asphalts.
- Conclued that the crystallizable components present in asphalt are largely found in the saturate fractions of the asphalt with some lesser amount in the naphthene-aromatics fraction.
- Melting of the crystalline fractions of the waxy asphalts took place over a broad range of temperature of 0 - 85°C

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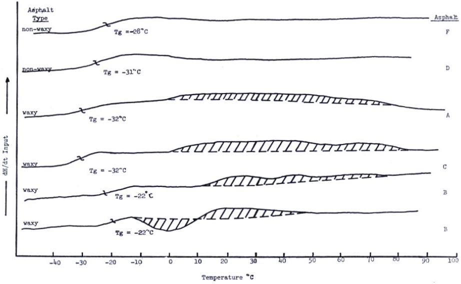
- Recorded for the first time cold crystallization (suppressed crystallization by quench cooling, results in metastable amorphous state below glass transition)



Noel and Corbett (1970), Journal of the Institution of Petroleum Technologists, 56, 261-268

Asphalt Transitions

- Mass fractions of the crystallized fractions can vary depending upon the asphalt type and the temperature
- Claudy (1992) - percentage of crystallized fractions varied from zero to 33.9 percent for different types of asphalts
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- What is the nature of the crystallized fractions in asphalt? - Essentially wax

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Asphalt Transitions

- Wax in bitumen
  1. Paraffin wax: Group of n-alkanes, crystallize in large flat plates or needles, also known as macro-crystalline wax
  2. Micro-crystalline wax: Aliphatic hydrocarbons with considerable iso and cyclic paraffins, crystallize in tiny microscopic needles.
  3. Certain aromatics and polar functional groups can also crystallize

- DSC techniques can be used to characterize the crystallization starting temperature (during cooling) and wax melting temperature (during heating).

Bitumen samples	Wax content (%)	Crystallisation starting temperature (°C)	Wax melting out temperature (°C)
B1	0	--	--
B2	4.0	30	63
B3	1.9	37	90
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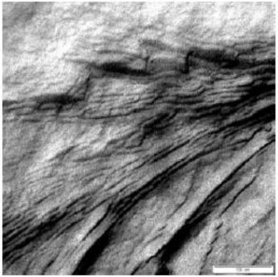
- Typical wax morphology



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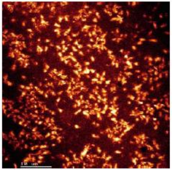
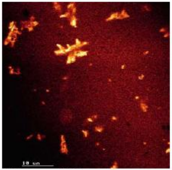


24 hours at 22°C



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Lu and Redelius (2006), ENERGY and FUELS 20 (2): 653-660

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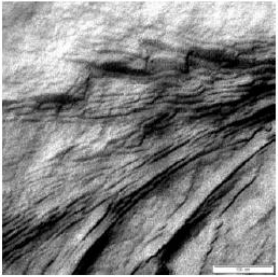

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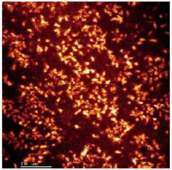

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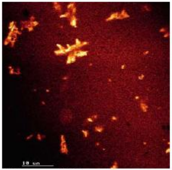

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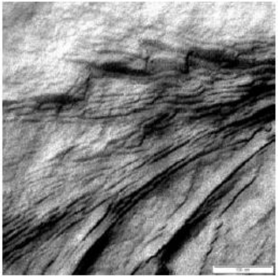

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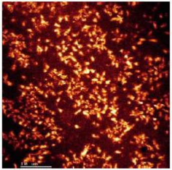

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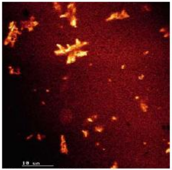

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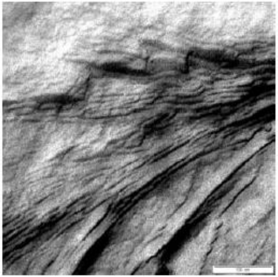

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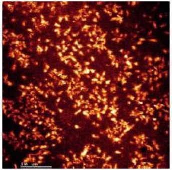

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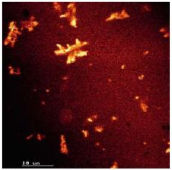

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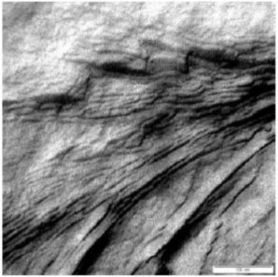

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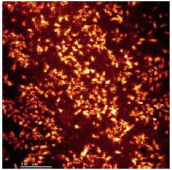

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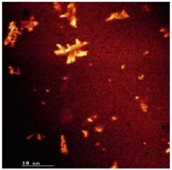

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Internal Structural Change of Asphalt with Time

- The internal structure of asphalt can develop and evolve if it is left undisturbed at a constant temperature.

  Reversible - Similar to physical aging of polymers ("*This phenomenon is the observed change in a property of the polymer as a function of storage time, at constant temperature, at zero stress, and under no influence from any other external conditions*" - Hutchinson (1995), Progress in Polymer Science)

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- Reversible Change in Internal Structure - Two mechanisms
  1. "Steric Hardening" - Takes place at room temperature, an extremely slow process taking from days to weeks to reach equilibrium conditions
  2. "Low Temperature Physical Hardening" - Takes place at temperatures near glass transition, is much more rapid and experimental investigations have reported that it takes normally 1 - 2 days at the temperature range of -15 to -35°C
- Clearly Arrhenius kind of relationship between rates and temperatures do not apply for asphalt.

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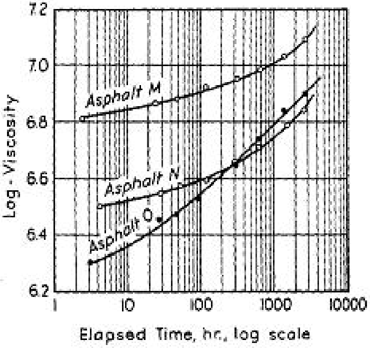
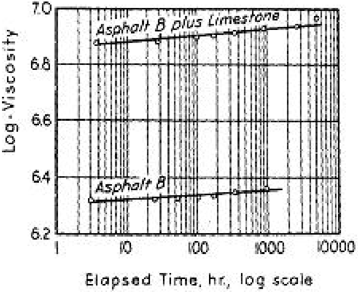
- Increase in the viscosity of asphalt kept in the viscometer for sufficiently long time

Traxler and Schweyer (1936), Proceedings of the American Society for Testing and Materials, 36, 544–551.





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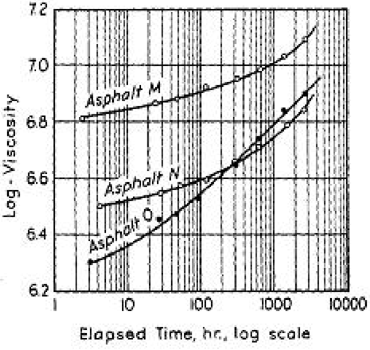

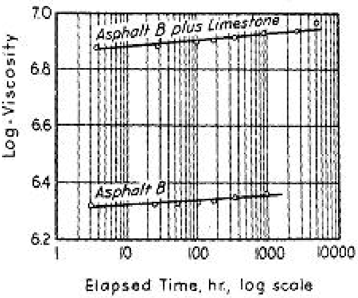

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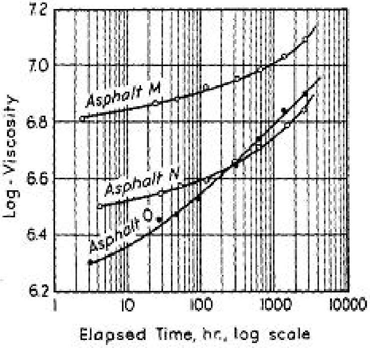

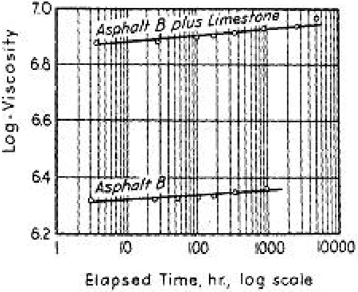

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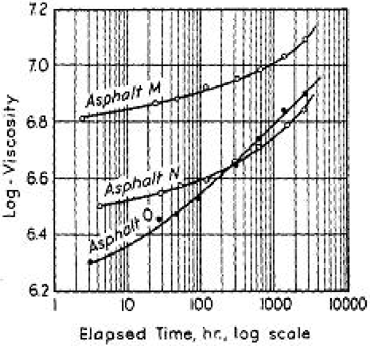

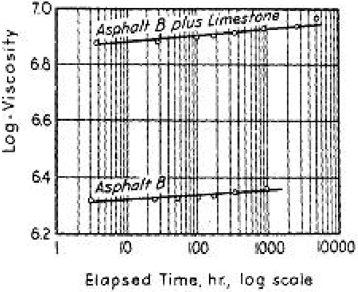

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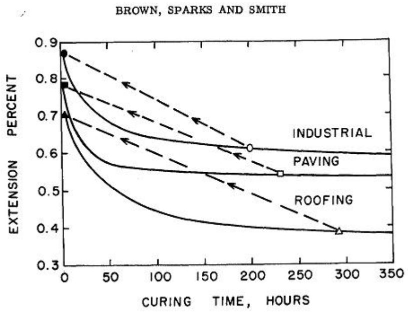
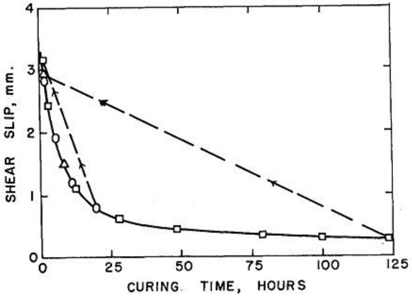
- Steric Hardening





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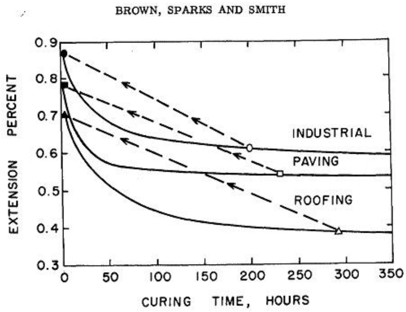

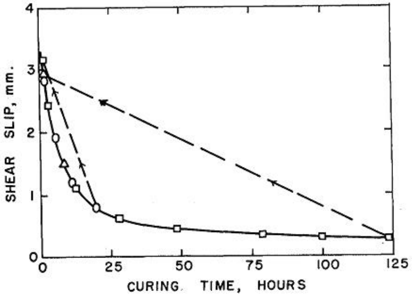

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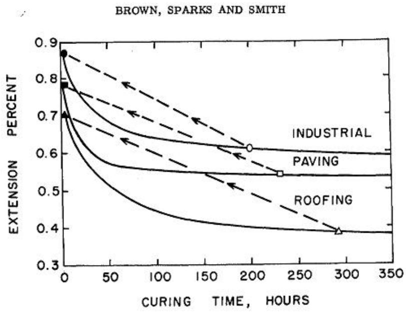

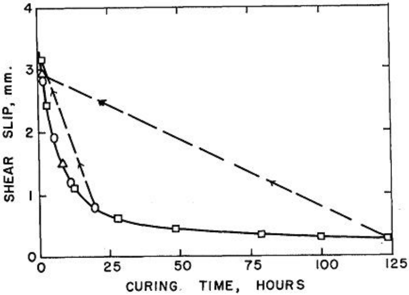

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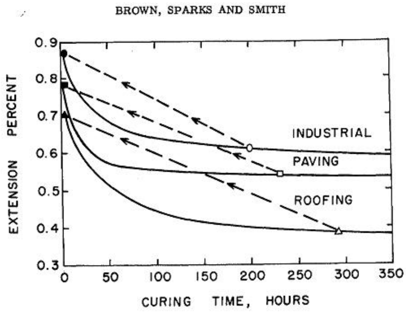

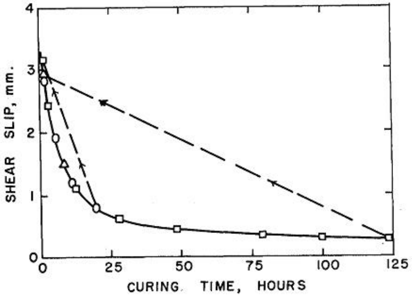

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Internal Structural Change of Asphalt with Time

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    1. Collapse of the 'free volume' as asphalt passes through glass transition (Bahia and Anderson, 1992)
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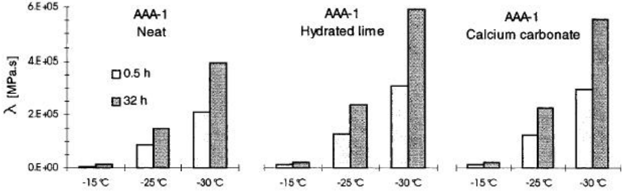

Johansson and Isacsson (1998), Construction and Building Materials, 12, 463-470.

Summary of the Issues in Modeling Asphalt

- The mechanical behavior of asphalt in the temperature regime of interest is quite complicated and not well understood,
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- Asphalt is a mixture of different chemical species and the different manifestations of the mechanical behavior of asphalt depends on the relative proportions of each of these species.
- The proportion of these different constituents as well as the potential for chemical interconversion depends to a large extent on the source of asphalt (crude source), the processing method etc.
- A complete and rigorous constitutive model should be able to take into account the multi-constituent nature of asphalt, the ability to interconvert as well as the influence of the crude source on the mechanical behavior of asphalt.
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Modeling of Asphalt

- The key element of the framework that we use is that a body can exist stress free in numerous natural configurations.
- We follow Rajagopal and Srinivasa (2000), Journal of Non-Newtonian Fluid Mechanics, 88, 207–227 for our modeling of asphalt.

$$\mathbf{x} = \chi_{\kappa_R}(\mathbf{X}, t). \tag{6}$$

$$\mathbf{F}_{\kappa_R} \equiv \frac{\partial \chi_{\kappa_R}}{\partial \mathbf{X}}. \tag{7}$$

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- Experimental studies on the compressibility of asphalt have pointed out that the change in the density is of the order of only 1.5 percent under normal temperatures and pressures and hence in this study, we assume asphalt to be incompressible.

$$\mathrm{div}\mathbf{v} = 0. \tag{10}$$

- The balance of linear momentum is

$$\rho\left[\frac{\partial \mathbf{v}}{\partial \mathbf{t}} + (\nabla \mathbf{v})\mathbf{v}\right] = \mathrm{div}\mathbf{T} + \rho\mathbf{g}, \tag{11}$$

- Reduced Energy-Dissipation Equation

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Constitutive Equation

- Helmholtz Potential

$$\psi = \frac{1}{2\rho} \sum_{i=1}^{n} \mu_{\mathrm{i}} \left(\mathrm{I}_{\mathrm{i}} - 3 \right), \tag{13}$$

- Rate of Dissipation

$$\xi = \sum_{i=1}^{n} \left(\eta_{\mathrm{i}} \mathbf{D}_{\kappa_{\mathrm{p}_{\mathrm{i}}(\mathrm{t})}} \cdot \mathbf{B}_{\kappa_{\mathrm{p}_{\mathrm{i}}(\mathrm{t})}} \mathbf{D}_{\kappa_{\mathrm{p}_{\mathrm{i}}(\mathrm{t})}} + \bar{\eta}_{\mathrm{i}} \mathbf{D} \cdot \mathbf{D} \right). \tag{14}$$

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Constitutive Equation

$$\mathbf{T} = -p\mathbf{1} + \sum_{i=1}^{n}\left(\mu_{\rm i}\mathbf{B}_{\kappa_{{\rm p}_{\rm i}(t)}} + \bar{\eta}_{\rm i}\mathbf{D}\right) \quad (15)$$

$$\frac{1}{2}\overset{\triangledown}{\mathbf{B}}_{\kappa_{{\rm p}_{\rm i}(t)}} = \frac{\mu_{\rm i}}{\eta_{\rm i}}\left[\frac{3}{{\rm tr}\left(\mathbf{B}^{-1}_{\kappa_{{\rm p}_{\rm i}(t)}}\right)}\mathbf{1} - \mathbf{B}_{\kappa_{{\rm p}_{\rm i}(t)}}\right], \qquad {\rm i} = 1, \ldots {\rm n}. \quad (16)$$

Some Experimental Corroboration

- Constant Extension Rate Test : Cheung and Cebon (1997)

$$\Lambda(t) = 1 + Kt, \tag{17}$$

where K is a constant. The velocity gradient for this motion is given by,

$$\mathbf{L} = \mathrm{diag}\left[\frac{-1}{2}\frac{K}{1+Kt}, \frac{-1}{2}\frac{K}{1+Kt}, \frac{K}{1+Kt}\right]. \tag{18}$$

$$\mathbf{B}_{\kappa_{\mathrm{p}(\mathrm{t})}} = \mathbf{1}, \quad \text{for} \quad t = 0. \tag{19}$$

Some Experimental Corroboration

For the case with single relaxation time, the constitutive equation is given by

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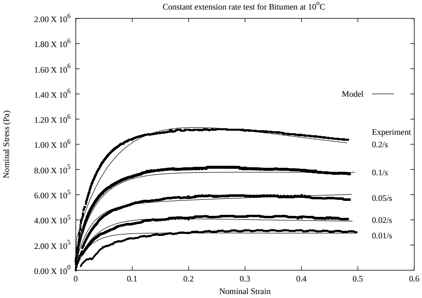

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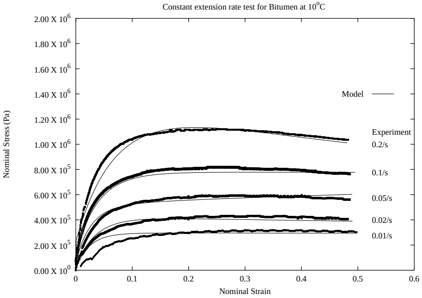

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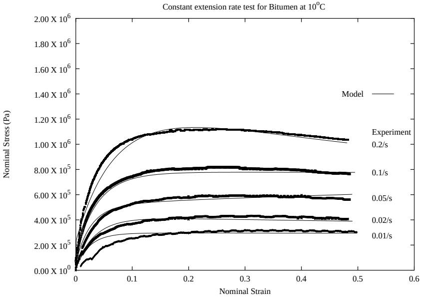

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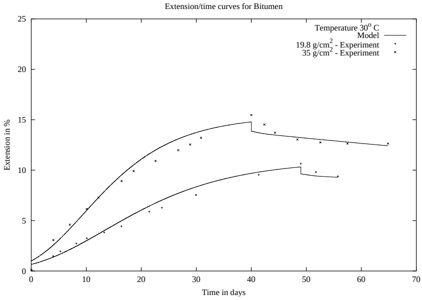

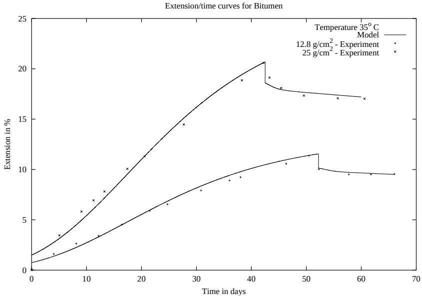

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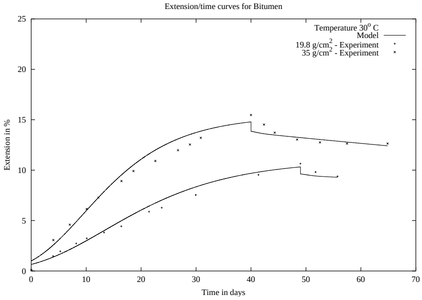

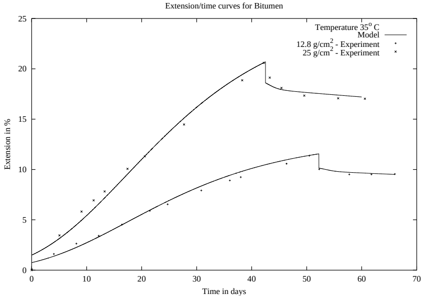

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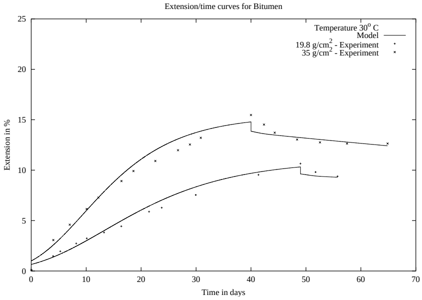

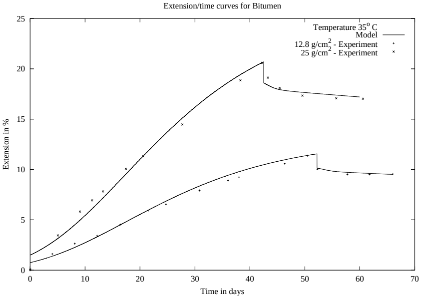

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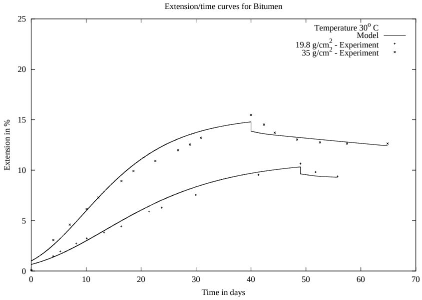

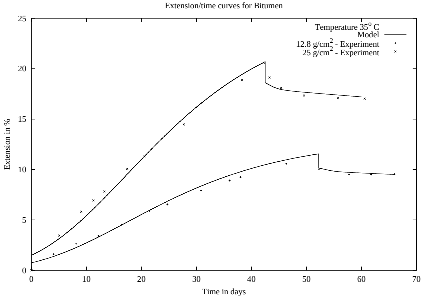

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Acknowledgments

Professor K. R. Rajagopal

Texas A&M University