Continuous Models for Characterizing Linear Viscoelastic Behavior of Asphalt Binders

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Why Model Rheological Behavior?

- Provide rational parameters that can be used to:
  - Explain and understand behavior of bitumen
  - Describe and/or predict the aging process
  - Provide rational parameters for use in the development of specifications
  - Link binder and mixture behavior
- Different applications may justify different model

Historical - Application to Specifications

- $PI_{R\&B}$ (Pfeiffer and van Doormaal, 1936
  - Ring and ball and pen
- PI_{logPen} (Huekelom and Klomp, 1964)
  - Slope of log pen vs temperature
- PVN (McLeod, 1972)
  - Pen at 25°C and viscosity at 60 or 135 60°C
- VTS (Puzinauskas)
  - Viscosity at 60 and 135 60°C

What Was Lacking in These Models?

- Provided point measurements
  - Did not provide mechanism for interpolation
  - Based on empirical measurements
  - Confounded time and temperature effects
- Significant but under appreciated development
  - Van der Poel's nomograph
  - Based on empirical measurements
  - Lacking in accuracy
  - Model never given in explicit form

Discrete Models

- Based on springs, dashpots, sliders, and other mechanical analogs
- Examples range from simple Maxwell model to multi-element Prony series
- Mathematically elegant and relatively easy to manipulate but
  - Elements/models lack a sense of intuitiveness
  - Such models are poor candidates for predicting aging or for relating to composition

Continuous Models

- Continuous function that defines the mastercurve and contains:
  - Minimal number of model parameters
  - Parameters that have a rational explanation
  - Parameters that can be related to binder composition and a molecular model
  - Parameters that can be related the aging process
  - Parameters that are useful in specification development
- Number of early examples in literature

Early Continuous Models

- Jongepier and Kuilman
  - Relaxation spectra as log normal distribution
- Dobson (1969)
  - Based on empirical relationships between modulus and phase angle
- Dickenson and DeWitt (1974)
  - Based on hyperbolic representation
  - Recognized relaxation spectra skewed

Christensen-Anderson LVE Model

- Original motive was to provide SHRP specification criteria for unmodified asphalt binders
  - Approach was discontinued in favor of point parameters such as $G^*/\sin\delta$, S(60s), etc.
- Based on the observation that the relaxation spectrum is a skewed function of time
  - Skewed logistic function gave best "fit"
- All other rheological functions can be generated from relaxation spectrum

Skewed Logistic Function

$$F(x) = \frac{m}{b}\exp\left\{\frac{x-a}{b}\right\}\left[1+\exp\left\{\frac{x-a}{b}\right\}\right]^{-(m+1)}$$

$F(x)$ = Probability density function

m = Skewness parameter

x = Independent parameter

b = Scale parameter

a = Location parameter

Through integration obtain cumulative distribution function

$$P(x) = 1 - \left[1+\exp\left\{\frac{x-a}{b}\right\}\right]^{-m}$$

CA Model for $G^*(\omega)$

- Substituting rheological parameters:

$$G^*(\omega) = G_g\left[1+\left\{\frac{\omega}{\omega_c}\right\}^{(\log 2/R)}\right]^{-R/\log 2}$$

$G^*(\omega)$ = Measured complex modulus

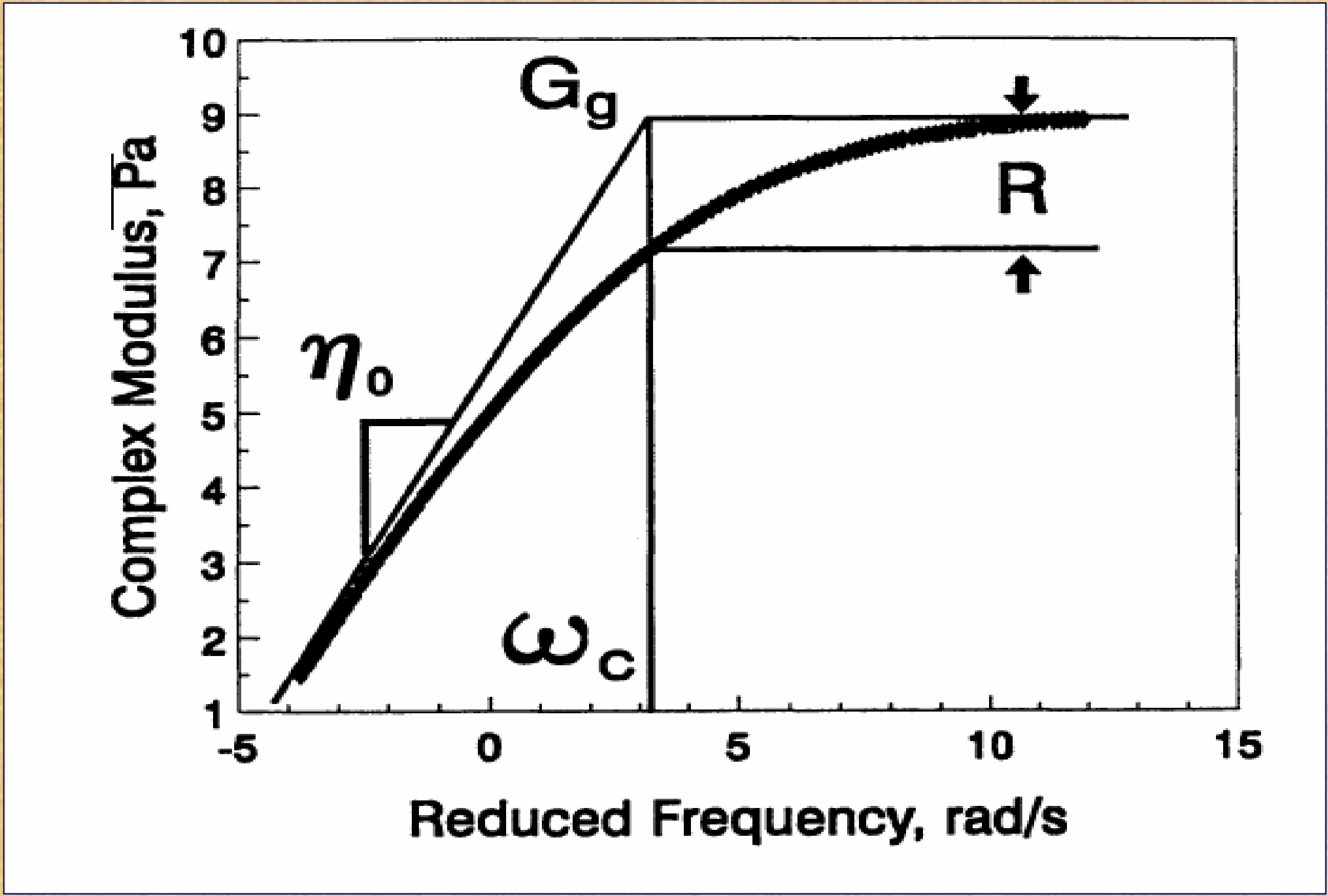
G_g = Glassy modulus

R = Rhelogical Index (shape factor)

ω = Test frequency

ω_c = Crossover frequency (location parameter)

Graphical Representation



CA Model for δ(ω)

- Rewriting and substituting rheological parameters:

$$\delta(\omega) = 90 / \left[1 + \left\{ \frac{\omega}{\omega_c} \right\}^{(\log 2)/R} \right]$$

$\delta(\omega)$ = Measured phase angle

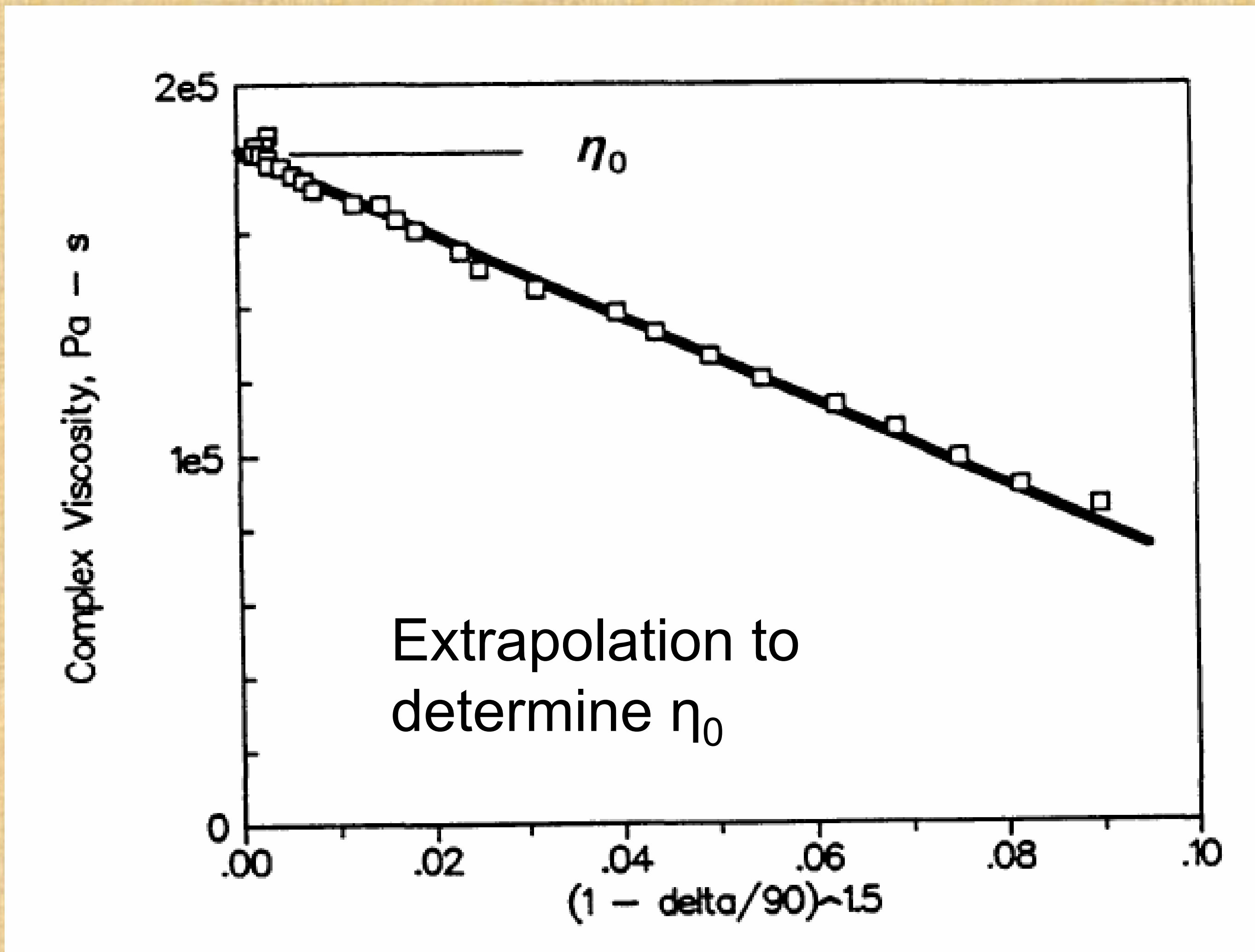
Time-Temperature Dependency

- Dependency above and Below T_g must be characterized with different algorithm
- WLF gives good results above T_g
  - Based on free volume concepts
- WLF not applicable below T_g due to physical hardening
  - Free volume is changing with time
  - Arrhenius gives better results
- Time-temperature dependency must consider T_g

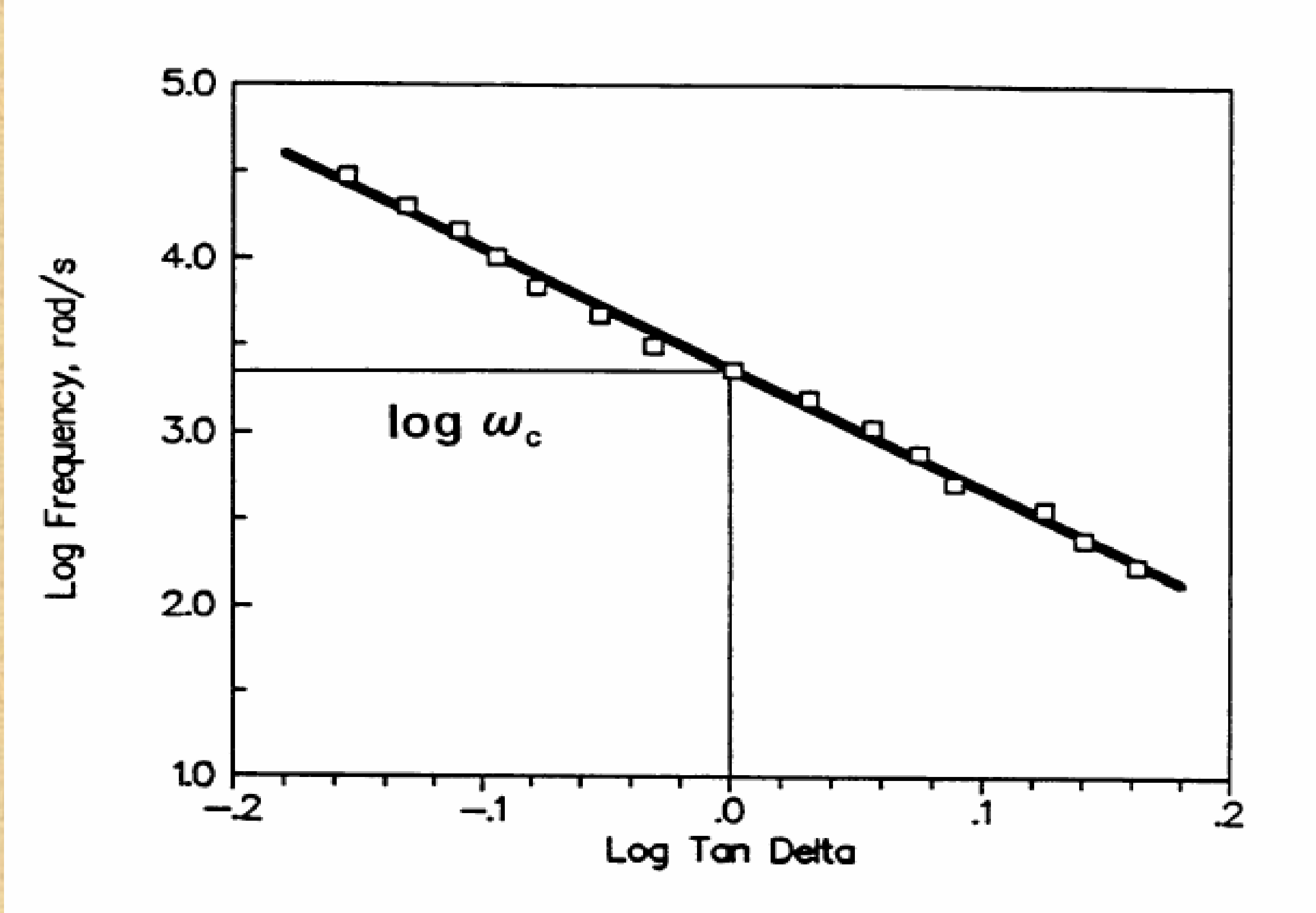
Short-cut Estimation of R and ω_c

- Full mastercurve is not needed to estimate model parameters
  - Shortcuts are especially useful in following aging studies where resources for full generation of mastercurve is impractical

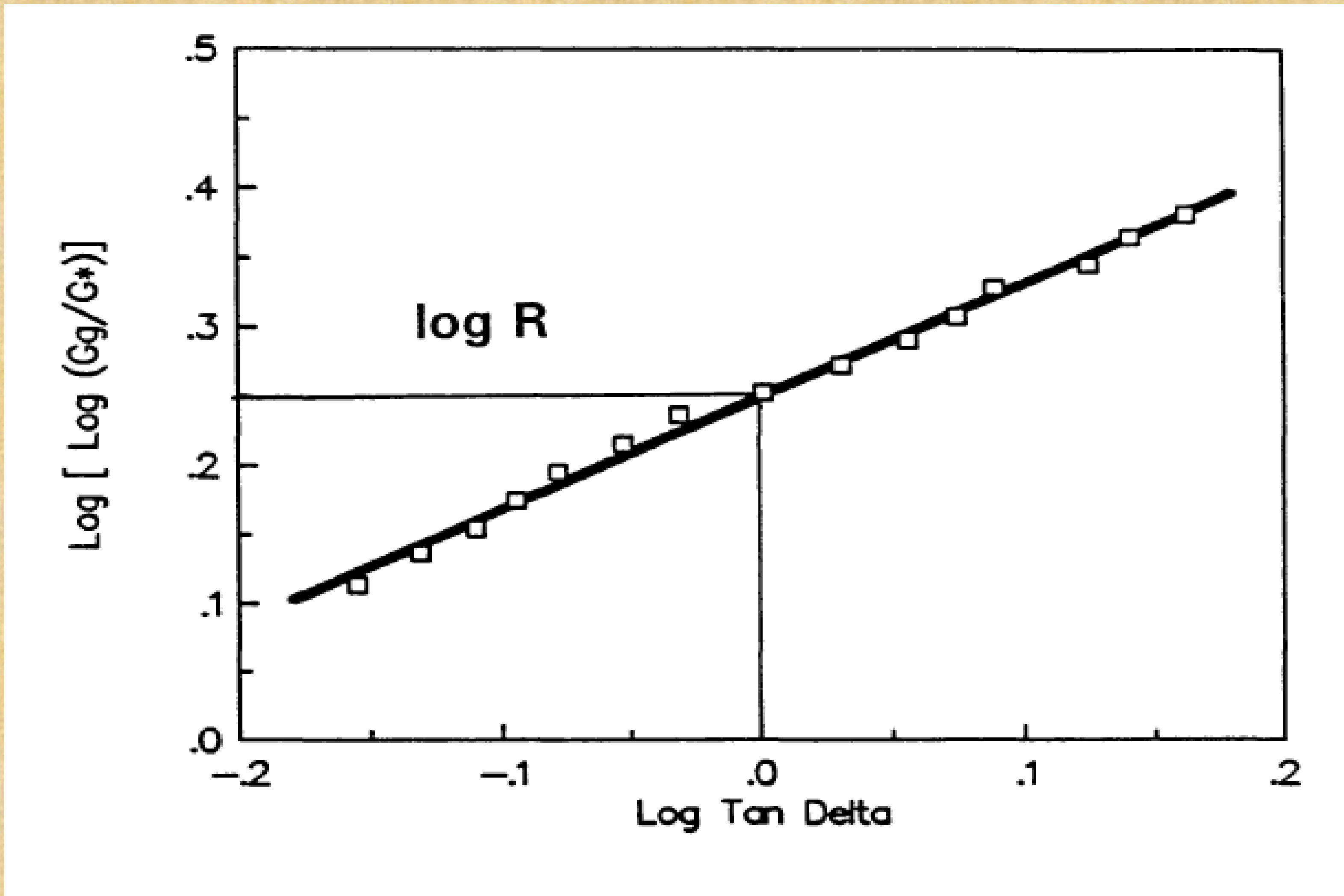
η^* vs. $(1- \delta/90°)^{1.5}$ gives η_0



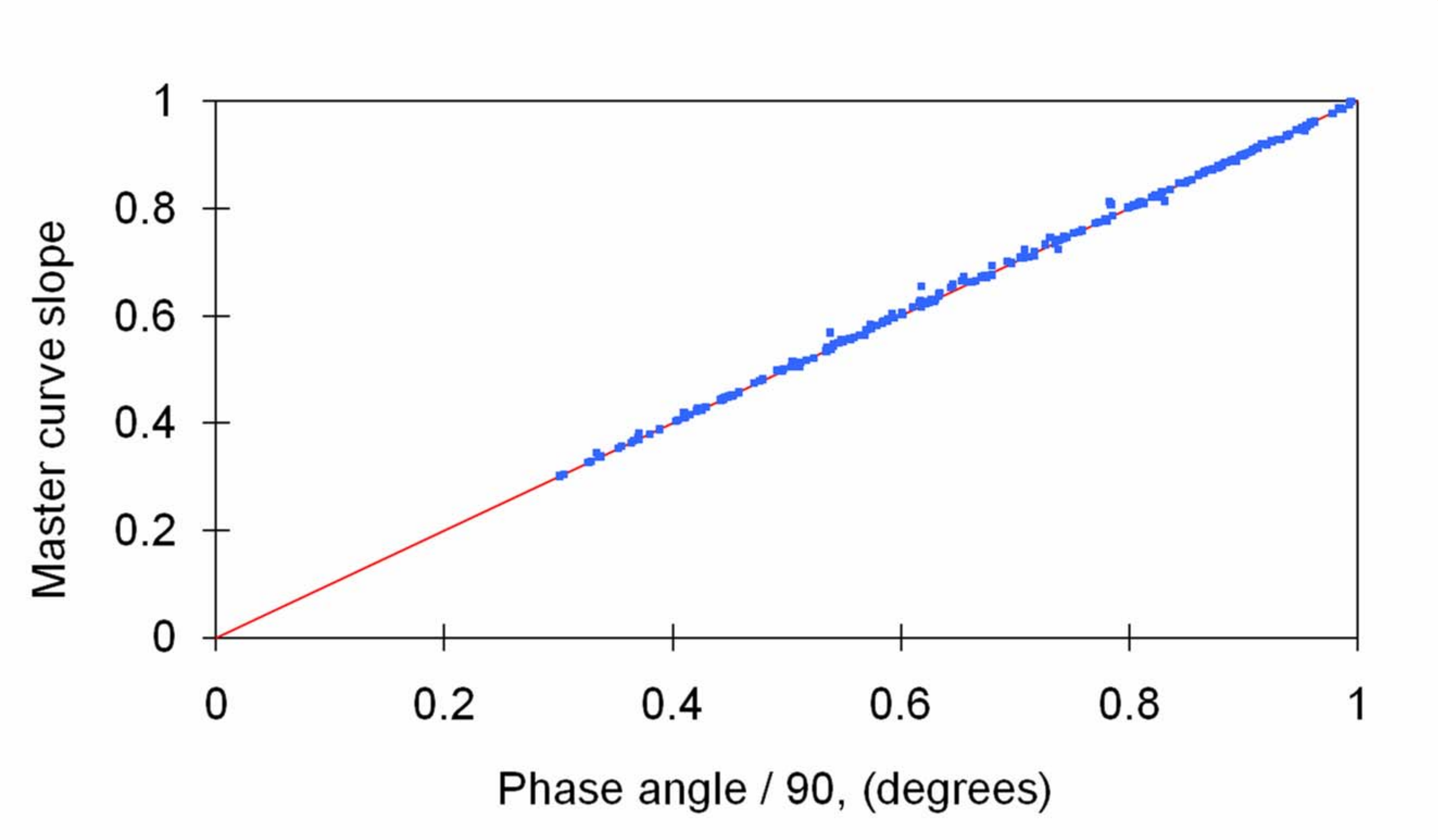
Log ω vs. log tanδ gives ω_c



Log log G_g/G^* vs. Log tan δ



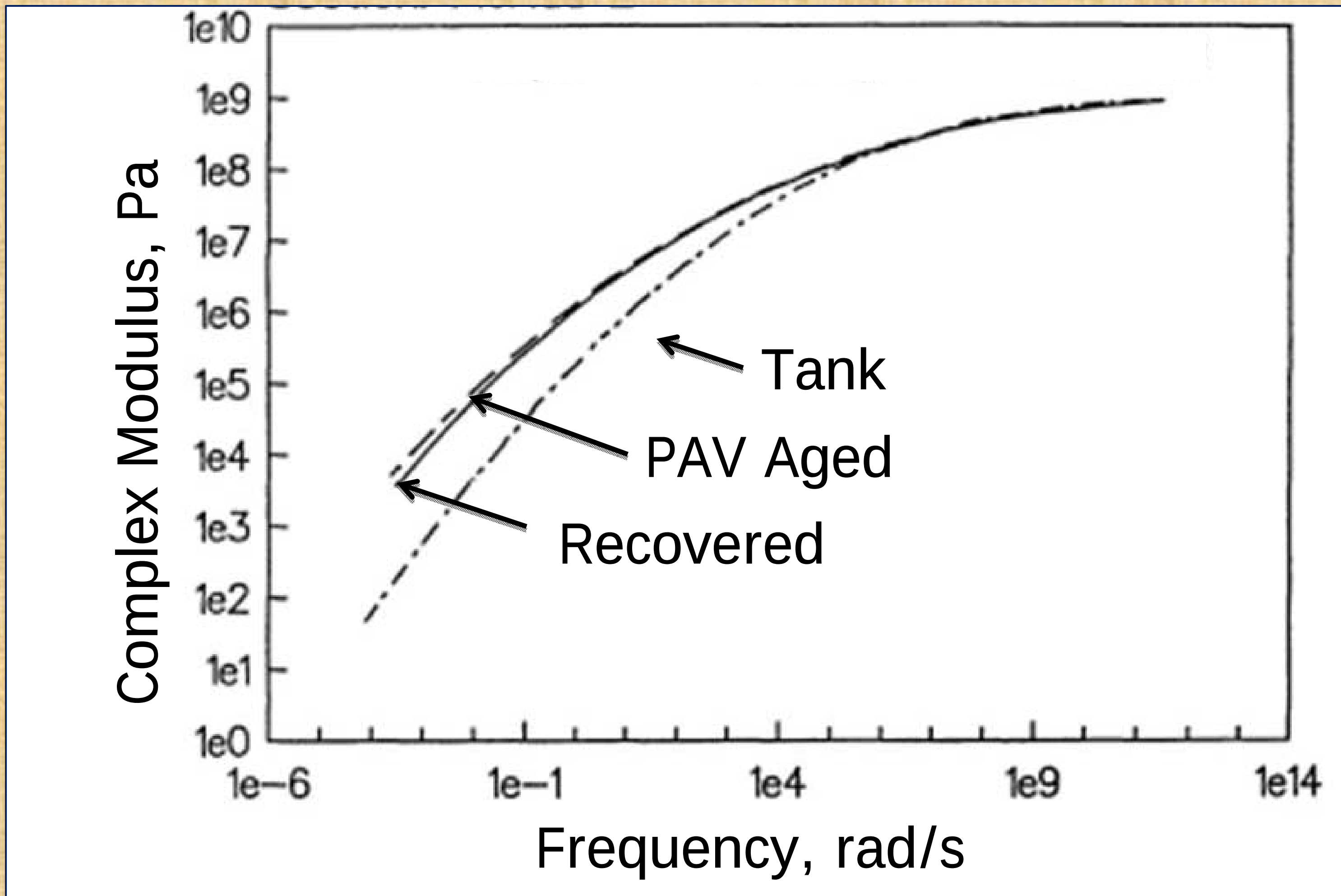
|G*| and δ Interrelation

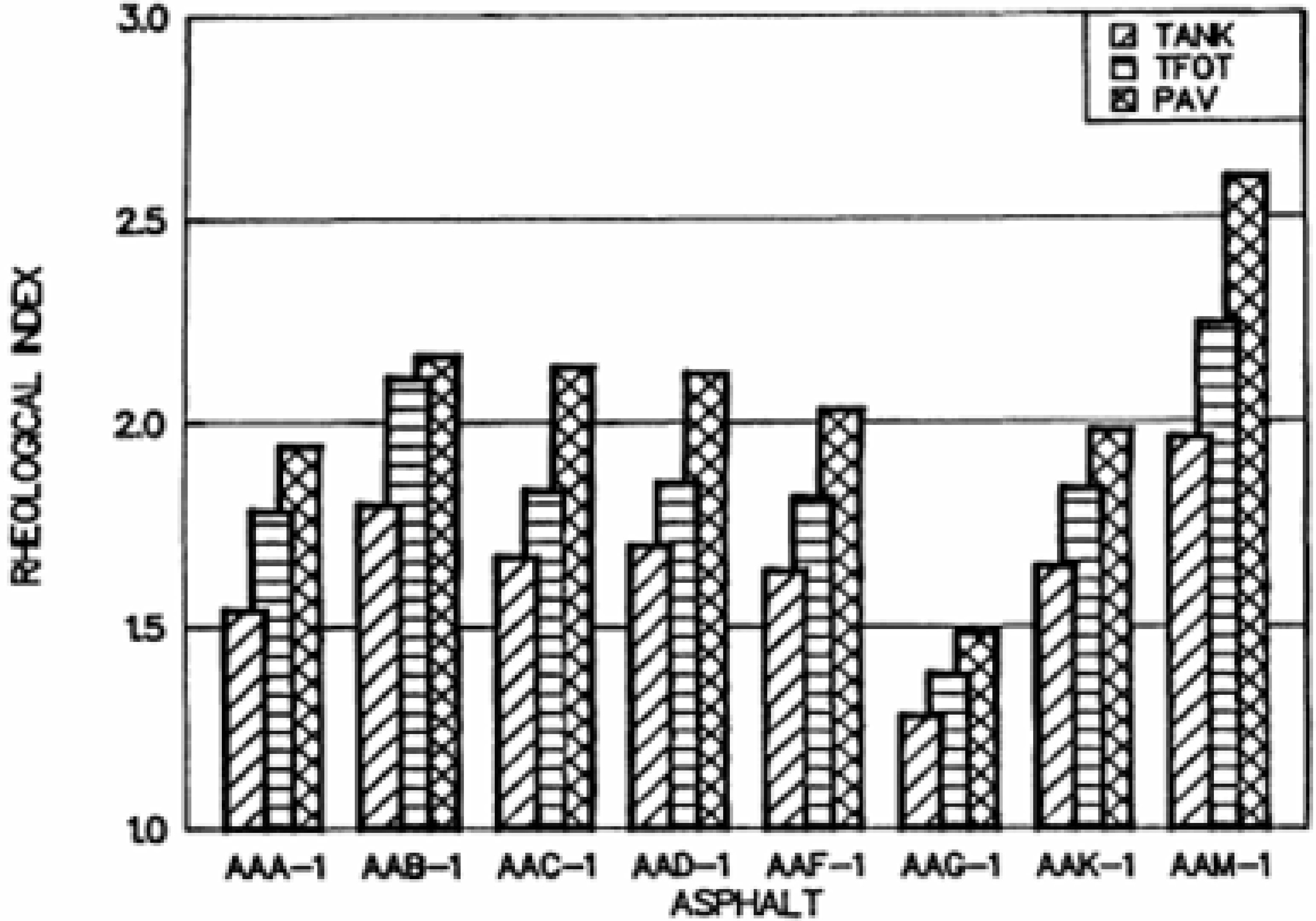


Changes in R and ω_c with Aging

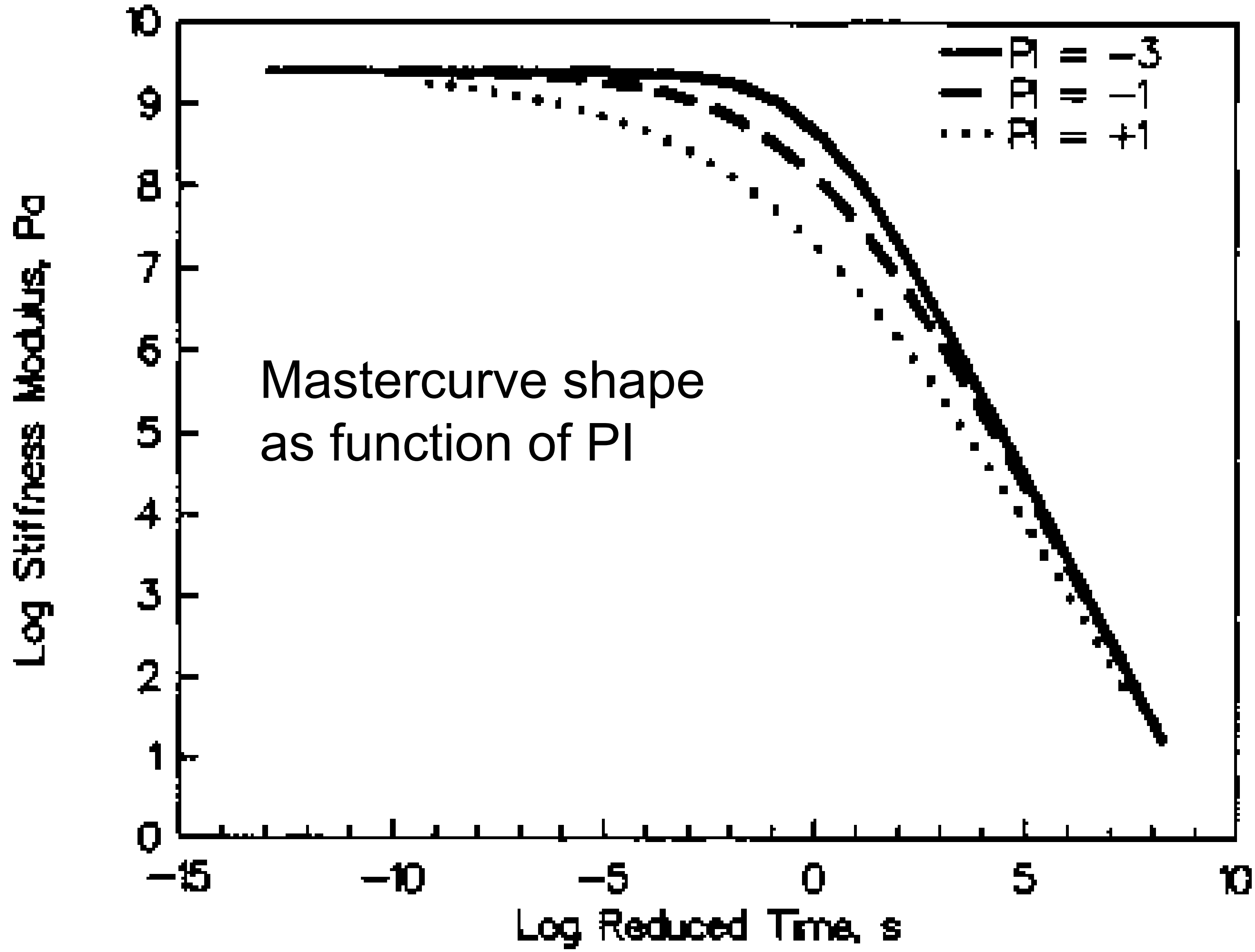
- Change in R reflects change in time dependency and relaxation spectrum
  - Mastercurve flattens with aging
  - R increases
- Change in ω_c reflects change in position of mastercurve
  - Mastercurve shifts to longer times or smaller frequencies
  - Reflects increase in η_0

Change in Mastercurve with Aging





3.0
2.5
2.0
1.5
1.0
RHEOLOGICAL INDEX
TANK
TFOT
PAV
AAA-1
AAB-1
AAC-1
AAD-1
AAF-1
AAG-1
AAK-1
AAM-1
ASPHALT



PI = −3
PI = −1
PI = +1
Mastercurve shape
as function of PI
Log Stiffness Modulus, Pa
Log Reduced Time, s
10
9
8
7
6
5
4
3
2
1
0
−15
−10
−5
0
5
10

Does It Work? Qualified Yes!

- Model was developed for unmodified binders
  - Model works well for unmodified binders if phase angle is less than approximately 70°
  - Need modification to better describe MC as approach 90°
- Model breaks down for modified binders at upper range of application temperatures
  - Elasticity of elastomeric modifiers disrupts shape of mastercurve
  - Need modification for modified materials

CA Model - Discussion

- CA model based on the assumption that the relaxation spectrum is a logistic function
- The model provides simple expressions for $|G^*|$ and δ

$$|G^*(\omega)| = G_g\,[1+(\omega_c/\omega)^{(\log 2)/R}]^{-R/(\log 2)}$$

$$\delta(\omega) = 90\,/\,[1+(\omega_c/\omega)^{(\log 2)/R}]$$

$|G^*|$ and δ Interrelation

- Booij and Thoone demonstrated that the real and imaginary parts are inter-related according to Kramers-Kronig functions; when applied to viscoelastic materials, under certain conditions, the Kramers-Kronig functions can be approximated by the following simple equations:

$$G'(\omega) \approx \frac{\pi}{2}\left(\frac{d\,G''(u)}{d\ln(u)}\right)_{u=\omega} \qquad (1)$$

$$G'(\omega) - G'(0) \approx -\frac{\omega\,\pi}{2}\left(\frac{d\,[G''(u)/u]}{d\ln(u)}\right)_{u=\omega} \qquad (2)$$

$$\delta(\omega) \approx \frac{\pi}{2}\left(\frac{d\ln|G^*(u)|}{d\ln(u)}\right)_{u=\omega} \qquad (3)$$

Relaxation Spectrum Approximation

- According to Williams and Ferry, the relaxation spectrum can be approximated as follows:

$$H(\tau) \approx \frac{\sin m\pi/2}{m\pi/2}\left[G' \frac{d\ln G'}{d\ln\omega}\right]_{\omega=1/\tau} \qquad (5)$$

where G' is the storage modulus and m is the estimated negative slope of $H(\tau)$ on a double logarithmic plot.

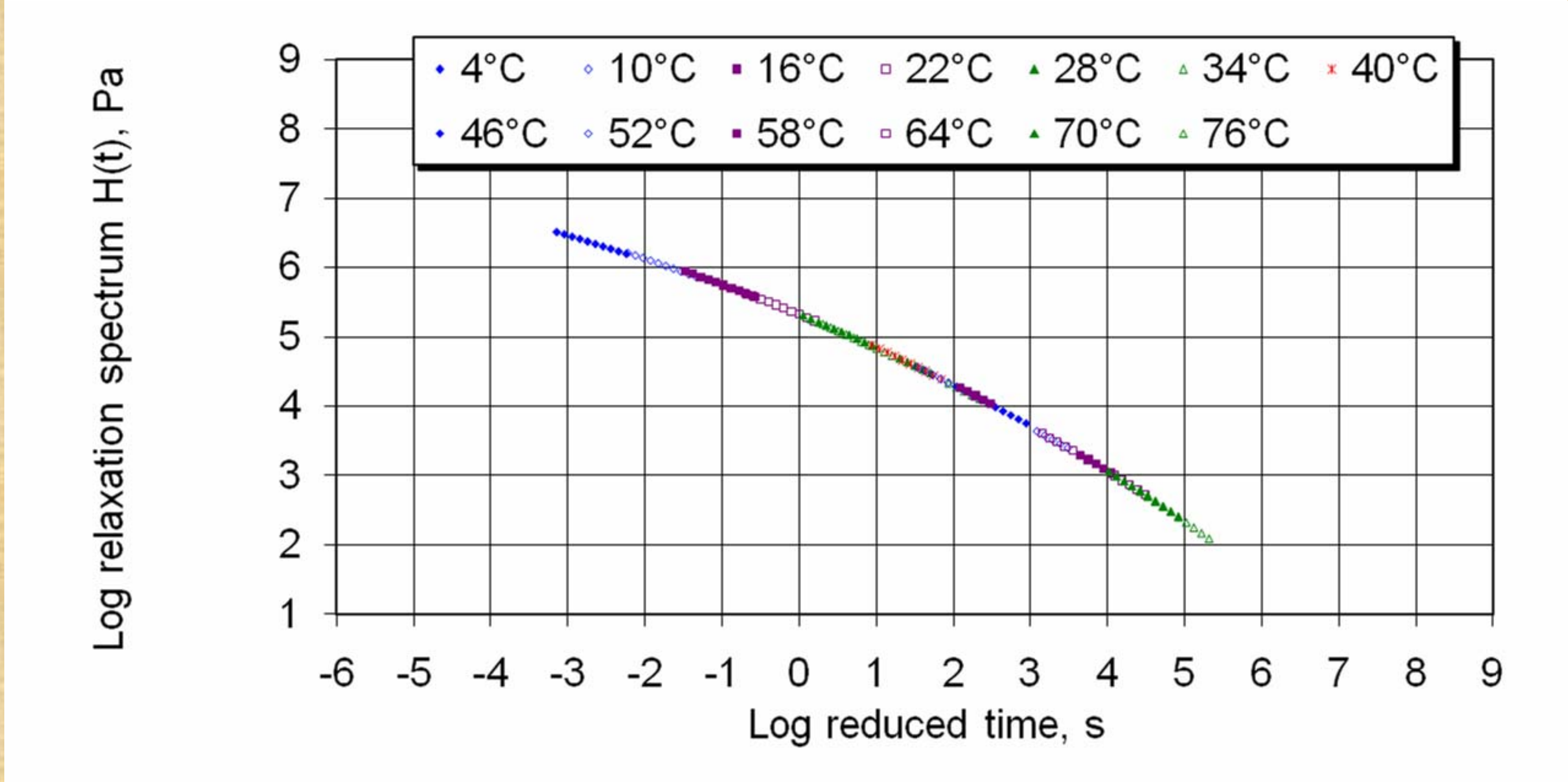
- Booij and Palmen applied equation 4 to equation 5 and obtained the following approximate expression

$$H(\tau) = \frac{\sin 2\delta}{2\delta}|G^*|\left[\frac{2\delta}{\pi} + \frac{d\ln\cos\delta}{d\ln\omega}\right]_{\omega=1/\tau}$$

Relaxation Spectrum Approximation

- This can be further approximated to:

$$H(\tau) \cong \frac{1}{\pi}\left[|G^*|\sin 2\delta\right]_{\omega=1/\tau}$$



CAM Model

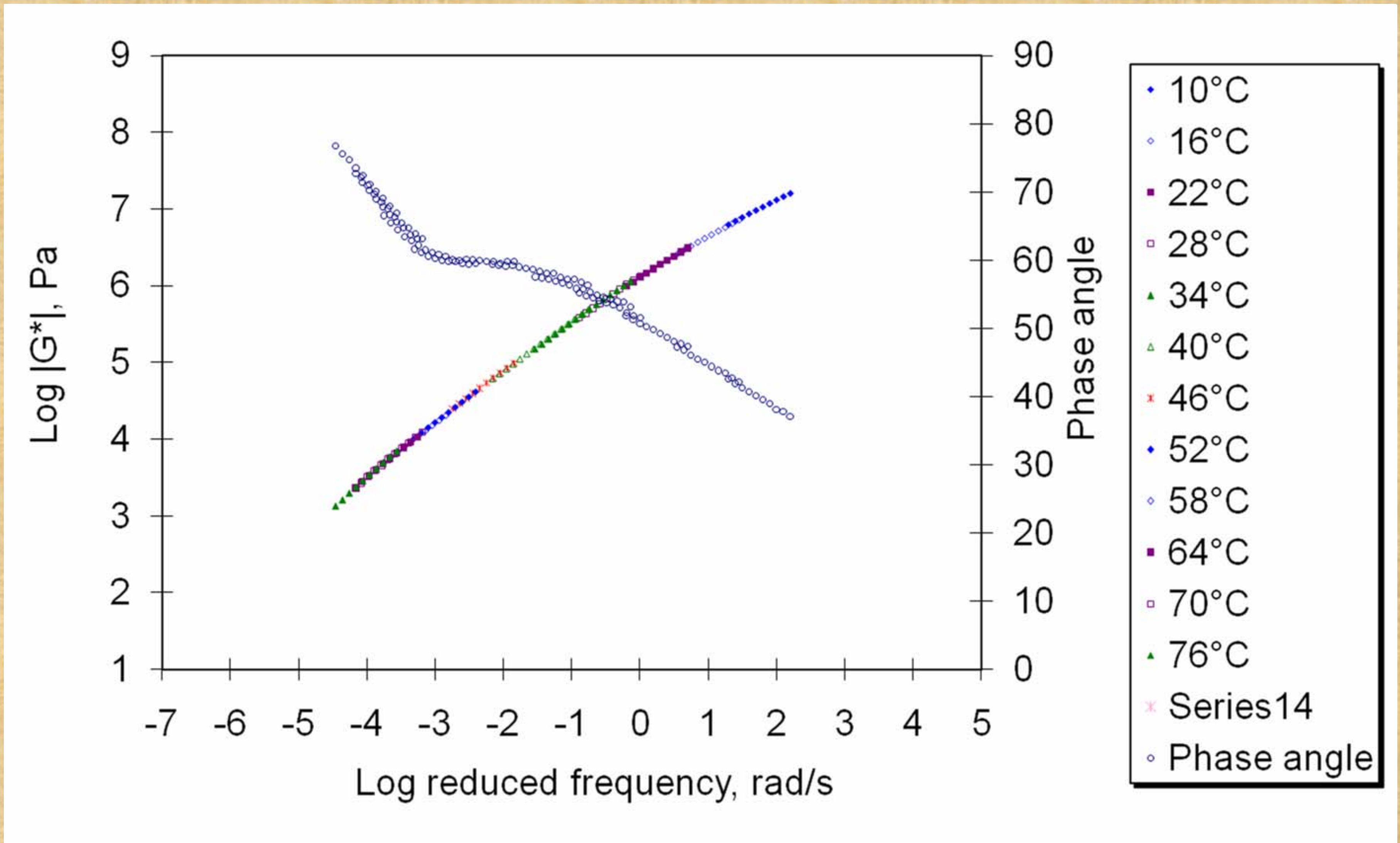
- CA model modified to improve fitting in the lower and higher zones of the frequency range
  - Authors applied Havriliak and Negami model to the |G*| resulting in the following expression:

$$|G^*(\omega)| = G_g [1 + (\omega_c / \omega)^v]^{-\frac{w}{v}}$$

$$\delta(\omega) = 90\, w / [1 + (\omega_c / \omega)^v]$$

- New parameter w describes how fast or how slow the phase angle data converge to the two asymptotes as frequency goes to zero or to infinity
- E.g., as frequency approaches zero, w > 1 characteristic of bitumen that reaches 90 degrees asymptote faster than a bitumen with w < 1

CAM Model



Log |G*|, Pa
Phase angle
Log reduced frequency, rad/s
9
8
7
6
5
4
3
2
1
90
80
70
60
50
40
30
20
10
0
-7
-6
-5
-4
-3
-2
-1
0
1
2
3
4
5
10°C
16°C
22°C
28°C
34°C
40°C
46°C
52°C
58°C
64°C
70°C
76°C
Series14
Phase angle

CAM Model

- Note that Leuseur used Havriliak and Negami model to represent the complex viscosity of bitumens
- By plotting data in Black space, he showed that not all bitumens are thermorheologically simple
  - This was noted previously where vertical shift factors were used in conjunction with the CA model and the vertical shift factors were related to wax content
  - This was also noted when using CAM model
    - Many models fit G" and G" simultaneously

Thermorheological Simplicity

- A linear viscoelastic material is thermorheologically simple if all characteristic functions (retardation, relaxation spectra, etc) meet the same time-temperature dependency
- Further developed by Ferry based on two assumptions:
  - Moduli are proportional to the product of temperature and density
  - Relaxation times depend on a single monomeric friction coefficient
- First condition implies that G''/G', which represents the tangent of the phase angle, is independent of temperature and density

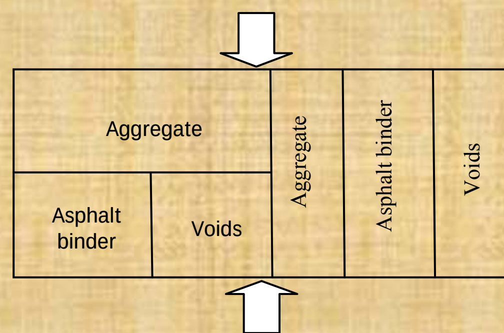
Thermorheological Simplicity

- Accordingly, the proper technique for generating master curves is to first superimpose the phase angle data to generate a set of horizontal shift factors
- $|G^*|$ data is then shifted with these horizontal shift factors and the vertical shift factors, if any, are determined by obtaining a smooth $|G^*|$ master curve

Using Models to Obtain Mixture Properties from Binder Properties (and vice-versa)

Semi-empirical model

- *Christensen et al.* (2003) proposed semi-empirical model to estimate extensional and shear dynamic modulus



$$E_{mix} = Pc\left[E_{agg}V_{agg} + E_{binder}V_{binder}\right] + (1 - Pc)\left[\frac{V_{agg}}{E_{agg}} + \frac{(1 - V_{agg})^2}{E_{binder}V_{binder}}\right]^{-1}$$

$$Pc = \frac{\left(P_0 + \dfrac{VFA \cdot E_{binder}}{VMA}\right)^{P_1}}{P_2 + \left(\dfrac{VFA \cdot E_{binder}}{VMA}\right)^{P_1}}$$

Pc-contact volume

P_0,P_1,P_2-constants

VFA-voids fill with asphalt

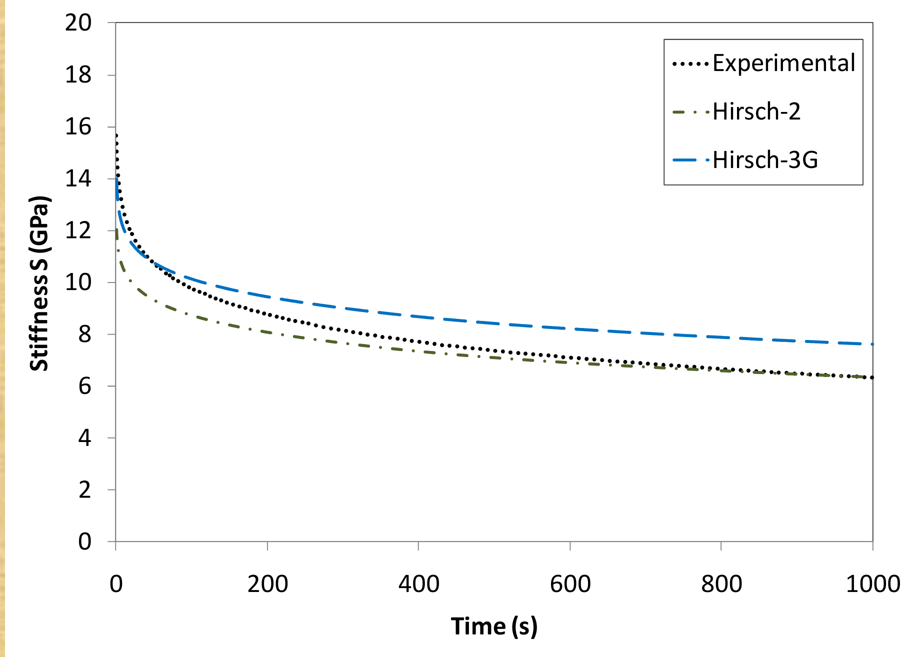
VMA- voids between aggregate

Zofka **(2007) proposed modification of Pc:**

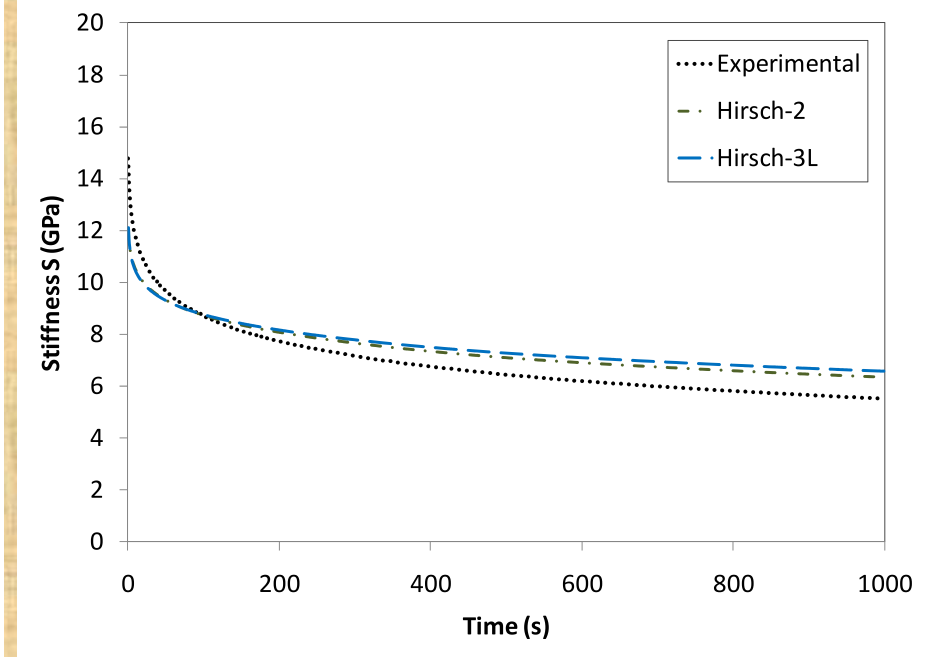
$Pc =$ [illegible] $\ln\left(E_{binder}/a\right) + 0.609$

Forward Problem - Hirsch Model

Granite



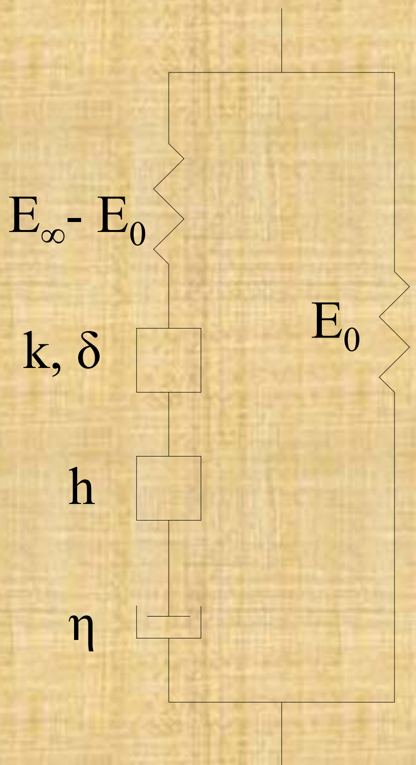
Limestone



Hirsch model for PG 58-34 M1 mixtures T=-24ºC

Analogical Models

➢ 2S2P1D Model (*Olard and Di Benedetto*, 2003)



$$E^*(i\omega\tau) = E_0 + \frac{E_\infty - E_0}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h} + (i\omega\beta\tau)^{-1}}$$

E^*	complex modulus,
E_∞	glassy modulus, $\omega\tau \rightarrow \infty$
E_0	static modulus, $\omega\tau \rightarrow 0$
h, k	exponents such that $0<k<k<1$
δ	dimensionless constant,
β	dimensionless parameter for the linear dashpot
ω	2π*frequency,
τ	characteristic time varying with temperature
t	time

No analytical expression for creep compliance in the time domain for this model.

Analogical Models

- 2S2P1D Model (*Olard and Di Benedetto*, 2003)
- Each mixture had the same parameters δ, k, h and β of the associated binder while only the static and glassy modulus (E_0 and E_∞) and τ_0 seemed to be binder and mixtures specific
- The values of E_0 and E_∞ for the mixtures were in the range of 250 to 1050MPa and 41500 to 45400MPa respectively
- Simple regression of the characteristic time of the mixture on the characteristic time of the corresponding binder at the reference temperature in log scale the authors found that:

$$\tau_{mix}(T) = 10^{\alpha}\,\tau_{binder}(T)$$

α regression coefficient depending on mixture and aging.

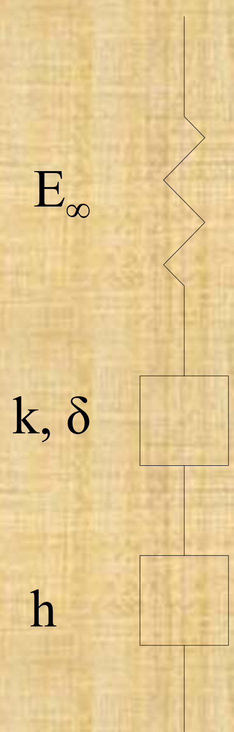
Analogical Models

- 2S2P1D Model (*Olard and Di Benedetto*, 2003)
- From the 2S2P1D model a relationship between the binder and the mix complex moduli was proposed. The expression is independent of the rheological model used to construct it.

$$E^*_{mix}(\omega,T) = E_{0mix} + \left[E^*_{binder}(10^{\alpha}\,\omega,T) - E_{0binder}\right]\frac{E_{\infty mix} - E_{0mix}}{E_{\infty binder} - E_{0binder}}$$

E^*_{mix}	complex modulus of the mixture,
E^*_{binder}	complex modulus of the binder,
$E_{\infty mix}$	glassy modulus of the mixture,
E_{0mix}	static modulus of the mixture,
$E_{\infty binder}$	glassy modulus of the binder,
$E_{0binder}$	static modulus of the binder,
T	temperature,
ω	2π*frequency,
α	regression coefficient depending on mixture and aging.

Huet Model ((Huet, 1963)



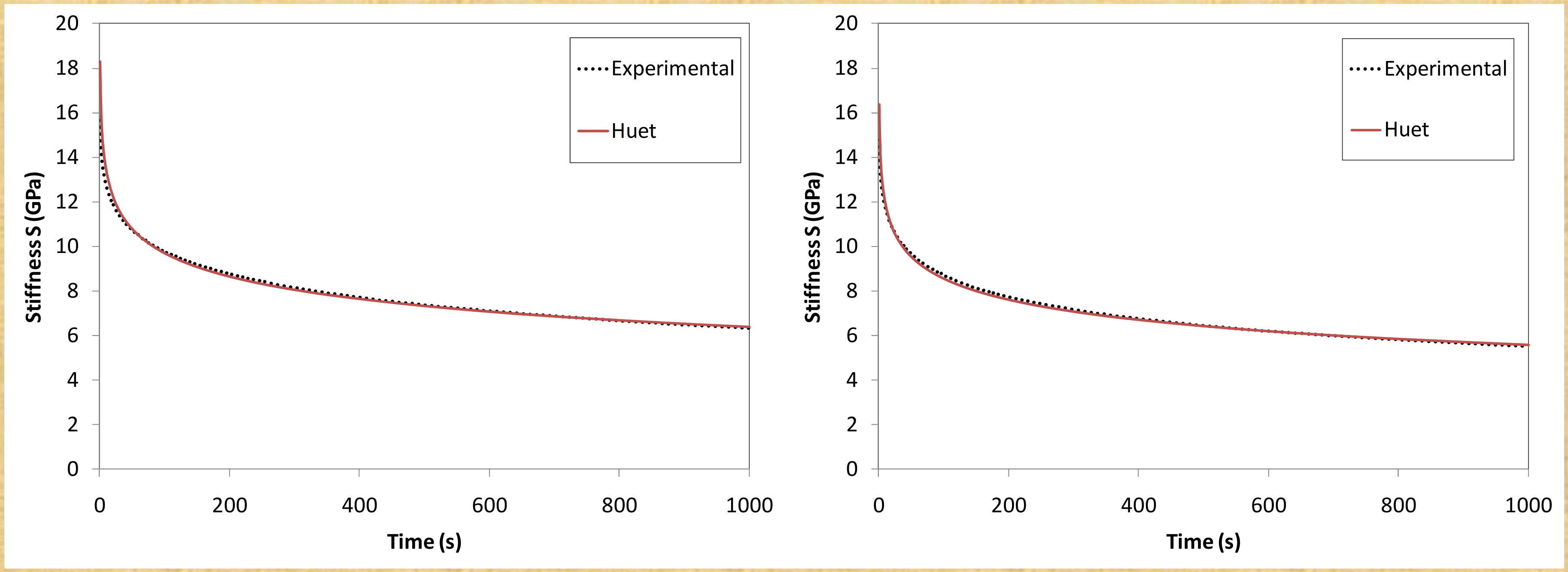
$$D(t) = \frac{1}{E_\infty}\left(1 + \delta\frac{(t/\tau)^k}{\Gamma(k+1)} + \frac{(t/\tau)^h}{\Gamma(h+1)}\right)$$

$$E^*(i\omega\tau) = \frac{E_\infty}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h}}$$

$D(t)$	creep function
E^*	complex modulus,
E_∞	glassy modulus,
h, k	exponents such that $0<k<h<1$
δ	dimensionless constant,
ω	2π*frequency,
τ	characteristic time varying with temperature
t	time
Γ	gamma function:

Forward Problem - Huet Model

Granite **Limestone**



Huet model for PG 58-34 M1 mixtures T=-24ºC

Forward Problem – Huet Model

Huet model parameters for four binder and corresponding granite mixture

Material		δ	k	h	E_∞(MPa)	Log(τ)
Binder	58-34:M1	2.42	0.18	0.60	3000	0.251
	58-34:M2	4.18	0.22	0.62	3000	0.497
	64-34:M1	3.50	0.21	0.64	3000	0.387
	64-34:M2	3.99	0.23	0.64	3000	0.328
Mixtures	58-34:M1:GR	2.42	0.18	0.60	28000	3.420
	58-34:M2:GR	4.18	0.22	0.62	30000	3.675
	64-34:M1:GR	3.50	0.21	0.64	30000	3.547
	64-34:M2:GR	3.99	0.23	0.64	29001	3.523

$$D_{binder}(t) = \frac{1}{E_{\infty\_binder}}\left(1+\delta\frac{(t/\tau_{binder})^k}{\Gamma(k+1)}+\frac{(t/\tau_{binder})^h}{\Gamma(h+1)}\right)$$

$$D_{mix}(t) = \frac{1}{E_{\infty\_mix}}\left(1+\delta\frac{(t/\tau_{mix})^k}{\Gamma(k+1)}+\frac{(t/\tau_{mix})^h}{\Gamma(h+1)}\right)$$

Forward Problem – Huet Model

- Based on the strong linear correlation found (R^2=0.98-0.99 for all the binders-mixtures), the following expression can be written to relate the characteristic time of the binders and corresponding mixtures with similar mix designs:

$$\tau_{mix} = 10^{\alpha}\,\tau_{binder}$$

τ_{binder}	characteristic time of binder,
τ_{mix}	characteristic time of mixture,
α	regression parameter, may depend on mix design

Forward Problem – Huet Model

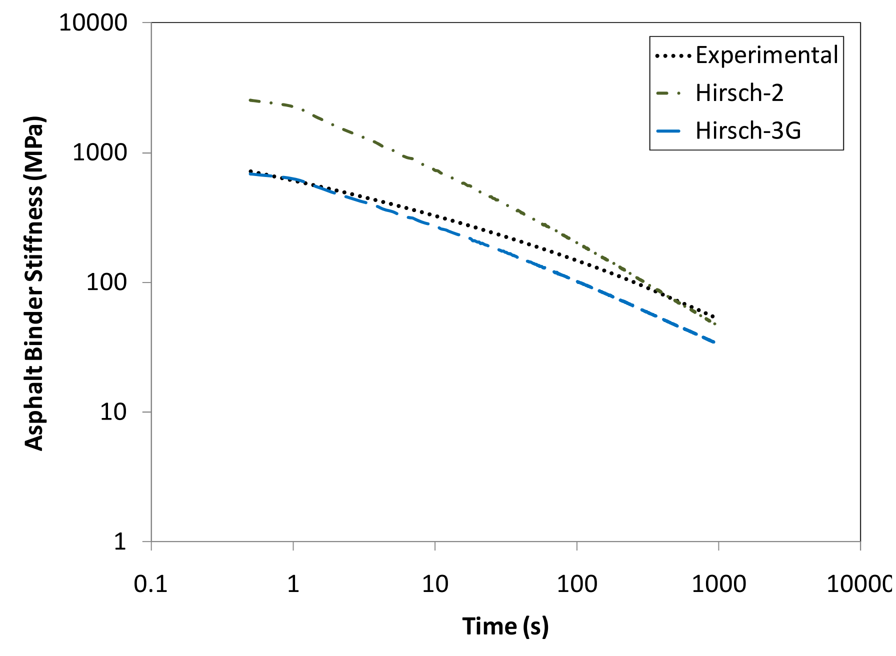
$$D_{mix}(t) = D_{binder}(t/10^{\alpha})\frac{E_{\infty\_binder}}{E_{\infty\_mix}}$$

$$S_{mix}(t) = S_{binder}(t/10^{\alpha})\frac{E_{\infty\_mix}}{E_{\infty\_binder}}$$

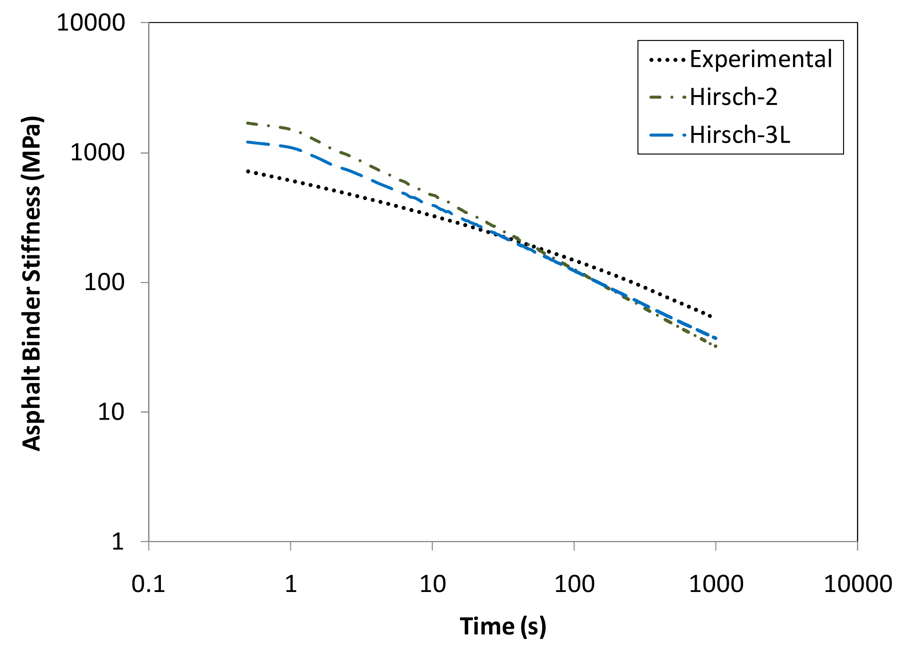
$D_{mix}(t)$	creep compliance of mixture,
$D_{binder}(t)$	creep compliance of binder,
$S_{mix}(t)$	creep stiffness of mixture,
$S_{binder}(t)$	creep stiffness of binder,
E_{∞_mix}	glassy modulus of mixture,
E_{∞_binder}	glassy modulus of binder,
α	regression parameter which may depend on mix design,
t	time

Inverse Problem- Hirsch Model

Granite



Limestone



Hirsch model for PG 58-34 M1 mixtures T=-24ºC

Inverse Problem - Huet Model

Based on the findings of Forward Problem:

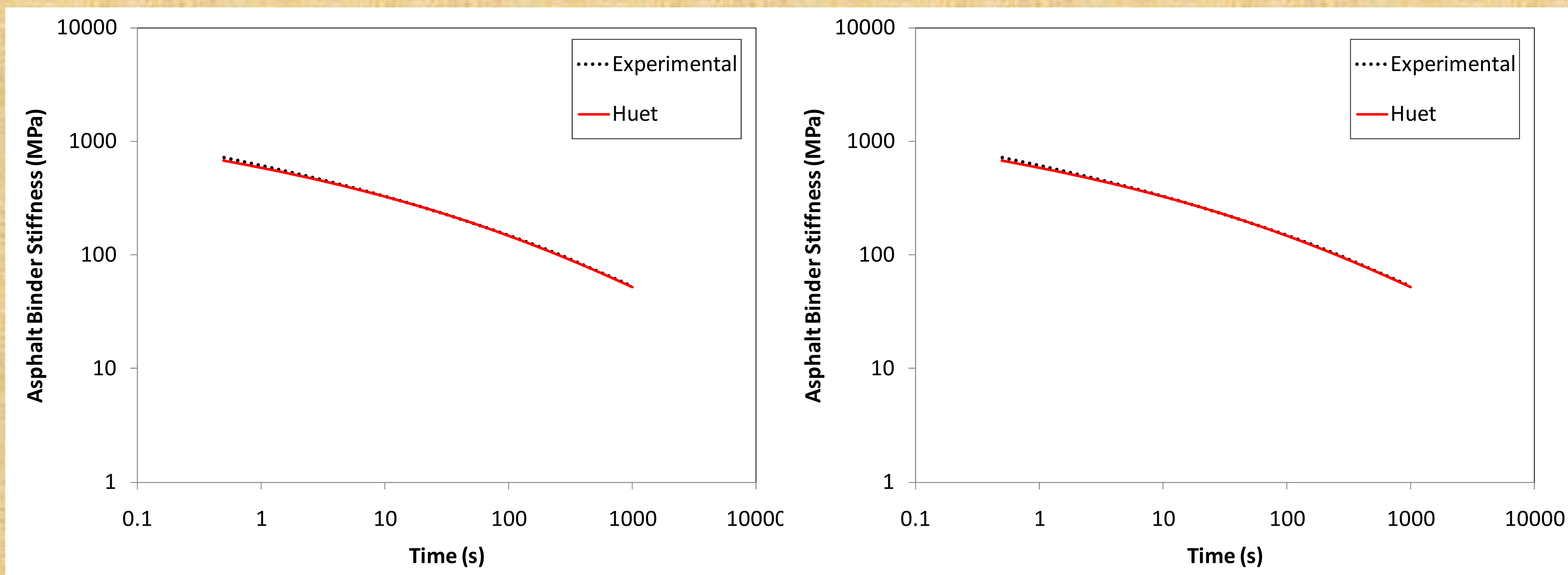
$$\tau_{binder} = 10^{-\alpha} \tau_{mix}$$

$$S_{binder}(t) = S_{mix}(t / 10^{-\alpha}) \frac{E_{\infty\_binder}}{E_{\infty\_mix}}$$

$S_{mix}(t)$	creep stiffness of mixture,
$S_{binder}(t)$	creep stiffness of binder,
E_{∞_mix}	glassy modulus of mixture,
E_{∞_binder}	glassy modulus of binder,
α	regression parameter which may depend on mix design,
τ_{binder}	characteristic time of binder,
τ_{mix}	characteristic time of mixture,
t	time.

Inverse Problem - Huet Model

Granite **Limestone**



Huet model for PG 58-34 M1 mixtures T=-24ºC

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