Application of Rheological Models to Modified Binders

48th Petersen Asphalt Research Conference

Organized by Western Research Institute

July 11-13 2011, Laramie, WY

Geoffrey M. Rowe, Abatech

Gaylon Baumgardner, Paragon

Mark. J. Sharrock, Abatech

Objectives

- To review types of models applied to modified binders
  - Discuss models
  - How shifting is done
  - Treatment of temperature
  - Treatment of BBR data
  - Shifting of DSR
- Review some changes in material properties
  - To explain what we are working on with regard to model development
  - To discuss how this applies to modified binders
  - What information may be obtained
  - How does our model fit work – limits
- Summary

Models is a “work in progress”

- No perfect model
- No answer that works well for all binders
- Contributions from many workers still needed

Types of rheological models

- Models to describe master-curves can generally be considered as:
  - functional forms (or equation)
  - mechanical element

Mechanical element models

1963	Huet Model
1967	Huet–Sayegh Model
1980's	Relaxation or retardation spectra/Prony series
1987	The 2S2P1D Model
2001	Di Benedetto and Neifar (DBN) Model

+ others

If constructed well forms a basis for computations in software etc

Functional forms and mechanical element models

- Functional forms and mechanical element models have “parameters” that are relatable to structural features used in numerical analysis methods
  - For example
    - MEPDG – E* model
    - CAM model – used in the assessment of critical cracking temperature of binder (AASHTO PP42/ASTM 6816)
    - Power law – low temperature cracking calculation of mix with IDT

Functional forms

- These generally offer a continuous models
- Can describe the properties over a very wide range of temperatures and frequencies
- The fitted functions can also be used to smooth and extend results thus providing better data for the subsequent fitting of mechanical models

Functional forms – some examples

Binders	
1969	Jongepier and Kuilman's
1969/72	Dobson's Model
1974	Dickinson and Witt's
1992	Christensen and Anderson (CA)
1999	Christensen, Anderson and Marasteanu (CAM)
2002	Matching Function - Al-Qadi and co-workers
Mixes	
1981-2005	Sigmoidal Model (Witczak)
2000	Hirsch model (Asphalt mixes)
Both binder/mix	
2001	NCHRP Report 429 (Bahia et al.)
2009	Generalized Logistic Sigmoidal Sigmoid (RBS)

+ others

Time-temperature superposition

- While a model might describe properties well at a single temperature we need a robust method to describe the time temperature shift parameters

Time-temperature superposition

- Free or model shifting
- Descriptive shift functions
  - Arrhenius
  - WLF
  - Polynomial
  - A+VTS
  - Kaelble

Shifting

- Free
- Functional form
- Functional form with descriptive shift function
- Shift function

Approach

- Use free shifting
- Adopt functional form approach
  - Descriptive information for sigmoid shape
    - G_e tends to zero for visco-elastic liquids
    - non-symmetrical
  - Sigmoid form for shift factor function
    - Inflection point similar to definition of T_d in SHRP A-369 report
- Use “Rouse” density adjustment

Rouse temperature adjustment

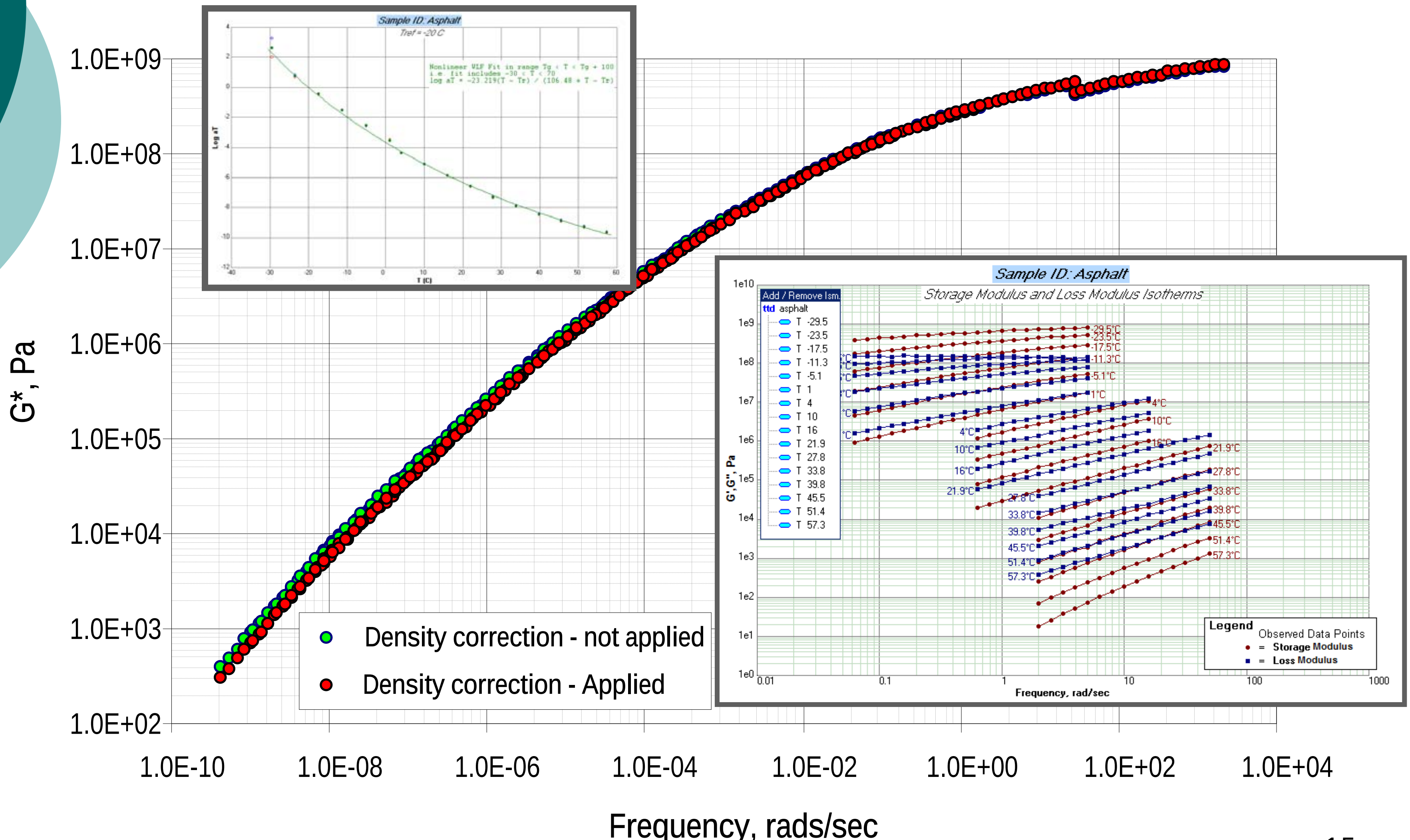
- What is this?

Normalized for density - vertical shift

- To enable all properties to be reported at the density corresponding to the reference temperature (Rouse, 1953)

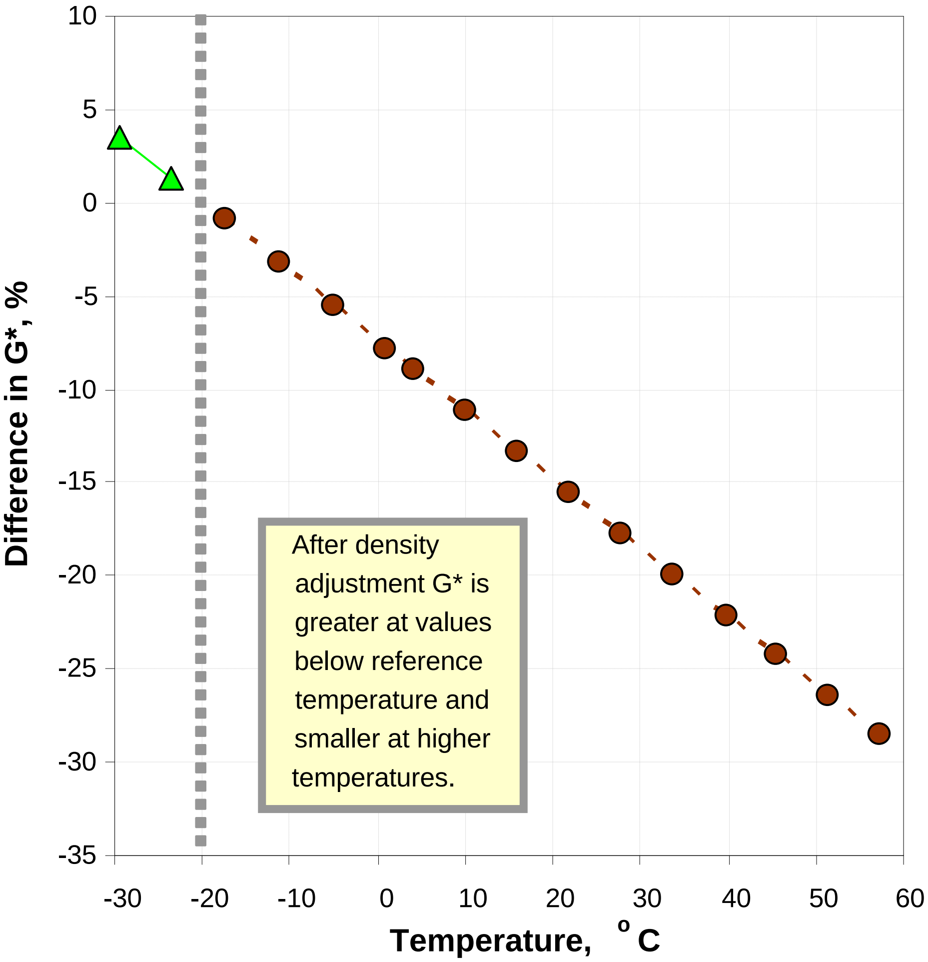
$$G(T_R, t) = \frac{T_R}{T} \frac{\rho(T_R)}{\rho(T)} G\left(T, \frac{t}{a_T}\right)$$

Effect of density adjustment on G*



Effect of density adjustment on G*

- Difference looks insignificant on log scale
- If a 50ºC shift is considered from the reference temperature then the error is -18.5% which equates to a temperature difference of approximately 1.14ºC
- Density correction is significant in our work with binder master curves



Just a word on other sigmoid methods

- Various other sigmoid forms used
  - MEPDG
  - NCHRP Report 429
  - Hirsch
- Problem with sigmoid fits is that they have some limited capability
  - Limits, symmetric, etc.
- Sigmoids only describe a sigmoid
  - Binders often have more complex behavior – ultimately we still need better models?!

What are characteristics

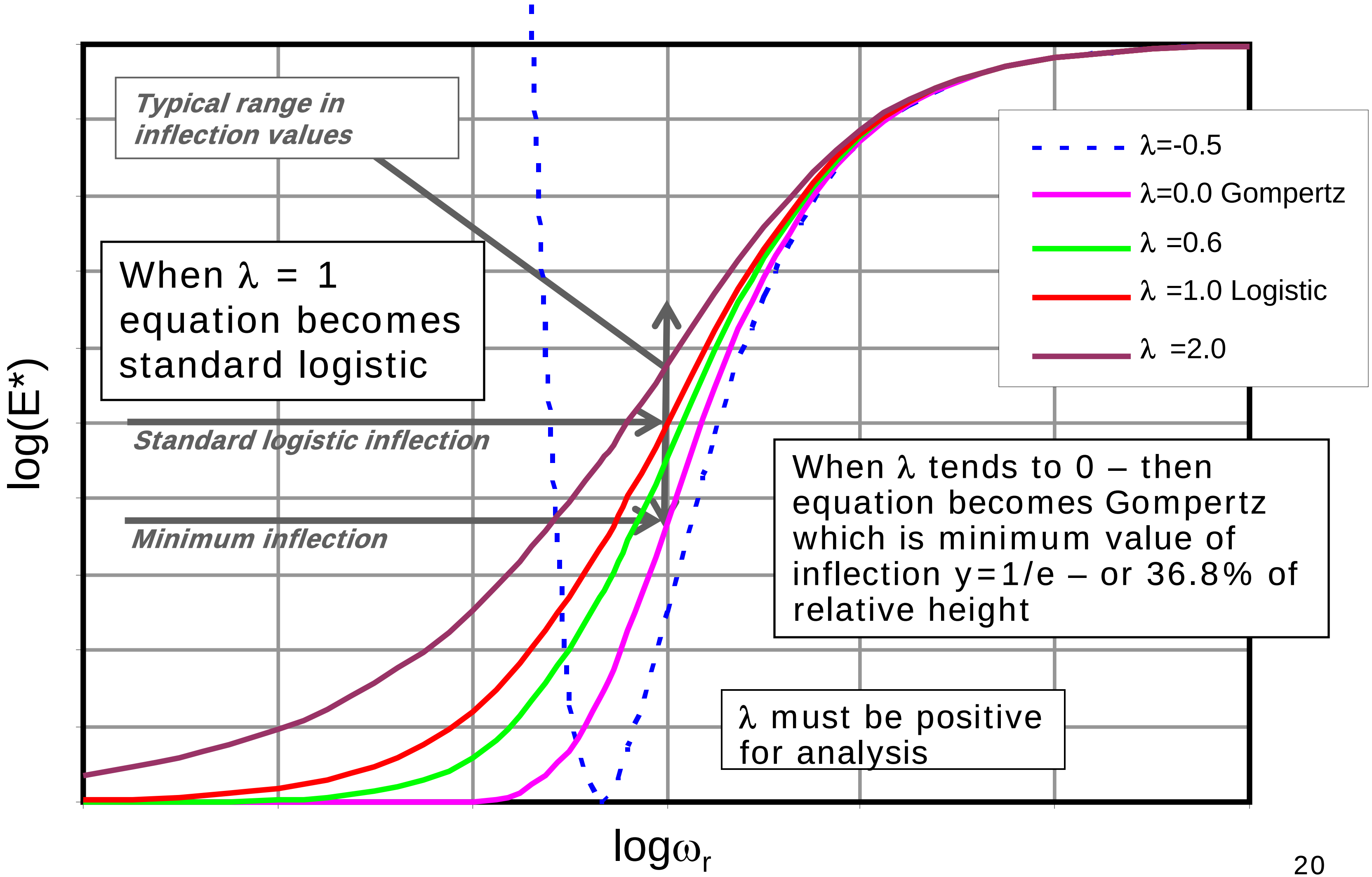
- Solid type behavior
- Phase angle will peak
- Two asymptotes – equilibrium modulus and glassy modulus
- Two crossover frequencies

Non-symmetric sigmoid

$$\log G^* = \delta + \frac{\alpha}{\left[1 + \lambda e^{(\beta + \gamma(\log \omega_r))}\right]^{1/\lambda}}$$

*E**	*complex extensional modulus*
ω_r	*reduced frequency in rads/sec*
δ	log equilibrium modulus, log G_e
α	log G_e – log G_g
G_g	glassy modulus
λ, β, γ	fitting parameters
$10^{(-\beta/\gamma)}$	inflection point/frequency
λ	controls height of inflection point

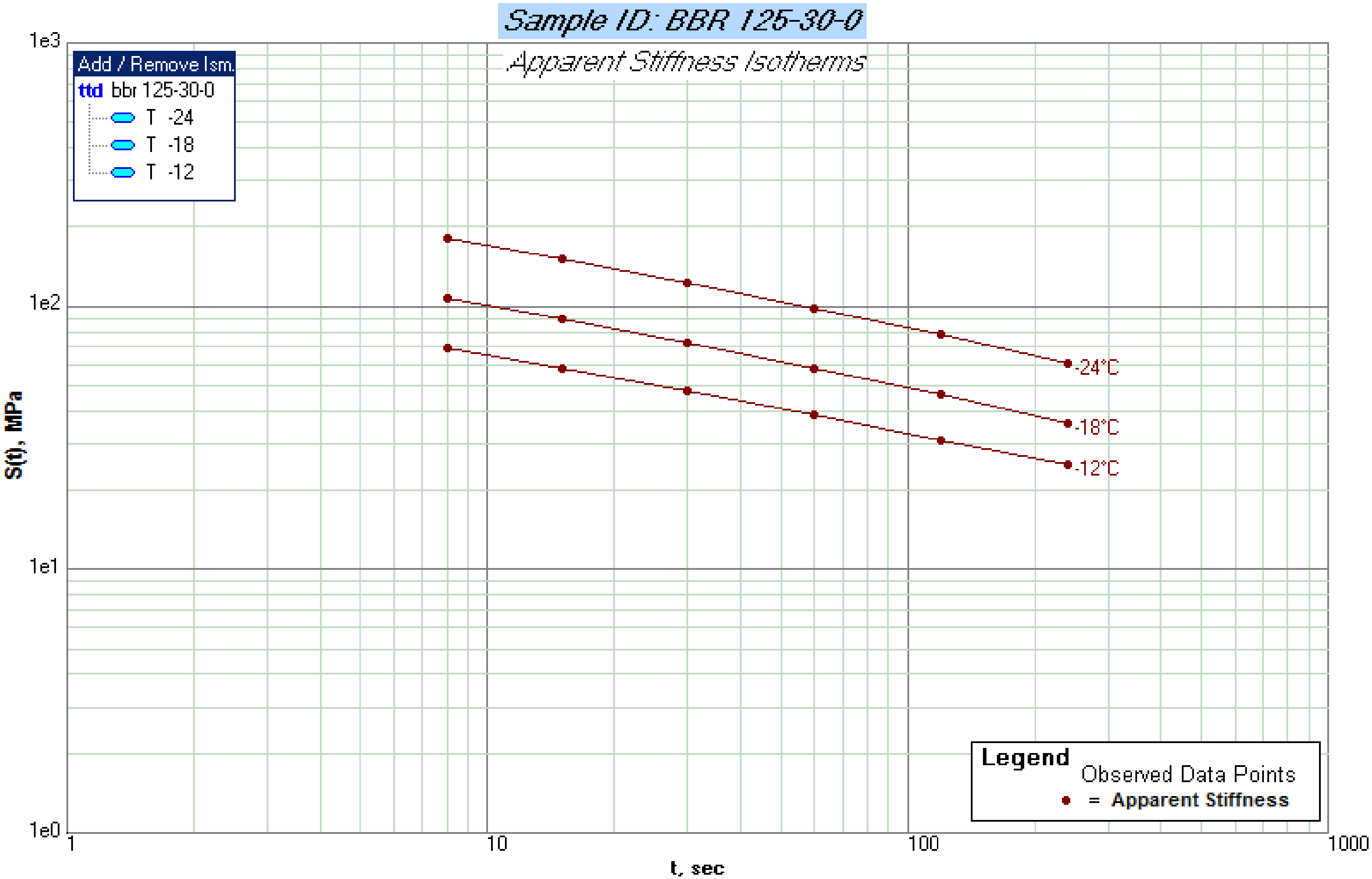
Non-symmetric sigmoid, λ



Example with high modification

- Data files
  - BBR -12, -18, -24^{o}C
  - DSR 0, 15, 3, 45, 60, 75, 90, 105, 120 and 135^{o}C
- BBR data converted to G', G"
- Combined data then shifted
  - Free shifting
  - Used complex modulus shift

BBR data



Sample ID: BBR 125-30-0
Apparent Stiffness Isotherms
Add / Remove Ism.
ttd bbr 125-30-0
T -24
T -18
T -12
-24°C
-18°C
-12°C
Legend
Observed Data Points
= Apparent Stiffness
1e3
1e2
1e1
1e0
S(t), MPa
1
10
100
1000
t, sec

BBR S(t) to G'G" conversion (1)

- Fit the BBR data is fitted with the CA, CAS and CAM model and determine the fit with the lowest error. This master-curve is adopted.
  - If material is a filled product then fit will most likely be CAS – enables higher glassy modulus
  - For most neat binders fit most likely will be CAM
- Hopkins and Hamming method is used to convert the master curve to the relaxation modulus E(t).

BBR S(t) to G'G" conversion (2)

- The Hopkins and Hamming algorithm provides a numerical solution to the convolution integral required to convert BBR creep stiffness (compliance, $D_{(\xi)}$, is first computed using model parameters, $D_{(\xi)} = 1/\ S_{BBR(\xi)}$) to relaxation modulus.
- The convolution integral is:

$$\int_0^t E(\xi)D(t-\xi)d\xi = t$$

BBR S(t) to G'G" conversion (3)

Hopkins and Hamming – numerical solution

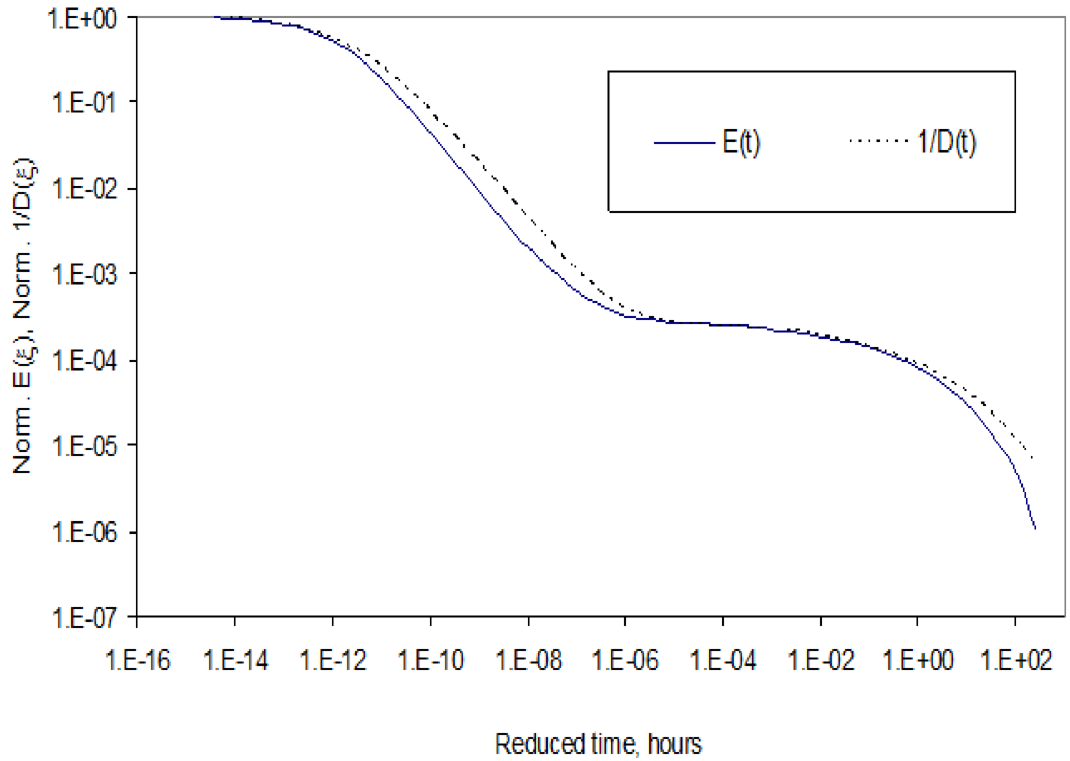
$$E(t_{n+\frac{1}{2}}) = \frac{t_{n+1} - \sum_{i=0}^{n-1} E(t_{i+\frac{1}{2}})\left[f(t_{n+1} - t_i) - f(t_{n+1} - t_{i+1})\right]}{f(t_{n+1} - t_n)}$$

$$f(t_{n+1}) = f(t_n) + \frac{1}{2}\left[D(t_{n+1}) + D(t_n)\right]\left[t_{n+1} - t_n\right]$$

The initial value f(t) at zero time is set as zero.

BBR S(t) to G'G" conversion (4)

- If E(t) is just taken as 1/D(t) then some significant errors can be introduced
- Example is PIB



BBR S(t) to G'G" conversion (5)

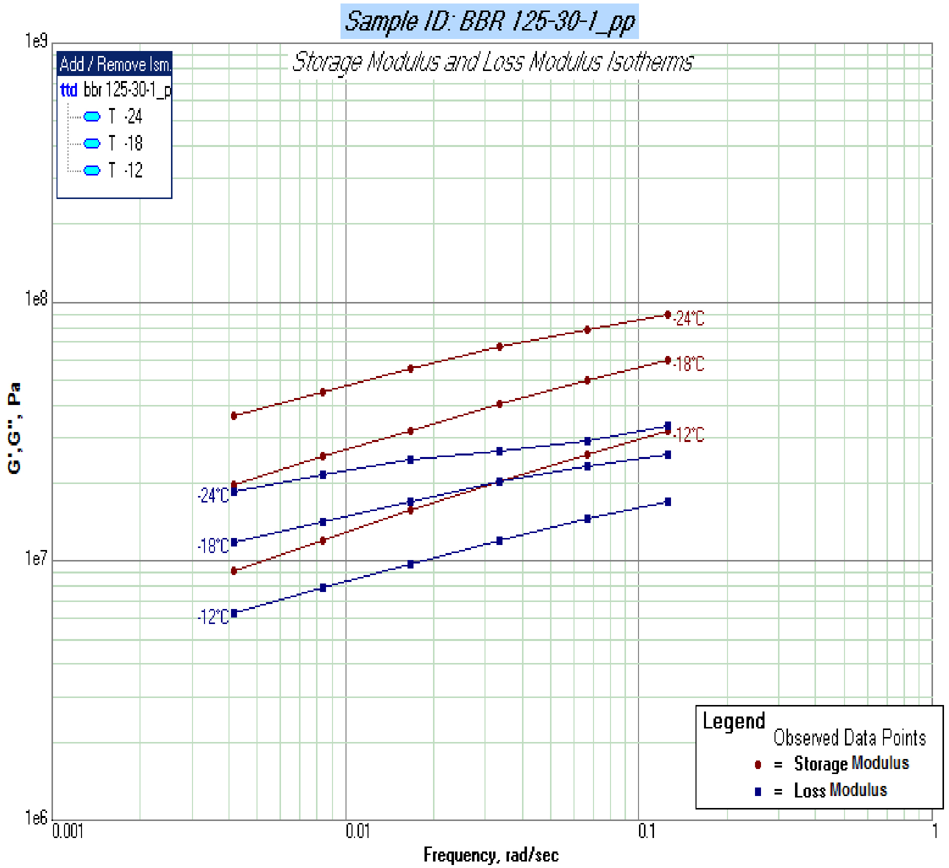
- Fit the E(t) data with a CAM model using the Glassy modulus determined from the previous fitting. This gives a function which describes a E(t) fit and essentially allows for a different glassy modulus if considered necessary from the earlier step.
- Calculate the discrete spectra for the E(t) fitted function.
- The reciprocal of the observed times are the substituted into the function to estimate the E', E" data points.

BBR S(t) to G'G" conversion (6)

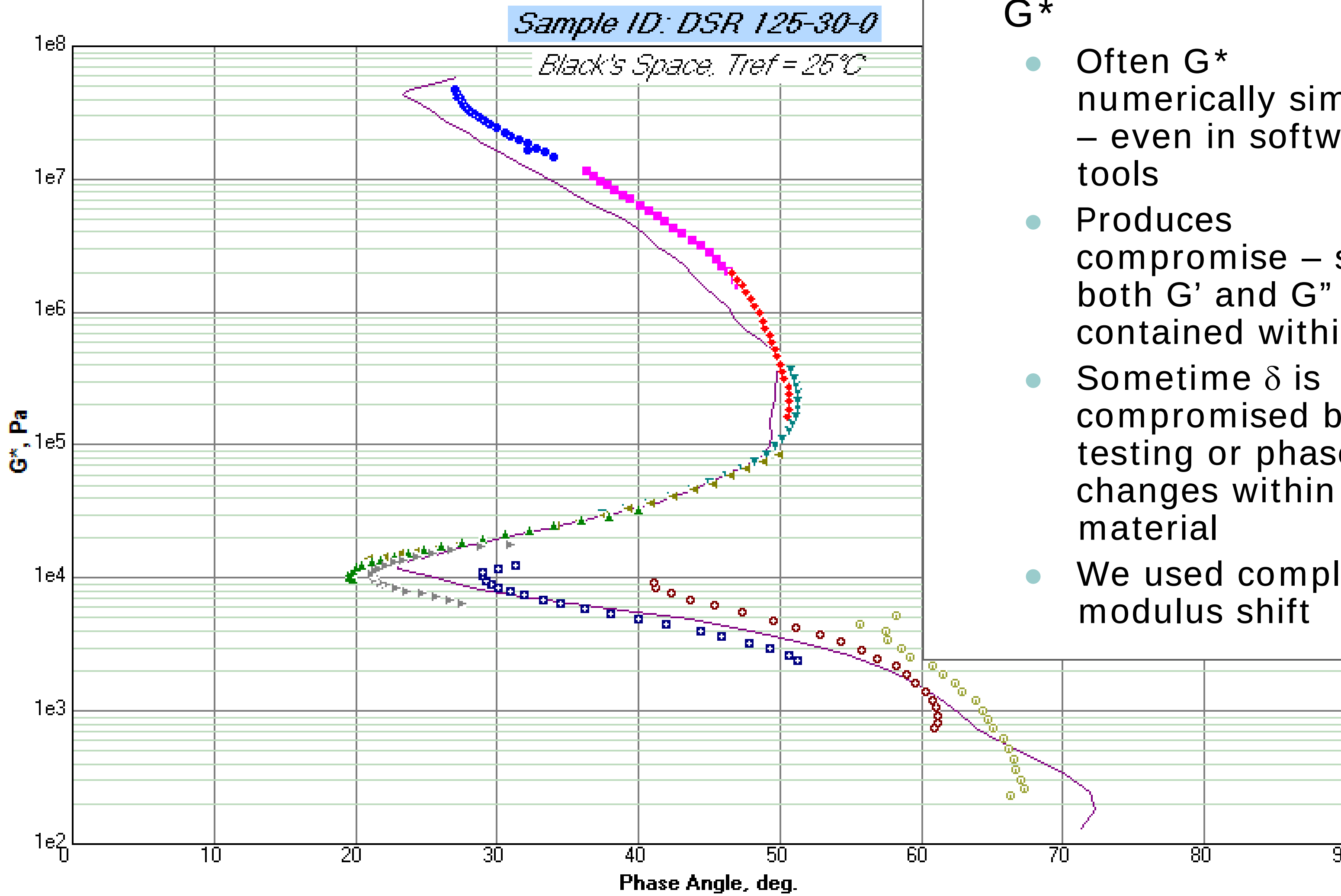
- The data points are shifted using the original shift values obtained along with a reverse density correction (Rouse) to obtain dynamic isotherms corresponding to the original data.
- Shear data is then obtained by converting to G', G" with a Poisson's ratio of 0.5.
  - This basically assumes no volume change which is reasonable for a liquid binder.

BBR S(t) to G'G" conversion (7)

- Process is implemented in software since it is quite numerically intensive
- RESULT→
- Can now merge this with other dynamic data

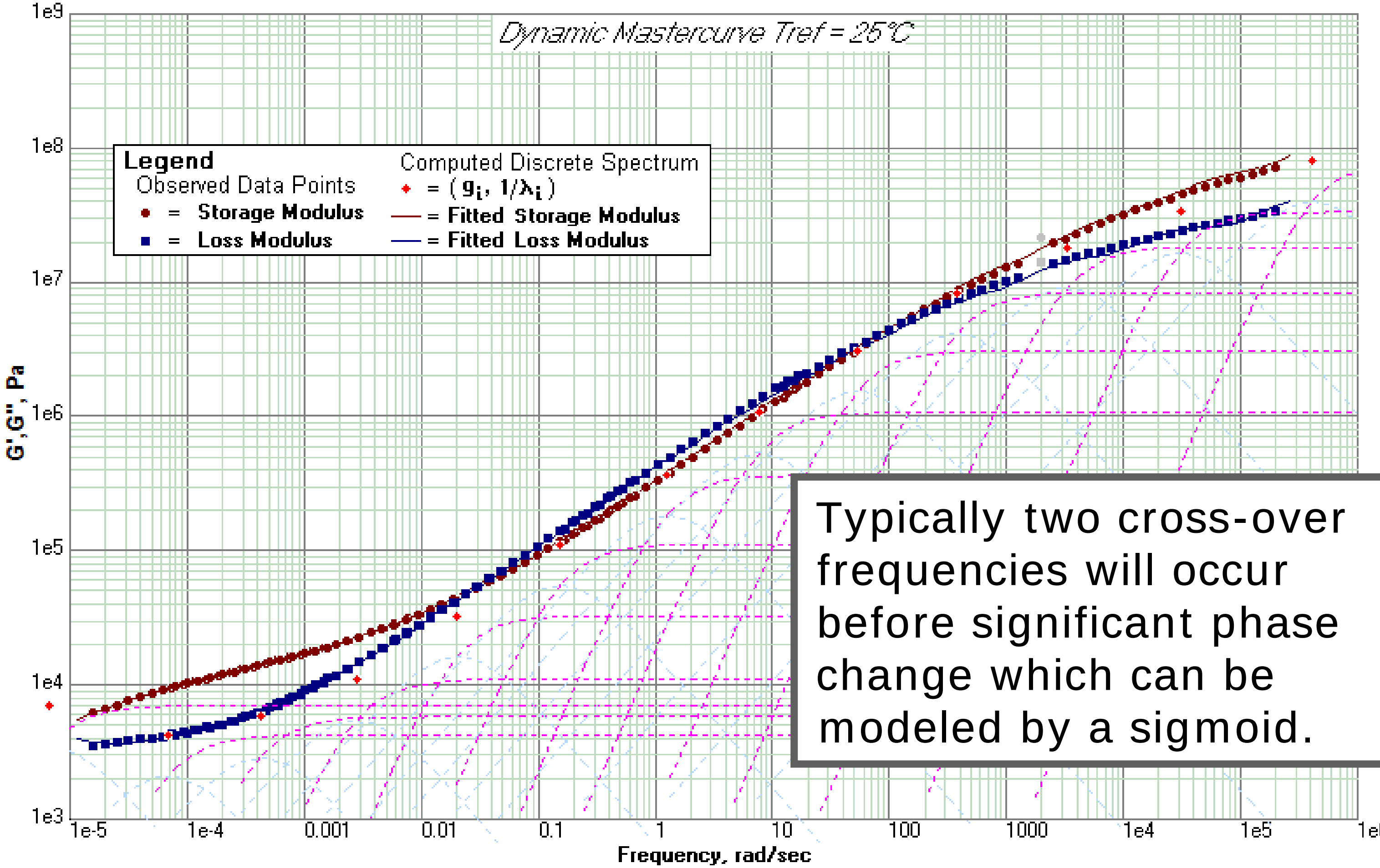


Shifting of DSR data



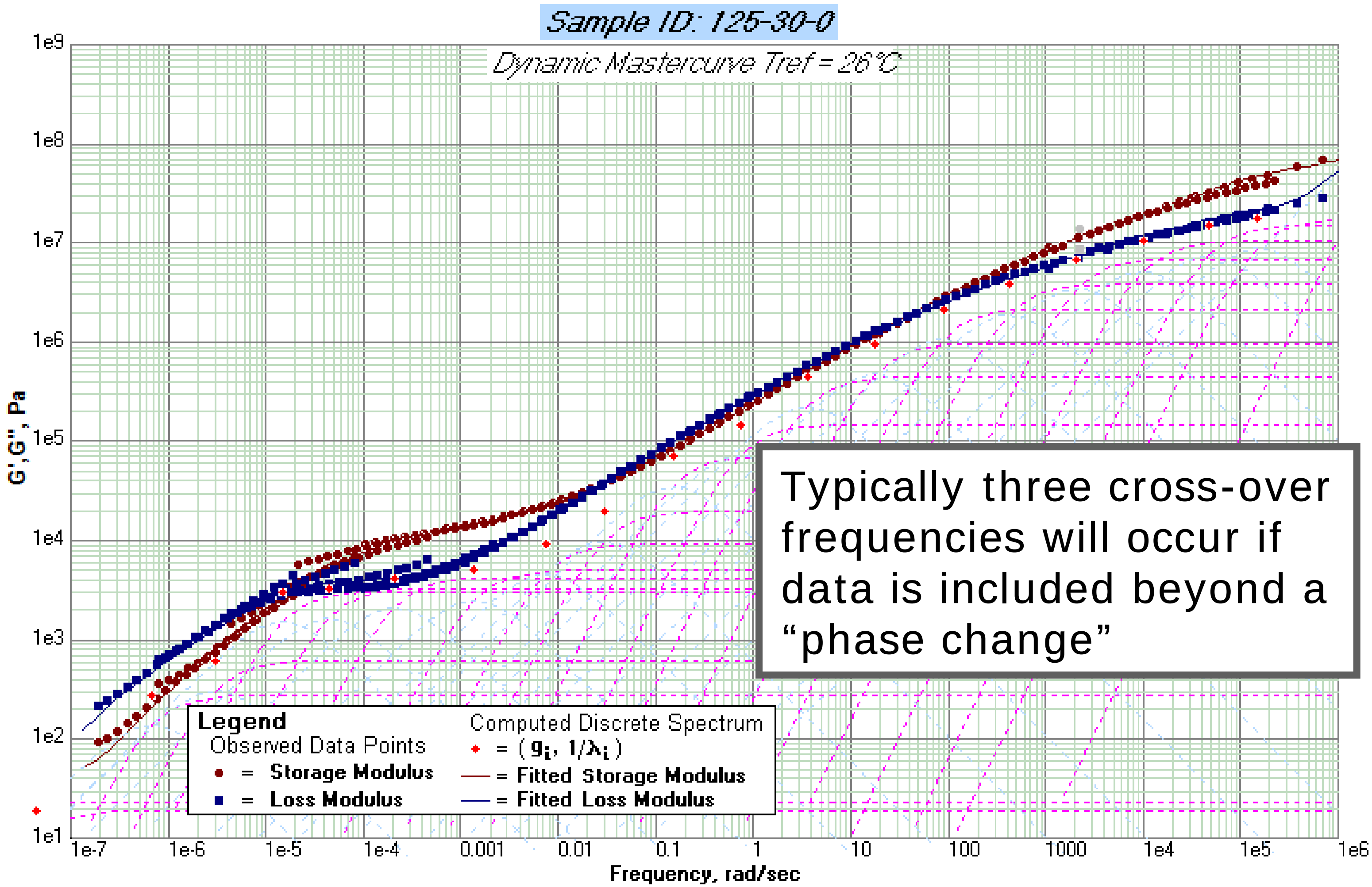
- Shift on G', G" – or G*
  - Often G* numerically similar – even in software tools
  - Produces compromise – since both G' and G" are contained within G*
  - Sometime δ is compromised by testing or phase changes within material
  - We used complex modulus shift

Crossover frequency (1) – to 90°C



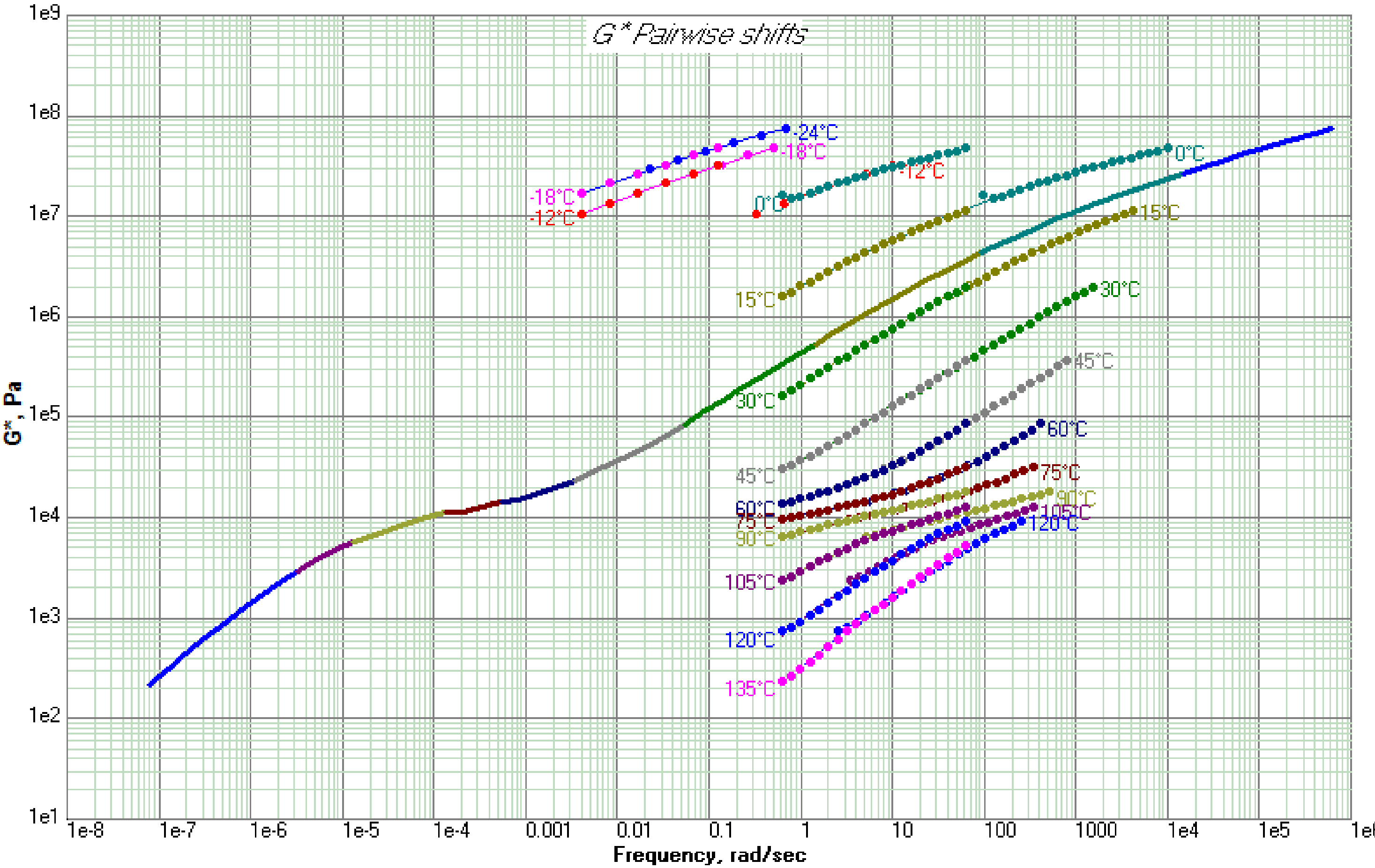
Typically two cross-over frequencies will occur before significant phase change which can be modeled by a sigmoid.

Crossover frequency (2) - to 135^{o}C

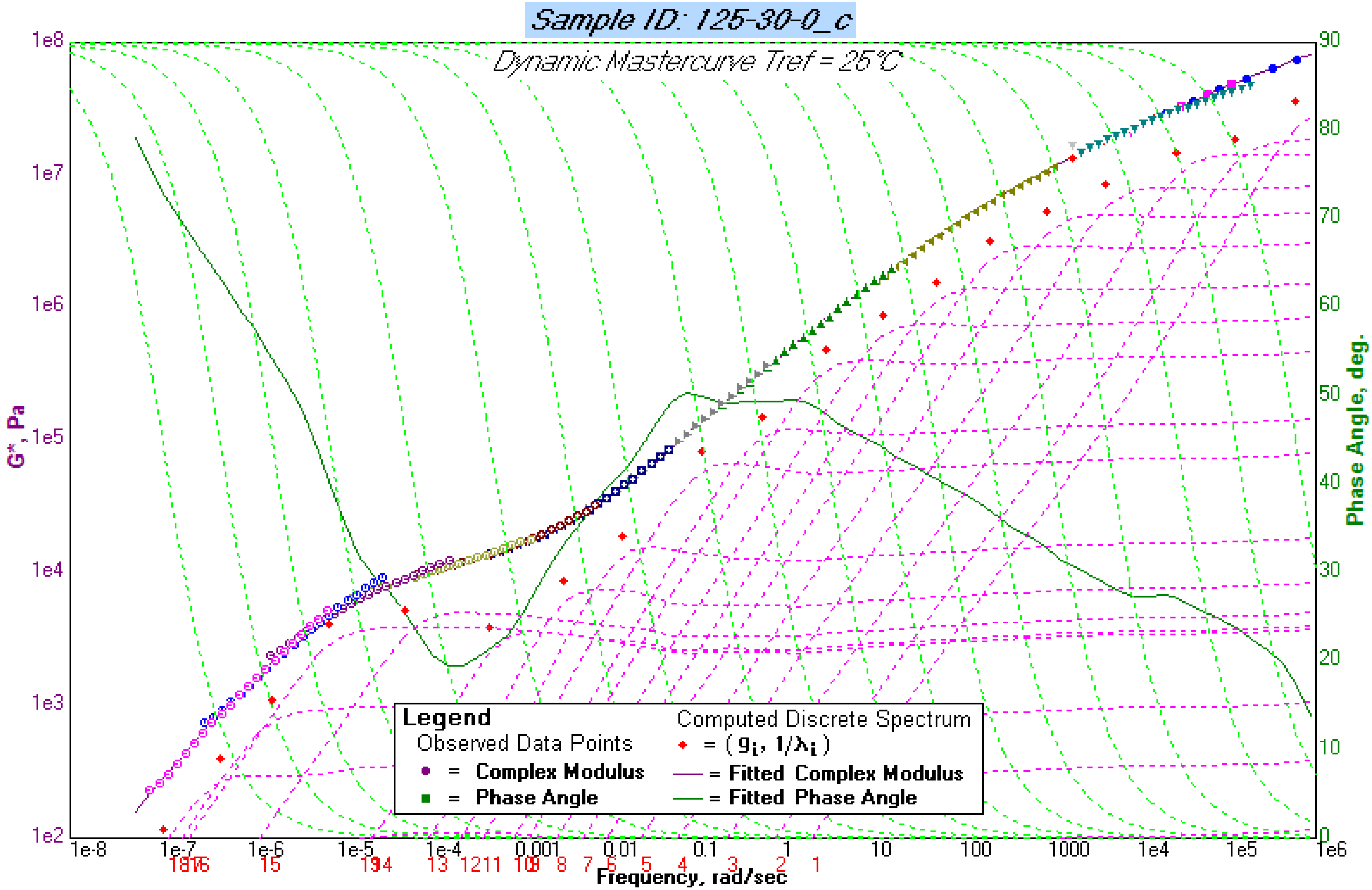


Typically three cross-over frequencies will occur if data is included beyond a “phase change”

Complex modulus Pairwise shift



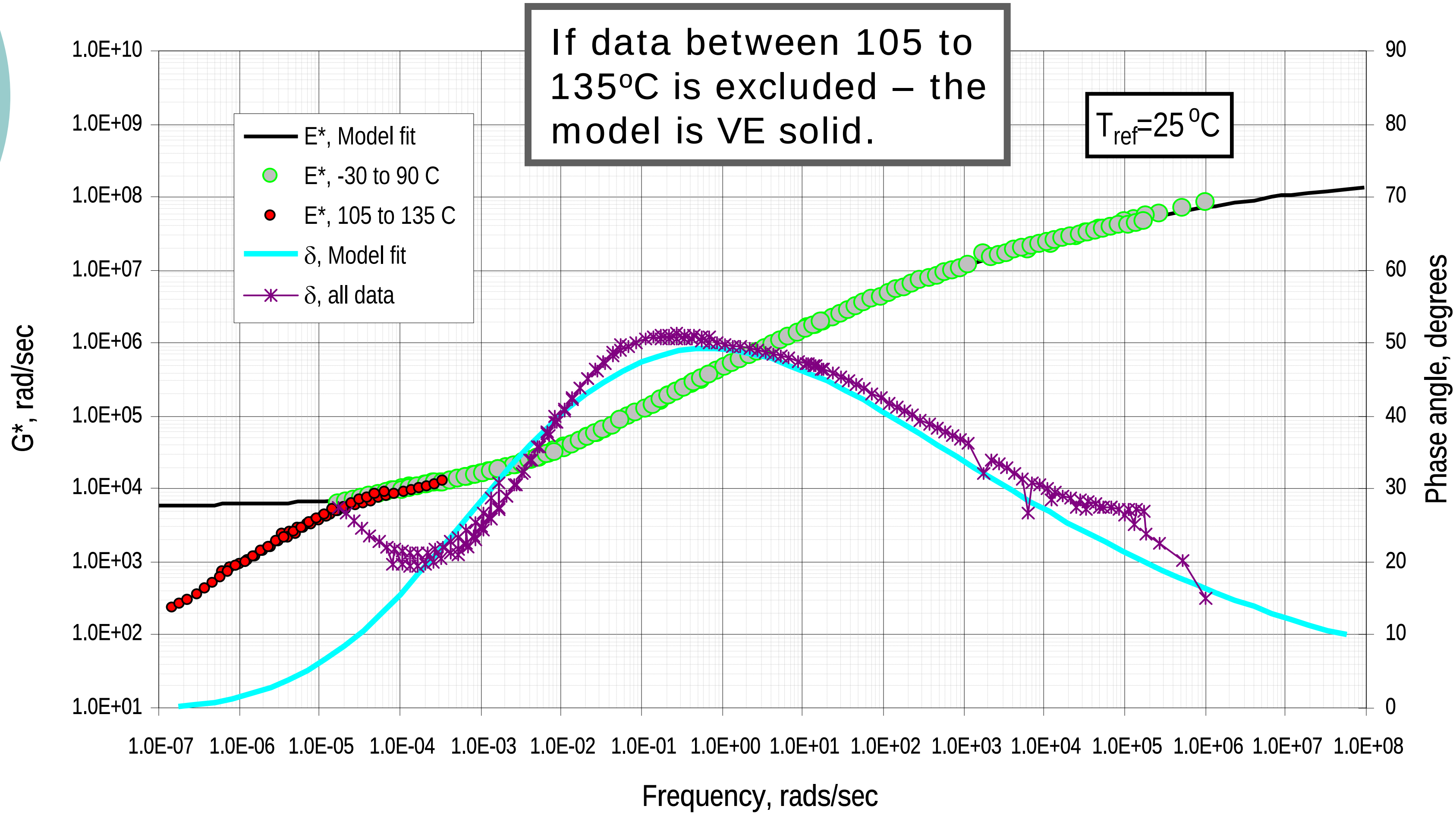
Complex modulus fit



Solid versus liquid model

- Solid model will only apply when evidence of solid type behavior
  - Plateau zone – G', G"
  - Phase angle starts to reduce
- If material transitions then liquid model re-applies – but no functional form

Solid versus liquid model



Model fit

- Fitted VE solid model

$$\log G^* = \delta + \frac{\alpha}{\left[1 + \lambda e^{(\beta + \gamma(\log \omega_r))}\right]^{1/\lambda}}$$

- If no solid fit
  - CAM type model

$$G^*(\omega_r) = G_g\,[1 + (\omega_c / \omega_r)^{\beta}]^{-\kappa/\beta}$$

- Used Kaelble shift

$$\log a_T = -C_1\left(\frac{T - T_d}{C_2 + |T - T_d|} - \frac{T_r - T_d}{C_2 + |T_r - T_d|}\right)$$

- Considered what is happing with cross-over frequency
  - Looked at that occurring at higher frequency since more likely to be dependent on binder
- Shape of model

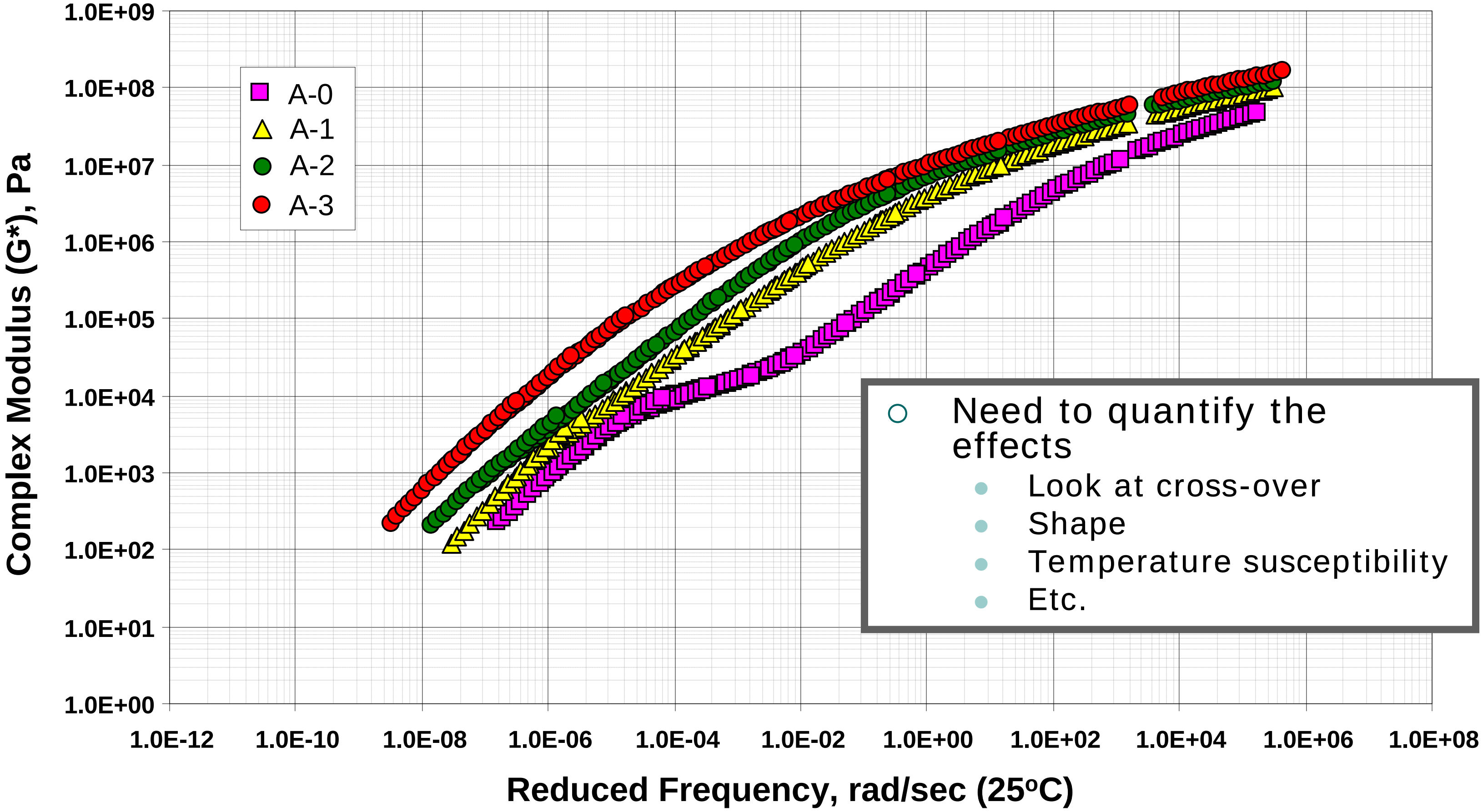
Materials evaluated

Material designation	Asphalt	SBS Content	SBS Type	Filler	Density
A	61.25% Vacuum Distilled Asphalt	8.75%	Radial	30% Calcium Carbonate Filler	1.26
B	61.25% Vacuum Distilled Asphalt	8.75%	Radial	30% Calcium Carbonate Filler 10.5% Flame Retardant Filler	1.26
C	56.87% Vacuum Distilled Asphalt	8.13%	Radial	35% Calcium Carbonate Filler	1.31
D	61.25% Vacuum Distilled Asphalt	4.38% 4.37%	Radial Linear	35% Calcium Carbonate Filler	1.31
E	60% Polyphosphoric Acid Catalytically Air Blown Asphalt (100°C SP/35 pen)	0	-	40% Calcium Carbonate Filler	1.37
F	Type IV Straight Air Blown Asphalt, No Filler	0	-	0	1.02

Aging

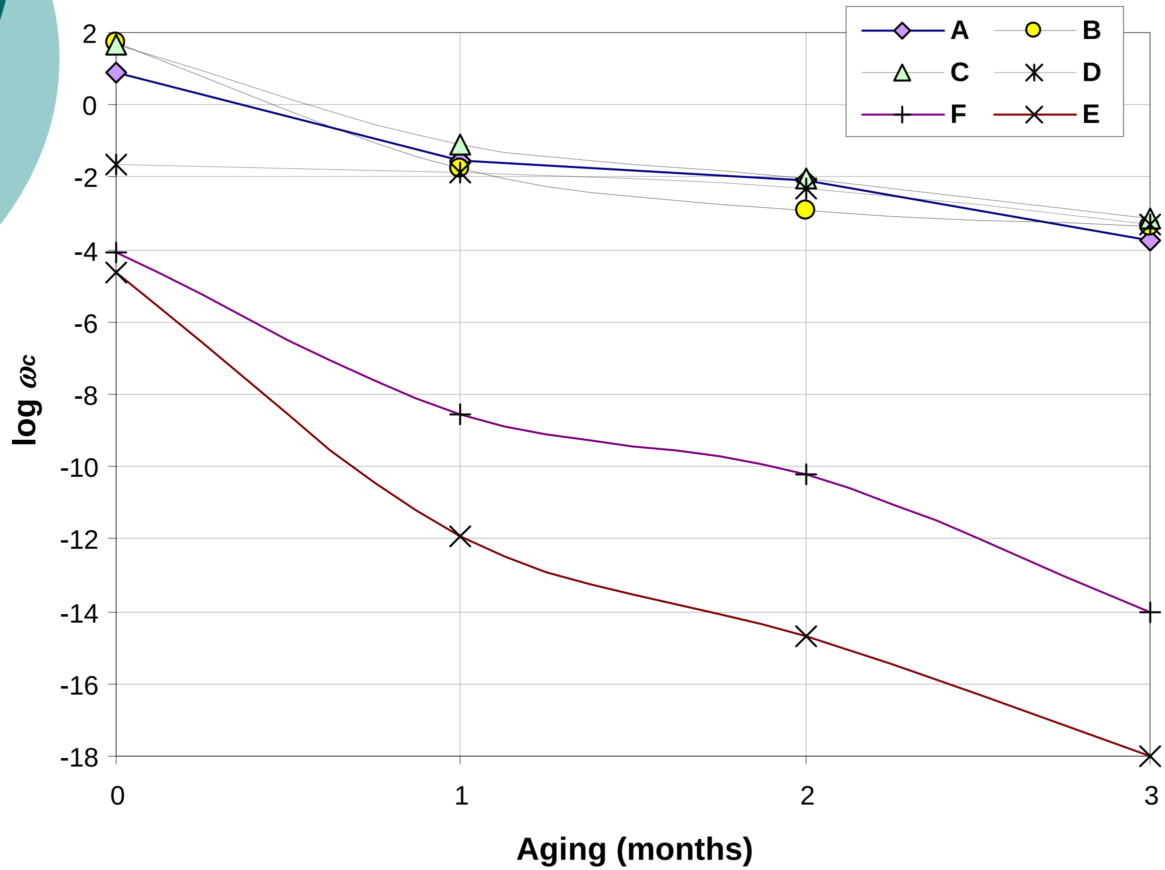
- Aging – 4 conditions
  - dark oven aging of 2 mm thick films aged in a dry, dark, forced draft oven at 80^{o}C
    - 0 – no ageing
    - 1 – one month
    - 2 – two months
    - 3 – three months

Effect of aging on G* master curve, A



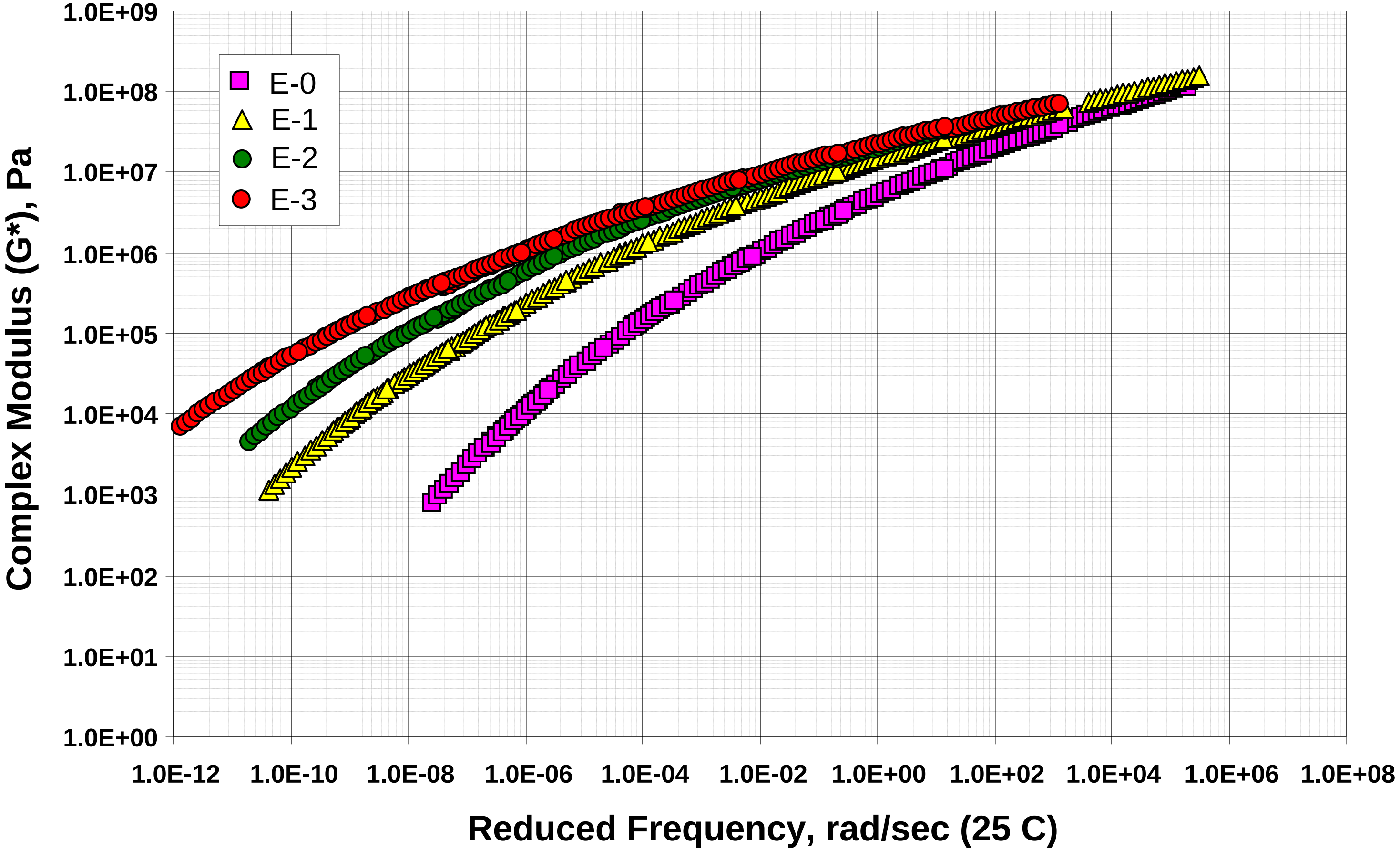
- Need to quantify the effects
  - Look at cross-over
  - Shape
  - Temperature susceptibility
  - Etc.

Cross over frequency



- Crossover frequency reduces as material ages
- Consistent with expectations
- Two of the products showed much larger increases – both air blown products

Effect of aging on G* master curve, E

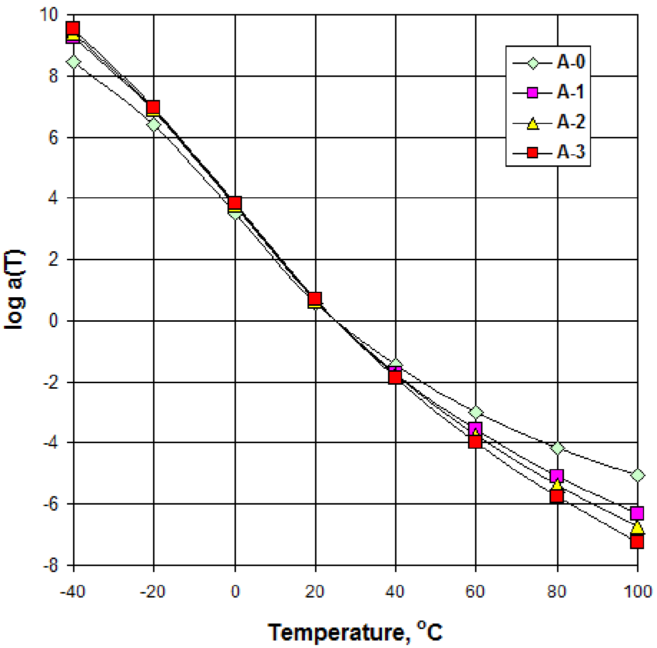


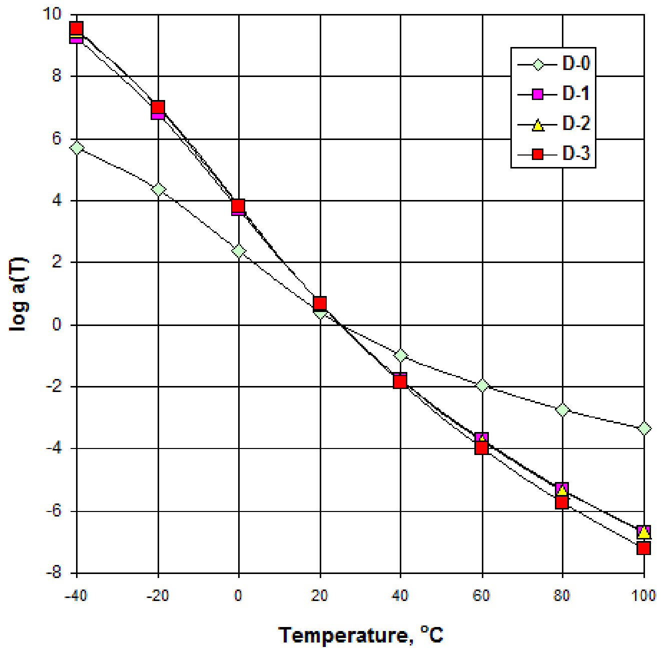
Change to G_e

- VE solid behavior cannot be modeled with some materials after aging has occurred – $G_e \rightarrow$ tends to zero
- Materials A, B, C and D – VE solid at 0 aging
  - VE liquid at 2 and 3 months

Temperature susceptibility

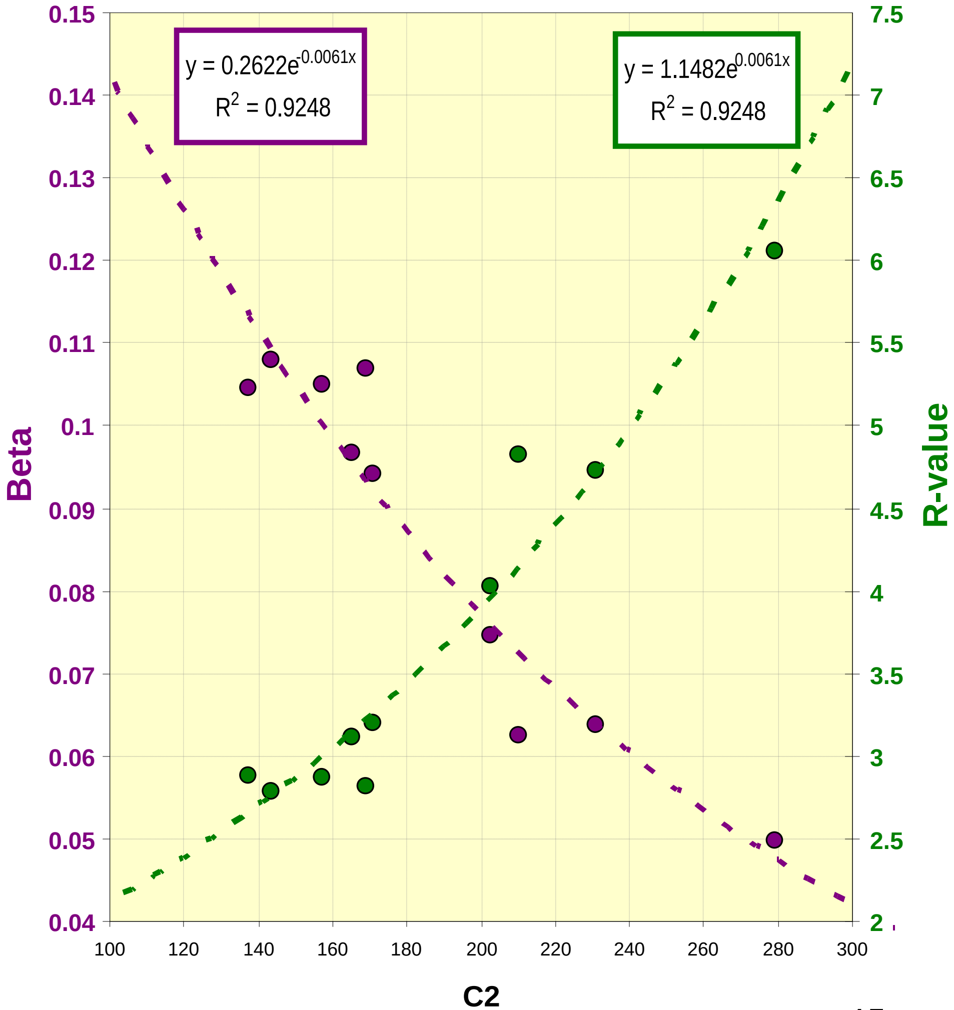
- Degree of shift changes between isotherms as material ages
- In all cases C2 increases – controls slope of WLF or Kaelble relationships





Temperature susceptibility

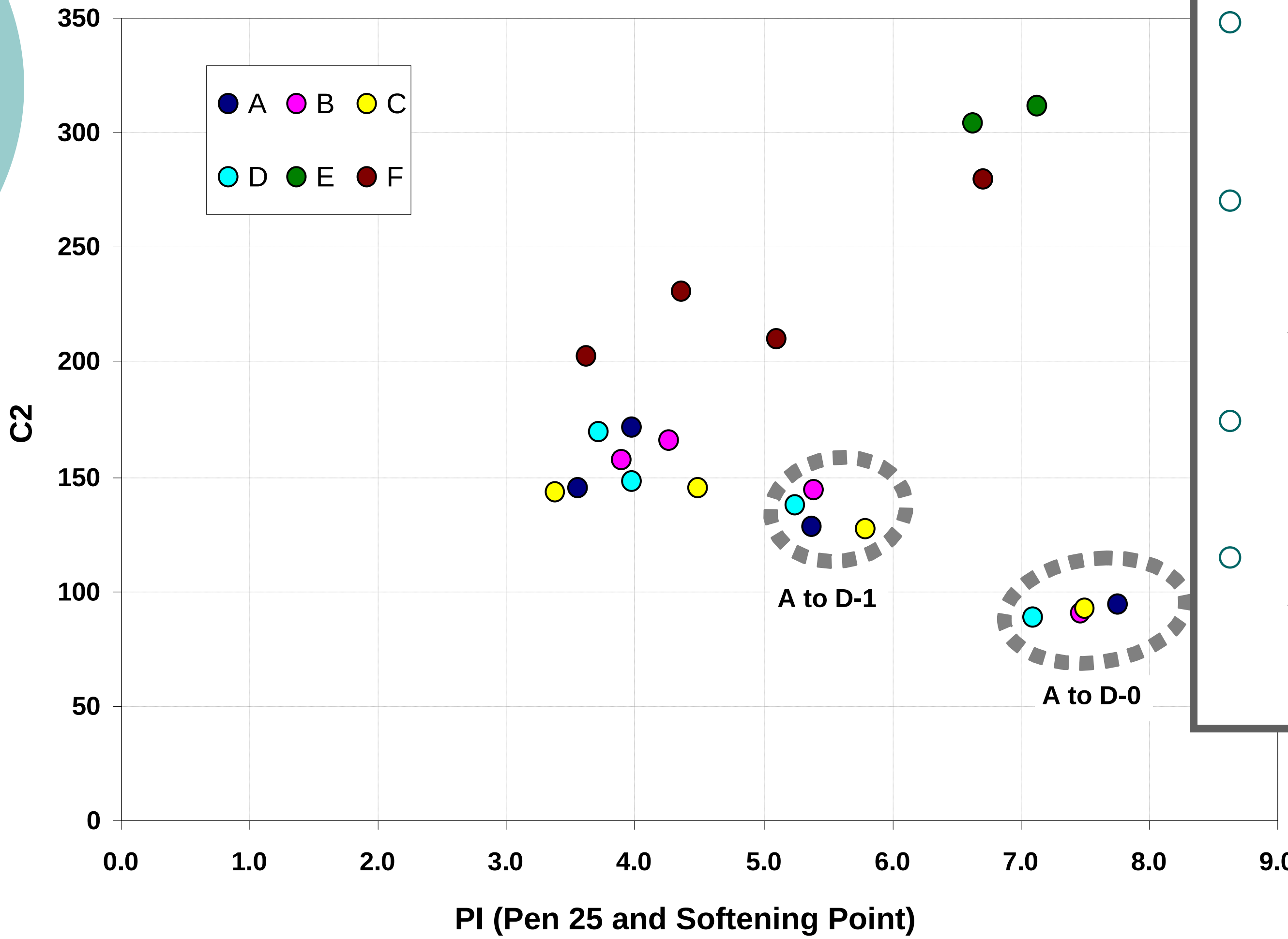
- Can consider three parameters for description of temperature susceptibility from rheology
- β and R (CA model) linked via simple relationship
  - R= log2/β
- C1 parameter in WLF/Kaelble sets location
- Note C1 and C2 are not constant values but depend upon material



Temperature susceptibility

- What about our old parameters
  - Measured Pen, 25 and 50^{o}C and ring & ball softening point
  - Calculated Penetration Index, PI
  - PI with SP provided best correlation with observed behavior

Temperature susceptibility



- Compare against old measures, for example = PI
- PI reduces for SBS modified materials as solid structure is lost with age
- May increase if further aged!!??
- For non-SBS in study PI increases with aging time

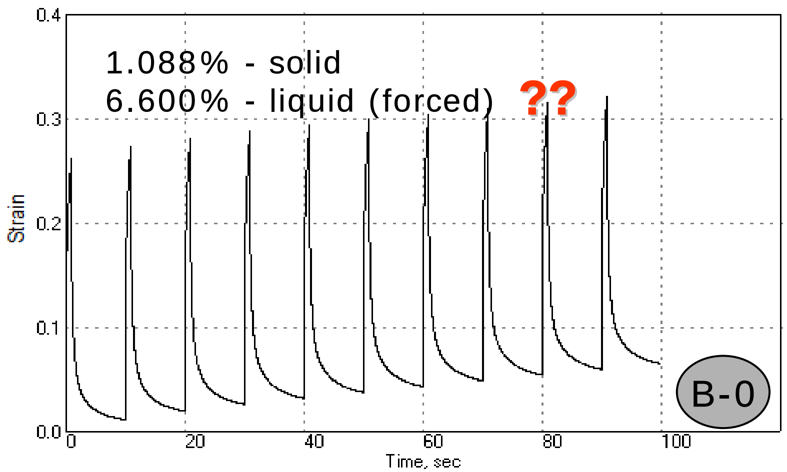
Temperature susceptibility

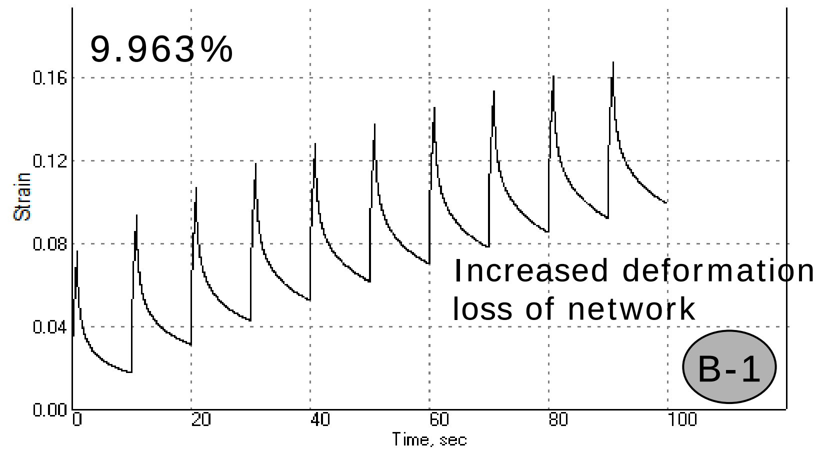
- With age
  - C2 increases
  - R-value increases
  - Beta –reduces
  - PI – can go either way
    - PI reduces as solid structure is lost
    - Increases as liquid structure hardens

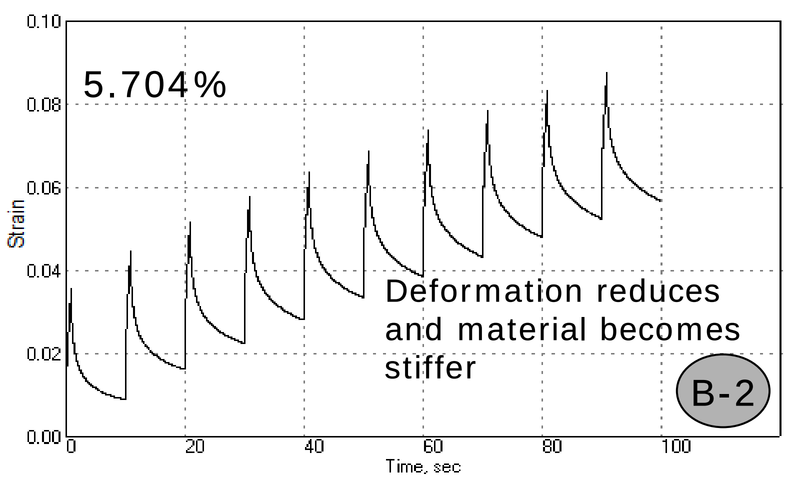
Deformation/flow potential

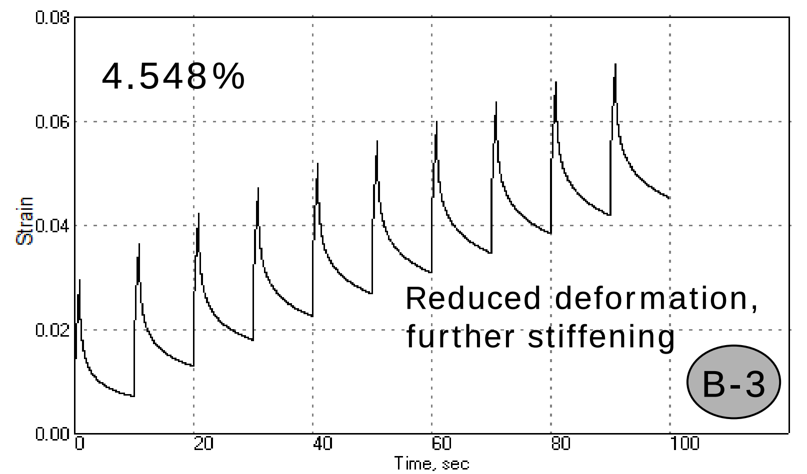
Simulated repeated creep – 3200 Pa

	B-0	B-1	B-2	B-3
G*/sin(δ), kPa @ 64°C	46.6	233.3	369.1	595.1









Summary 1

- Can use a non-symmetric sigmoid to describe behavior
  - Shifting – standards need to be very specific on assumptions
  - Many ways to develop data
- Liquid behavior – CAM type model does a reasonable job
  - Must use variable G_g modulus with modified materials
  - β and R-value – in various model forms related by $R=\log 2/\beta$
- β, R and C2 all related to temperature sensibility
- Temperature correction is important in the development of master curves

Summary 2

- A model format VE solid is discussed the properties of many highly-modified products to be modeled effectively between -40 and +90°C.
- The six products evaluated can be described either by the VE solid model (RBS) or the VE liquid model (CAM).
- For the SBS modified materials considered in this analysis the polymer network degrades with age resulting in a solid model being no longer applicable to define the rheology of the materials
  - The aged materials are behaving like stiff visco-elastic liquids
- The cross-over frequency is significantly affected as the material ages as is the β parameter that defines the rheological type of the binder
  - Both of these changes are anticipated

Summary 3

- The temperature susceptibility as defined by the shift factors needed to produce master curves changes significantly with aging
- Shape and position of master curves change
- Work in progress…..

The end

- Thanks for listening!

Greetings from all of us too!