A Generalized Logistic Function to describe the Master Curve Stiffness Properties of Binder Mastics and Mixtures

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Generalized logistic

Richards curve

$$\log(E^*) = \delta + \frac{\alpha}{(1+\lambda e^{(\beta+\gamma\log\omega)})^{1/\lambda}}$$

Master curve functions

- Objectives
  - Review how robust mastercurve forms are for different material types
  - Materials
    - Polymers
    - Asphalt binders
    - Asphalt mixes
      - Hot Mix Asphalt
      - Mastics and filled systems
  - Observation – different functional forms offer more flexibility with complex materials

Need for evaluation

- Work with various roofing materials and materials used for damping indicated that application of some standard sigmoid functions would not describe functional form for materials

Overview

- Shifting
  - “Free shifting” – Gordon and Shaw
  - Functional form shifting
- Master curve functional forms
  - CA
  - Sigmoid
    - MEPDG
    - Richards etc
- Discussion
  - Relevance to materials

Master curves

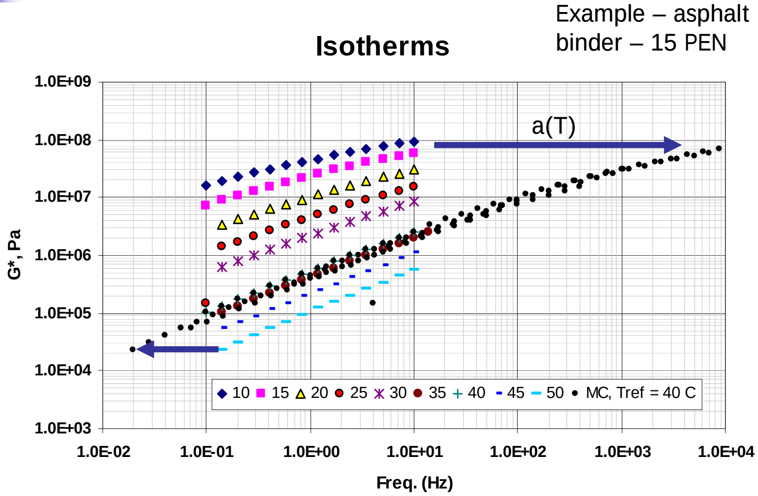
- A system of reduced variables to describe the effects of time and temperature on the components of stiffness of visco-elastic materials
- Also
  - Thermo-rheological simplicity
  - Time-temperature superposition
- Produces composite plot – called master curve

Simple master curve

- Use of EXCEL spreadsheet to manually shift to a reference temperature

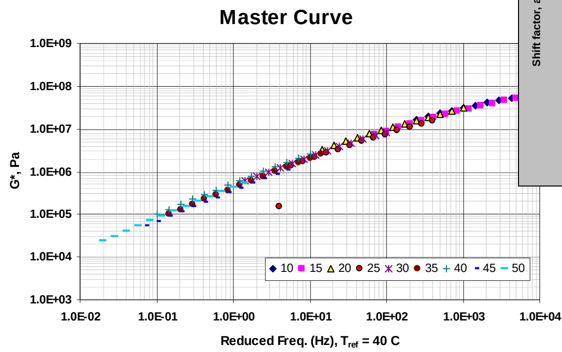
Simple master curve

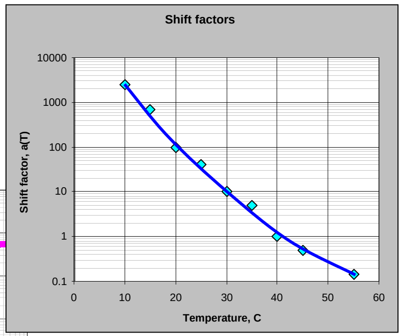
Example – asphalt binder – 15 PEN



Two parts – curve and shifts

- Shift factor relationship is part of master curve numerical optimization





Both curves can be fitted to functional forms to describe inter-relationships

Sifting schemes

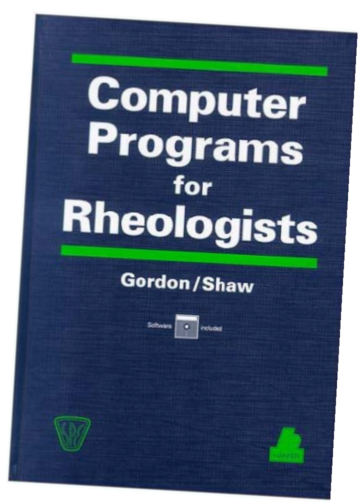
- Shifting schemes improve accuracy
- Enable assessment of model choice
- Can look at error analysis

Shifting choices

- Use a shift not dependent upon a model
  - "Free shifting"
  - Gordon and Shaw's scheme good for this
- Model shifting
  - Shift data using underlying functional model
  - Makes shift easier when less data available
  - Assumption is that model form is suitable for data

Gordon and Shaw Method

- Gordon and Shaw method relies upon reasonable quality data with sufficient data points in each isotherm to make the error reduction process in overlapping isotherms work well
- Gordon and Shaw used since good reference source for computer code



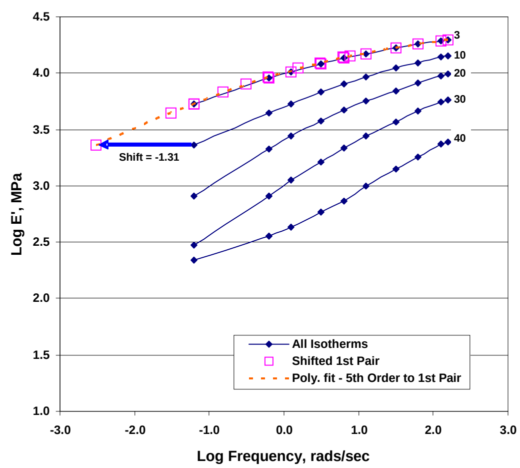
Master Curve Production

Shifting Techniques (Gordon/Shaw)

- Determine an initial estimate of the shift using WLF parameters and standard constants
- Refine the fit by using a pairwise shifting technique and straight lines representing each data set
- Further refine the fit using pairwise shifting with a polynomial representing the data being shifted
- The order of the polynomial is an empirical function of the number of data points and the decades of time / frequency covered by the isotherm pair
- This gives shift factors for each successive pair, which are summed from zero at the lowest temperature to obtain a distribution of shifts with temperature above the lowest
- The shift at T_{ref} is interpolated and subtracted from every temperature's shift factor, causing T_{ref} to become the origin of the shift factors

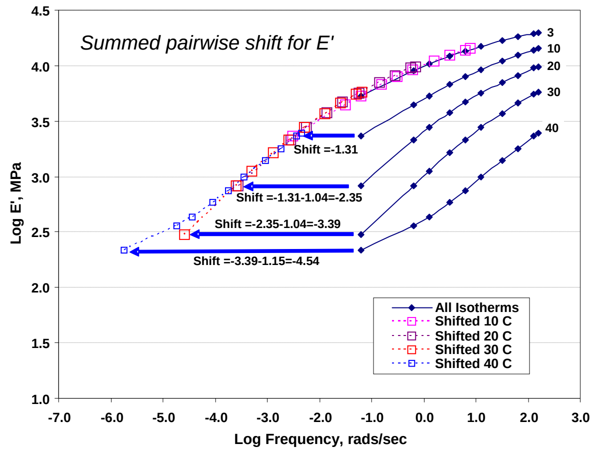
Gordon and Shaw

- After 1st estimate – the polynomial expression is optimized using nonlinear techniques
- 1st pairwise shift starts from coldest temperature isotherm
- Procedure is done for both E' and E"
- Could do on just E*, E(t), G(t), D(t), G* if these are all that is available – but default is to do on loss and storage parts of complex modulus



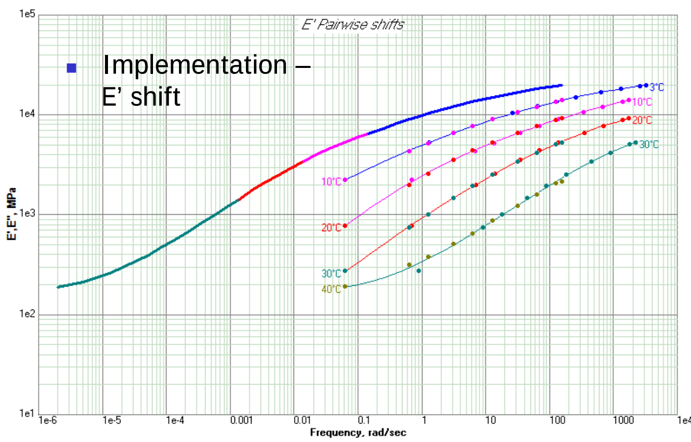
Gordon and Shaw

- Each pairwise shift is determined



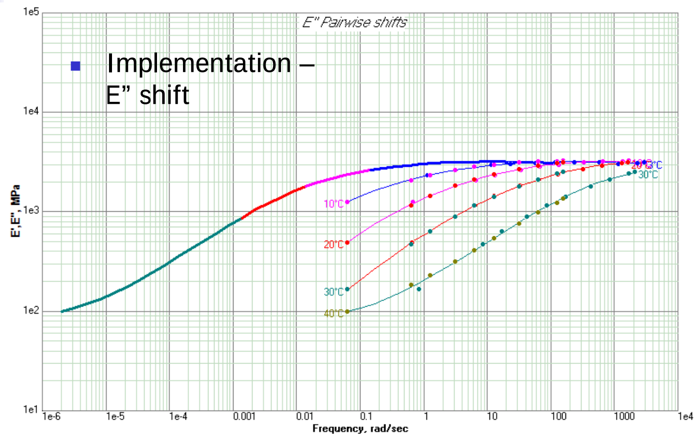
Gordon and Shaw – E'

- Implementation – E' shift



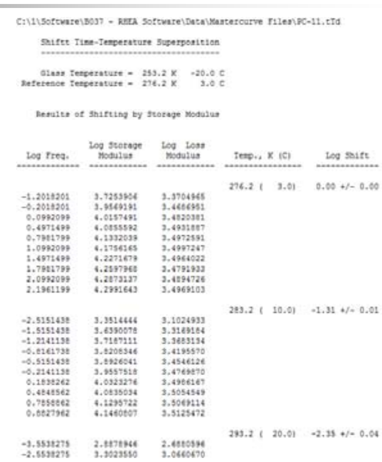
Gordon and Shaw – E”

- Implementation – E” shift



Gordon and Shaw – stats

- +/- 95% confidence limits (t-statistic) – based on Gordon and Shaw book
- Gives values for both E’, E” and average
- Comparison of shift factors also plotted



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Shiftt Time-Temperature Superposition

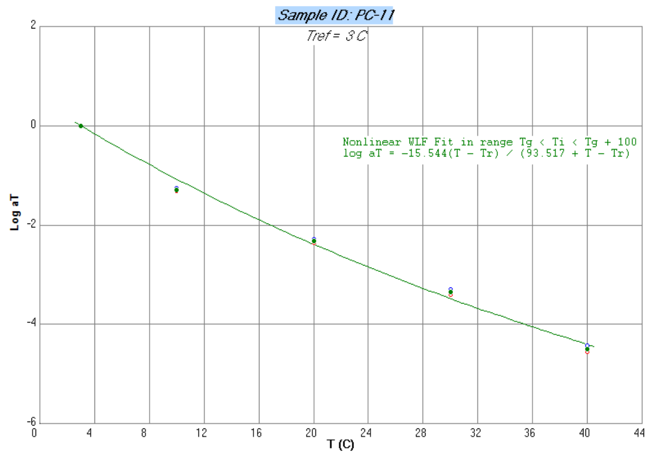
Glass Temperature = 253.2 K -20.0 C
Reference Temperature = 276.2 K 3.0 C

Results of Shifting by Storage Modulus

Log Freq.	Log Storage Modulus	Log Loss Modulus	Temp., K (C)	Log Shift
			276.2 (3.0)	0.00 +/- 0.00
-1.2018201	3.7253906	3.3704965		
-0.2018201	3.9569191	3.4486951		
0.0992099	4.0157491	3.4820381		
0.4971499	4.0855592	3.4931887		
0.7981799	4.1332039	3.4972591		
1.0992099	4.1756165	3.4997247		
1.4971499	4.2271679	3.4964022		
1.7981799	4.2597968	3.4791933		
2.0992099	4.2873137	3.4894726		
2.1961199	4.2991643	3.4969103		
			283.2 (10.0)	-1.31 +/- 0.01
-2.5151438	3.3514444	3.1024933		
-1.5151438	3.6390078	3.3169184		
-1.2141138	3.7187111	3.3683134		
-0.8161738	3.8208346	3.4195570		
-0.5151438	3.8926041	3.4546126		
-0.2141138	3.9557518	3.4769870		
0.1838262	4.0323276	3.4986167		
0.4848562	4.0835034	3.5054549		
0.7858862	4.1295722	3.5069114		
0.8827962	4.1460807	3.5125472		
			293.2 (20.0)	-2.35 +/- 0.04
-3.5538275	2.8878946	2.4880596		
-2.5538275	3.3023550	3.0660670		

Gordon and Shaw – shifts factors

- If shift factors are very different for E’ and E” then shifting may not have worked very well
- Maybe need to consider some other type of shifting



Model shifting

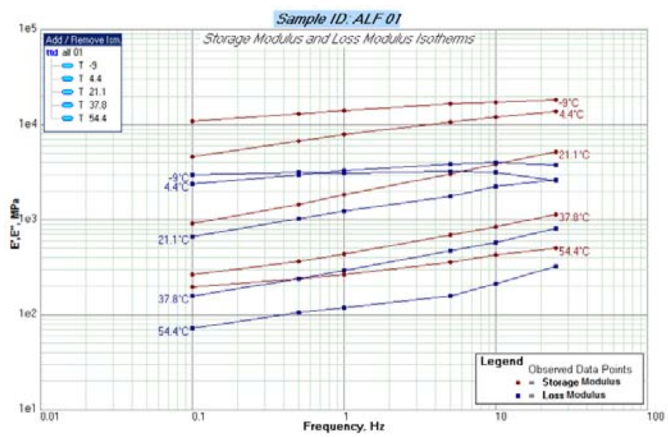
- Shifting to underlying model
- If material behavior is known, it can assist the shift by assumption of underlying model
  - Why would I do this?
  - Example – EXCEL solver used to give shift parameters

Model shifting

- Why?
  - If data is limited to extent that Gordon and Shaw will not work or visual technique is difficult
  - For example – mixture data collected as part of MEPDG – does not have sufficient data on isotherms to allow Gordon and Shaw to work well in all instances – 4 to 5 points per decade is best

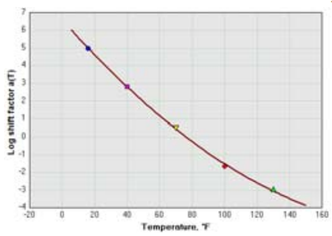
Typical mix data

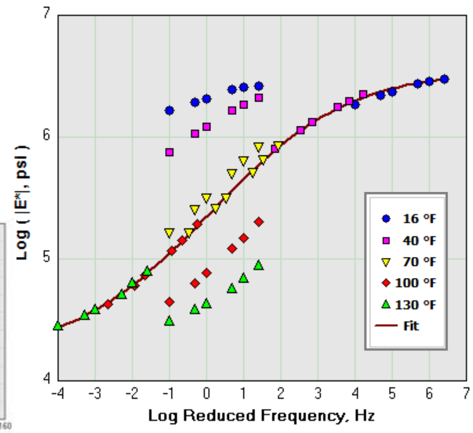
- Example mix data set collected for MEPDG analysis
- Note – on log scale data has non-equal gaps with only two points per decade



Model fit

- Model shift provides the result to be used in a specific analysis





Models

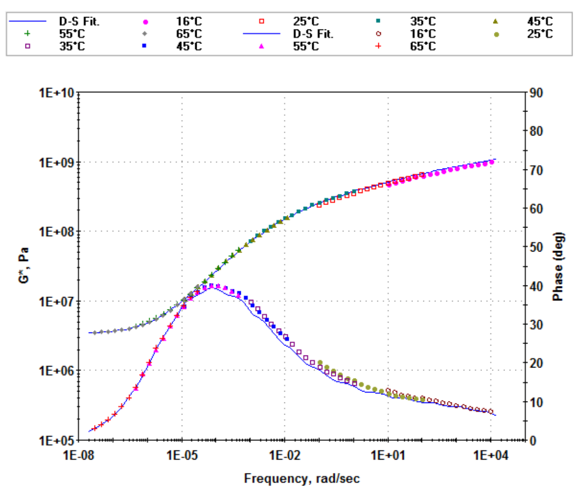
- Why we needed to consider different models?
  - Working with some complex materials we noted that the symmetric sigmoid does not provide a good fit of the data
  - We then started a look at other fitting schemes

Complex materials

- Asphalt materials can be formulated which have complex master curves
  - Roofing compounds
  - Thin surfacing materials
  - Damping materials
  - Jointing/adhesive compounds
  - HMA with modified binders

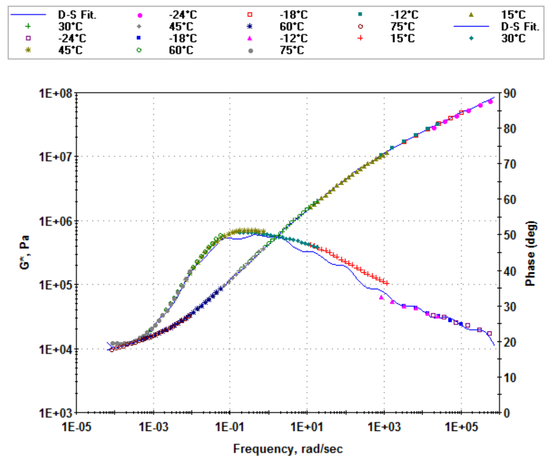
Example – thin surfacing on PCC

- Material mixed with aggregate and used as a thin surfacing material on concrete bridge decks



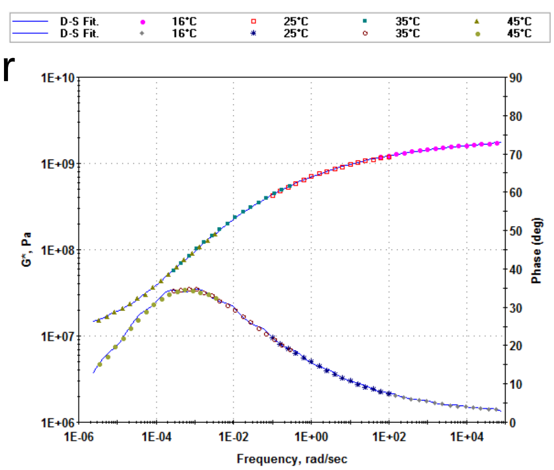
Example – roofing product

- Roofing material
  - 8.75 % Radial SBS Polymer
  - 61.25 % Vacuum Distilled Asphalt
  - 30 % Calcium Carbonate Filler
- Master curve considered in range -24 to 75ºC – this range gives a good fit in linear visco-elastic region
- After 75ºC structure in material starts to change and material is not behaving in a thermo-rheologically simple manner



Example – adhesive product

- Master curve for a material used for fixing road markers



Models – on these products

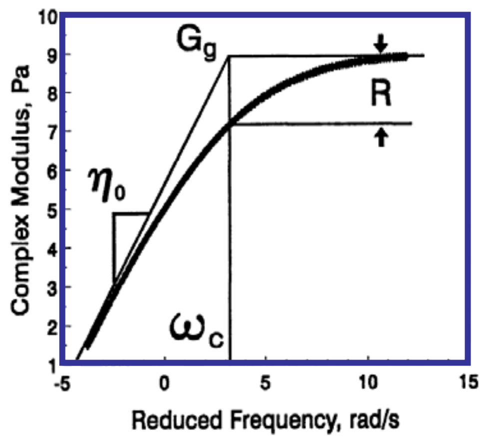
- On the three previous examples it was observed that the master curve is not a represented by a symmetric sigmoid or CA style master curve
- Need to consider something else!

Christensen-Anderson

- CA, CAM
- Idea originally developed by Christensen and published in AAPT (1992)
- Work describes binder master curve and works well for non-modified binders

Asphalt binder models, SHRP

- Christensen-Anderson - CA model (1993)
  - Relates $G^*(\omega)$ to G_g, ω_c and R
  - Model for phase angle
  - Model works well for non-modified binders
  - Model is similar for G(t) or S(t) format
  - Relates to a visco-elastic liquid whereas materials shown in previous slides show more solid type behavior



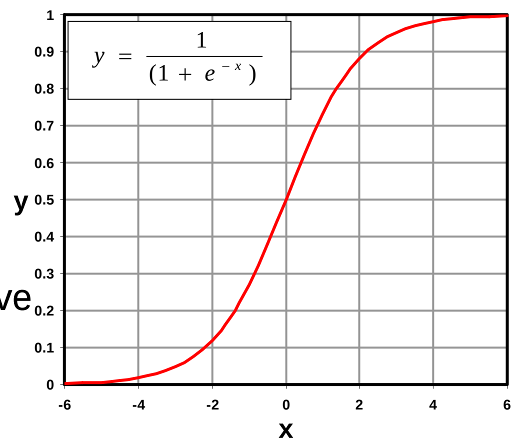
Sigmoid - logistic

- Standard logistic (Verhulst, 1838)
  - Originally developed by a Belgium mathematician
  - Used in MEPDG
  - Has symmetrical properties
  - Applied to a wide variety of problems

Pierre François Verhulst

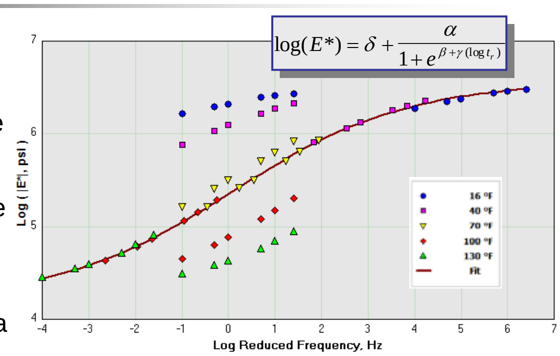
Mix models - Witczak

- Basic sigmoid function
- Basis of Witczak model for asphalt mixture E* data
- Parameters introduced to move sigmoid to typical asphalt mix properties



Witczak model

- Witczak model parameters define the ordinates of the two asymptotes and the central/inflection point of the sigmoid, as follows:
  - 10^{δ} = lower asymptote
  - $10^{(\delta+\alpha)}$ = upper asymptote
  - $10^{(\beta/\gamma)}$ = inflection point
- Empirical relationships exist to estimate δ α β and γ
- Model is limited in shape to a symmetrical sigmoid
- Sigmoid has characteristics of a visco-elastic solid



Other models

- Standard logistic will not work for all asphalt materials - what other choices do we have?
  - CAS
    - Christensen-Anderson modified by Sharrock
    - Allows variation in the glassy modulus – useful for filled systems below a critical amount of filler – where the liquid phase is still dominant. Have used for roofing materials and mastics.

$$S(\xi) = S_{glassy}[1+(\xi/\lambda)^{\beta}]^{-1/\beta}$$

  - Gompertz (1825)
    - Works well for highly filled/modified systems. Filled modified joint materials and sealants.

$$y(t) = ae^{be^{ct}} + d$$

Benjamin Gompertz

  - Richards model (1959)
    - Allows a non-symmetrical model format. Gives a better fit for some jointing compounds and hot-mix-asphalt.

$$Y = A + \frac{C}{(1+Te^{-B(X-M)})^{1/T}}$$

  - Weibull (1939)
    - Allows non-symmetric behavior
    - Added as an additional method

$$\log(E^*) = A + B\left[C - e^{-\left(\frac{x+D}{E}\right)^{F}}\right]$$

Note – these are being used to describe the shape of master curve

Sigmoid - generalized logistic

- Generalized logistic (Richards, 1959)
  - Introduces an extra parameter to allow non-symmetrical slope
  - Parameter introduced that allows inflection point to vary
  - Analysis also yields – Standard logistic (as used in MEPDG) and Gompertz (as special case) when appropriate by data

A Flexible Growth Function for Empirical Use

F. J. RICHARDS

(Research Institute of Plant Physiology, Imperial College of Science, London, S.W. 7)

SUMMARY

The application of an extended form of von Bertalanffy's growth function to plant data is considered; the equation has considerable flexibility, but is used only to supply an empirical fit. In order to aid the biological analysis of such growth data as are capable of representation by the function, general rate parameters are deduced which are related in a simple manner to its constants.

The many attempts which have been made to simulate curves of limited growth by mathematical formulations either aim at accounting for their form through certain fundamental postulates about the growth process, or else are severely practical in scope and inspired by the desire to obtain any relatively simple equation which contains the essence of the numerical data. In the empirical approach the magnitudes of the constants in the fitted equations may be used to assess the importance in growth of experimentally controllable factors, but the constants themselves are not regarded as having any absolute significance for the theory of growth. Obviously the usefulness of any empirical equation is enhanced if its constants yield easily information of direct biological interest.

The three best-known 'growth functions' are as follows:

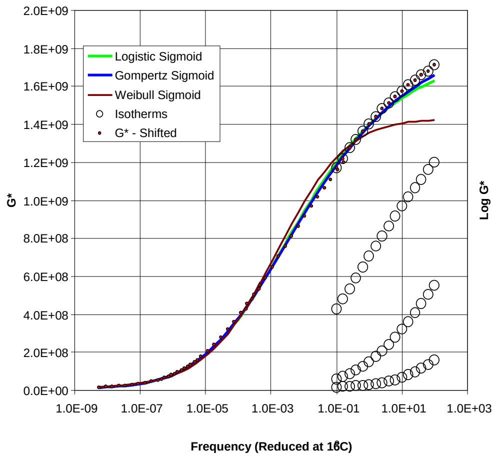
	Monomolecular	Autocatalytic	Gompertz
Equation	$W = A(1-be^{-kt})$	$W = A/(1+be^{-kt})$	$W = Ae^{-be^{-kt}}$
Growth-rate	$k(A-W)$	$kW(A-W)/A$	$kW\log_e(A/W)$

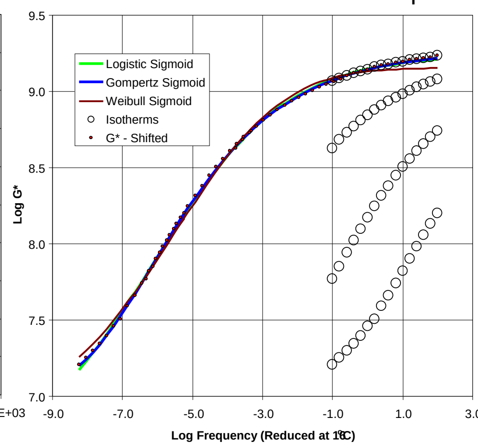
Here W represents the size at time t and A its ultimate limiting value; k is the 'rate constant' which determines the spread of the curve along the time axis. The magnitude of b is usually unimportant biologically, since it reflects only the choice of the zero of time. The monomolecular function has no point of inflexion, its growth-rate declining linearly with increasing W; it is used sometimes (cf. Gregory, 1928) to represent the later portions of life history. The autocatalytic or 'logistic' curve is symmetrical round its point of inflexion; its *relative* growth-rate declines linearly with increasing W. It has been used widely both from a theoretical standpoint (e.g. Robertson, 1923) and as a convenient empirical curve. The Gompertz curve resembles the autocatalytic in many features, but is asymmetrical, inflecting at $W = A/e$, or 0·368 A; linear relations exist both between its relative growth-rate and log W, and between the logarithm of its relative rate and time. This curve has been used more extensively in population studies and to represent the course of animal growth than it has by botanists; it was deduced as a theoretical curve

Journ. of Experimental Botany, Vol. 10, No 29, pp. [illegible], June 1959.

Example – thin surfacing on PCC

Best fit is Gompertz

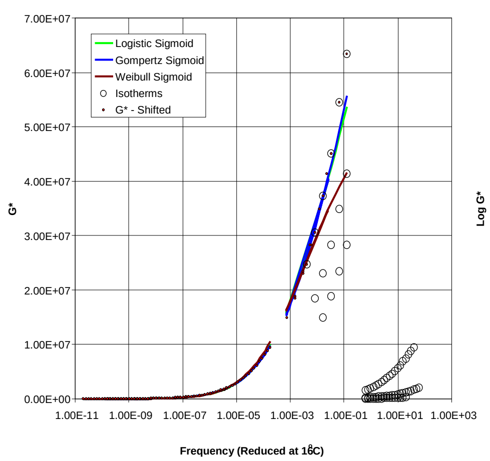


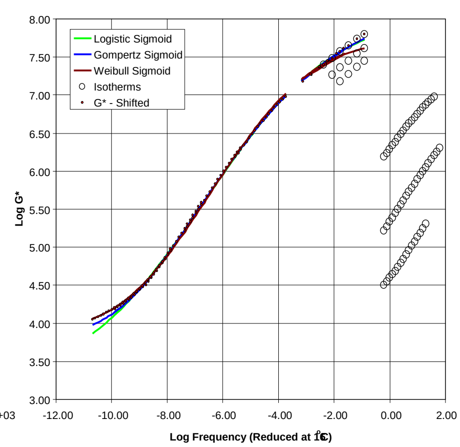


G*=Pa

Example – roofing product

Low stiffness=Weibull, high stiffness=Gompertz, best fit=Gompertz

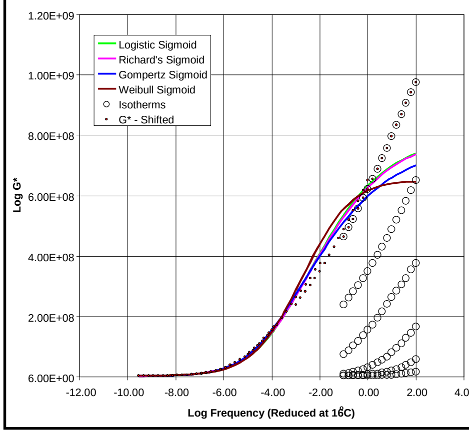


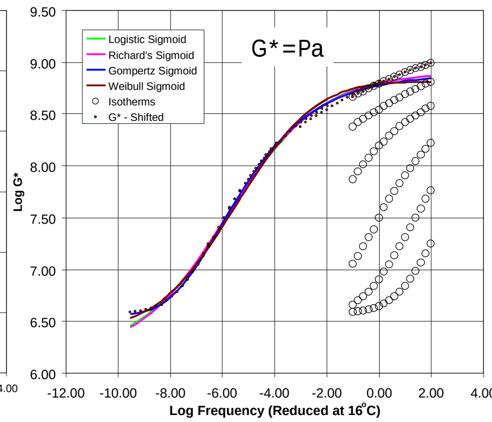


G*=Pa

Example – adhesive product

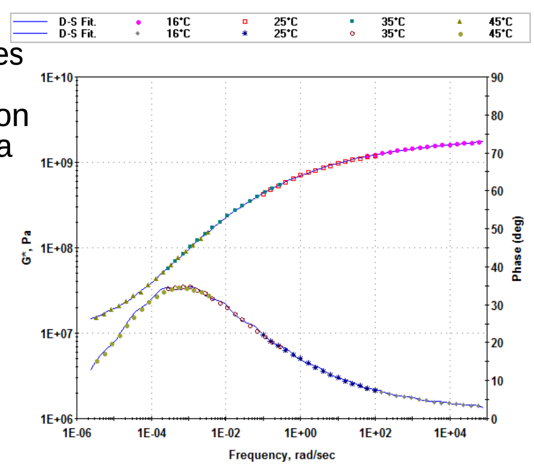
Low stiffness=Gompertz, high stiffness=logistic, best fit=Gompertz
High stiffness appears to have some errors!





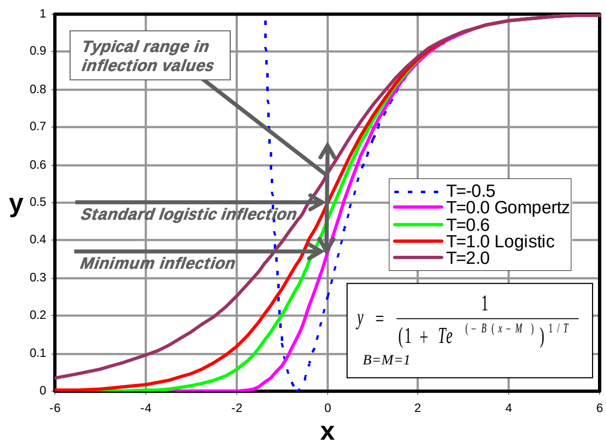
Prony series/D-S fits

- In each of the examples the data is fitted to Prony series – relaxation and retardation spectra with good fits
- If data is extended by use of a “sound” functional form model, this enables extension of calculations in regions not tested by the rheology measurements



Generalized logistic

- Generalized logistic curve (Richard's) allows use of non-symmetrical slopes
- Introduction of additional parameter T
  - When T = 1 equation becomes standard logistic
  - When T tends to 0 – then equation becomes Gompertz
  - T must be positive for analysis of mixtures since negative values will not have asymptote and produces unsatisfactory inflection in curve
  - Minimum value of inflection occurs at 1/e – or 36.8% of relative height



HMA – Standard vs. Generalized

- Based on standard (logistic) sigmoid the generalized sigmoid formats are:-

Standard logistic | **MEPDG FORMAT** | Generalized logistic

$$\log(E^*) = \delta + \frac{\alpha}{1+e^{(\beta+\gamma\log\omega)}} \qquad \log(E^*) = \delta + \frac{\alpha}{(1+\lambda e^{(\beta+\gamma\log\omega)})^{1/\lambda}}$$

ALTERNATE FORMAT

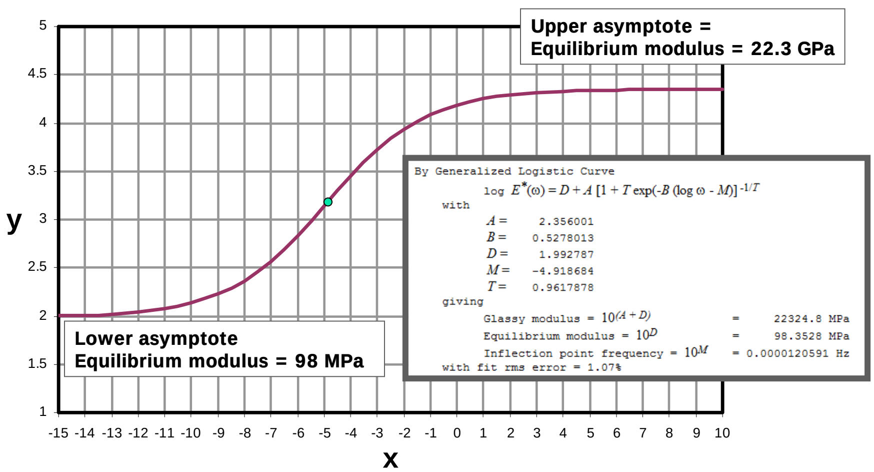
$$\log(E^*) = D + \frac{A}{1+e^{-B(\log\omega - M)}} \qquad \log(E^*) = D + \frac{A}{(1+T\exp(-B(\log\omega - M)))^{1/T}}$$

δ=D, α=A, β= BM
γ= -B, λ=T

δ = lower asymptote
δ+α = upper asymptote

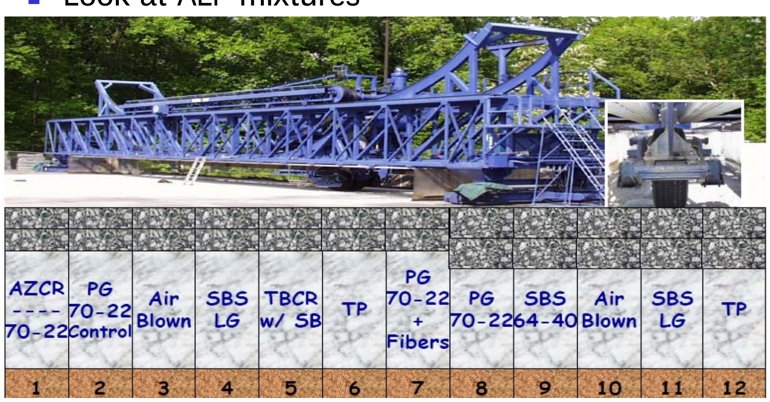
–(β/γ) = inflection point/frequency

Generalized logistic example

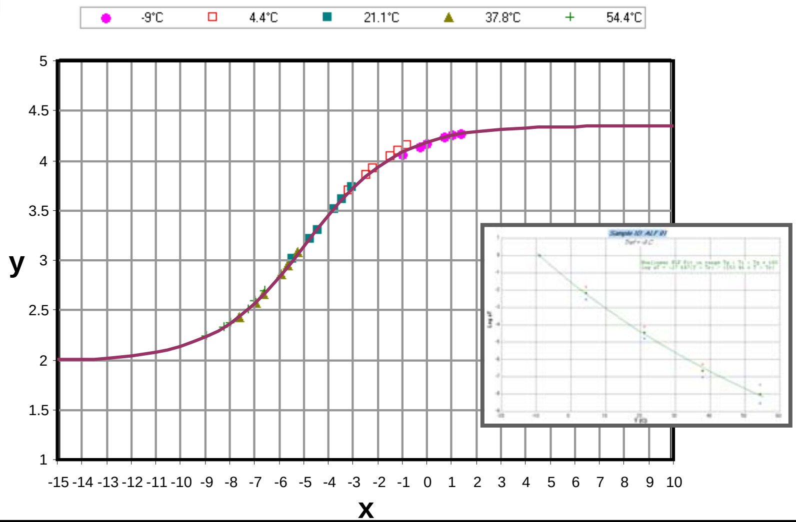


Extension to HMA mixtures

- Do the generalized sigmoid enable a better definition of HMA mixes
- Look at ALF mixtures



Generalized logistic example



Model fit

- Compare errors from different model fits to assist with determination of correct form of shifting

Complex Modulus Fit

By Generalized Logistic Curve

$$\log E^*(\omega) = D + A\,[1 + T\exp(-B\,(\log\omega - M)]^{-1/T}$$

with

$A =$ 2.356001
$B =$ 0.5278013
$D =$ 2.045066
$M =$ 0.0785282
$T =$ 0.9617878

giving

Glassy modulus = $10^{(A+D)}$ = 25180.7 MPa
Equilibrium modulus = 10^{D} = 110.934 MPa
Inflection point frequency = 10^{M} = 1.1982 Hz
with fit rms error = 1.07%

ALF1
AZCR 70-22

By Standard Logistic Curve

$$\log E^*(\omega) = D + A\,[1 + \exp(-B\,(\log\omega - M)]^{-1}$$

with

$A =$ 2.363261
$B =$ 0.5321055
$D =$ 2.035833
$M =$ 0.08976333

giving

Glassy modulus = $10^{(A+D)}$ = 25066.5 MPa
Equilibrium modulus = 10^{D} = 108.601 MPa
Inflection point frequency = 10^{M} = 1.2296 Hz
with fit rms error = 1.07%

Model fit

- Different modifiers may need different models to define mix behavior

Complex Modulus Fit

By Generalized Logistic Curve

$$\log E^*(\omega) = D + A\,[1 + T\exp(-B\,(\log\omega - M))]^{-1/T}$$

with

$A =$ 2.060639
$B =$ 0.3576573
$D =$ 2.315308
$M =$ -1.107036
$T =$ 0.01266578

giving

Glassy modulus = $10^{(A+D)}$ = 23765.5 MPa
Equilibrium modulus = 10^{D} = 206.685 MPa
Inflection point frequency = 10^{M} = 0.0781563 Hz
with fit rms error = 1.79%

By Standard Logistic Curve

$$\log E^*(\omega) = D + A\,[1 + \exp(-B\,(\log\omega - M))]^{-1}$$

with

$A =$ 2.288005
$B =$ 0.4570379
$D =$ 2.023987
$M =$ -0.7401943

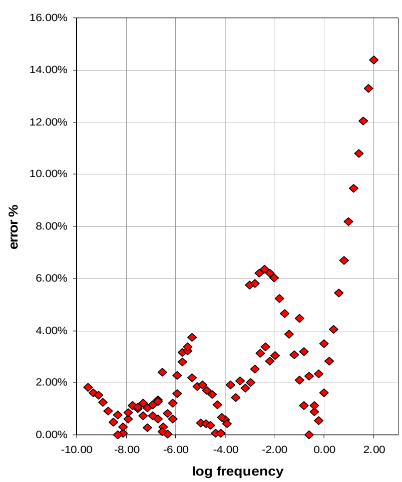
giving

Glassy modulus = $10^{(A+D)}$ = 20511.2 MPa
Equilibrium modulus = 10^{D} = 105.679 MPa
Inflection point frequency = 10^{M} = 0.181889 Hz
with fit rms error = 2.85%

ALF7
PG70-22 + Fibers

Error

- Need to develop better way of considering errors since most of error tends to occur at limits
- rms% values tend to be low because of adequate fit for large amount of central data



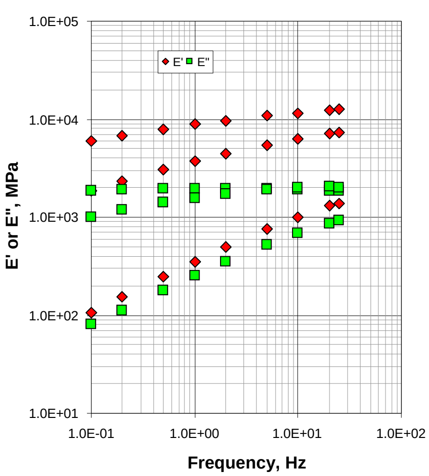
Applied to ALF study

- When methods applied to ALF data only one data set – previous example – is close to symmetrical – standard logistic
- Most data sets are better represented by Richards or Gompertz (special case of Richards - three examples)
- In most cases inflection point is lower than $(G_{glassy} + G_{equilbrium})/2$

ALF	Binder System	T or γ	Note
1	AZCR 70-22	0.962	
2	PG70-22 Control	0.001	Gompertz
3	Air Blown	3.464	
4	SBS LG	0.180	
5	TBCR w/ SB	0.156	
7	PG70-22 + Fibers	0.012	
8	PG70-22	1.421	
9	SBS 64-40	0.001	Gompertz
10	Air Blown	0.260	
11	SBS LG	0.001	Gompertz
12	TP	0.088	

Data quality

- More recent testing on master curves for mixes enables more data points to be collected and with better data quality further assessment of models can be considered
- Number of test points/isotherm in present MEPDG scheme is limited resulting in numerical problems in some shifting schemes
- Need in many cases to assume model as part of shift development



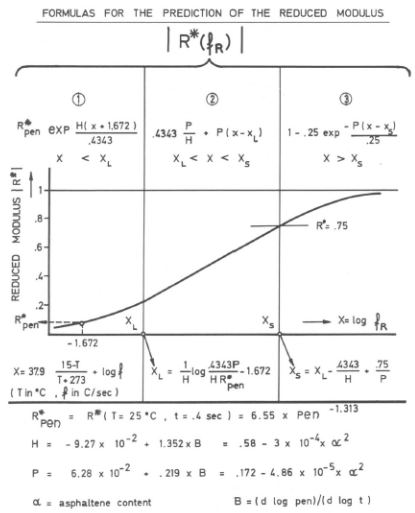
Objective of better models

- Leads to better calculations
  - Spectra calculations and interconversions
  - Better definition of low stiffness and high stiffness properties are critical if considering pavement performance
  - Work with damping calculations
  - Work looking at obtaining binder properties from mix data
  - Phase angle interrelationships
  - Considerable evidence that we should be using a non-symmetrical sigmoid function

Other non-symmetrical models

Francken and Verstaeten, 1974

- Non-symmetrical sigmoid model
- $E^*=E_\infty \times R^*(f_R)$
  - R* - sigmoid function – varies between 0 and 1



Bahia et al., 2001

- NCHRP-Report 459 – Bahia et al.

$$G^* = G_e^* + \frac{G_g^* - G_e^*}{\left[1 + (f_c/f')^k\right]^{m_e/k}}$$

where

$G_e^* = G^*(f \to 0)$, equilibrium complex modulus, $G_e^* = 0$ for binders and $G_e^* > 0$ for mixtures in shear;
$G_g^* = G^*(f \to \infty)$, glass complex modulus;
f_c = location parameter with dimensions of frequency;
f' = reduced frequency, function of both temperature and strain; and
k, m_e = shape parameters, dimensionless.

Summary

- Standard logistic symmetric sigmoidal
  - Data on more complex materials clearly does not conform
  - Obvious when looking at phase angle data versus reduced frequency
  - For HMA – same conclusion when apply “free shifting”
    - A few cases the generalized logistic gave a result close to the standard logistic
  - Standard binder – uses a non-symmetric function to describe behavior – CA model – this aspect is missing with the standard logistic in HMA model
- Generalized logistic non-symmetric sigmoid
  - Provides a more comprehensive analysis tool
  - Builds on work of Fancken et al. and Bahia et al.
  - Parameter introduced to allow variation of inflection point
  - Anticipated to become more important with more complex modified binders
  - In most cases considered for HMA the inflection point is below the mean of the Glassy and Equilibrium modulus values
  - Generalized logistic reduces to Gompertz at lower acceptable value of T or γ