Advanced Rheological Analysis

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OBJECTIVES

To present methods for advanced rheology

Why?....

- to improve understanding of materials
- enables better analysis
- better computation of specification parameters

..... better master curves and better analysis of results

This presentation in 2 parts – 1) Building Master Curves and 2) Examples
What is needed for t-T superposition

• Minimum data – 5 data points equally spaced on log scale in each isotherm
• Sufficient temperatures to enable over-lap
• Shifting – Gordon and Shaw method recommended
  • Others often used with poor understanding of consequences
TESTING STIFFNESS AT DIFFERENT RATES AND TEMPERATURES – DATA SET FROM DSR

Shift factors used to slide data along horizontal axis to make smooth curve.
Testing stiffness at different times and temperatures – data set from BBR

Shift factors used to slide data along horizontal axis to make smooth curve.

Sample ID: Test Section #5

RTFO Aged Samples

Creep modulus CAM, Rms En 0.59

$T_{ref} = -20 \, ^\circ C$

Arrhenius Fit: $E^* = 0.9973$

$\ln(\sigma(T)) = +27500.6 \ (1/T - 1/T_{ref})$
Several methods have been applied in past

- Use of shift constant factors, constant factors for Arrhenius and WLF equations
  - Pro - easy to use and implement
  - Con – assumes temperature susceptibility is known

- Use a master curve shape and a functional form to define the expected shape of the shift factor and material behavior, in bitumen commonly used with Christensen-Anderson model, in mixtures used commonly with Witczak model
  - Pro – assists with gaps in data sets, easy to implement in spreadsheet
  - Con – often mixes parameters that define temperature and time susceptibility into a single analysis

- Free shifting and post model fit, uses rules and small curve fits to fit adjacent pairs of isotherms
  - Pro – better distinction of time and temperature effects, better computation of visco-elastic model parameters
  - Con – more stringent data requirements and if data quality not present shifting may fail

Each method has been used in the analysis of asphalt materials – often papers and publications fail to provide sufficient detail on methods, each method will give different results
WHICH DATA IS SHIFTED

G’ and G”
- Generally preferred by rheologists
- Equal weight given to elastic and viscous components of stiffness
- Each is shifted independently and then averaged

G*, E*, S(t)
- G*, E* also contains both viscous and elastic components
  - In some cases mix data is poor with gaps resulting in need to use E* if free shifting is used
- S(T) used in BBR analysis – like the G* or E* - S(t) contains components of viscous and elastic behavior
FREE-SHIFT METHOD

• Free-shift method that is generally adopted is based on the book published by Gordon and Shaw
• Gordon and Shaw method requires reasonable quality data with sufficient data points in each isotherm to numerically make the error reduction process work well
• Does not require overlapping isotherms but works better if overlap exists
• Gordon and Shaw used since good reference source for computer code
Determine an initial estimate of the shift using Kaelble modification to the WLF equations with standard constants of 17.4 and 51.6.
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 being taken as the maximum value between
  - number of the augment $3\sqrt{n}$
  - maximum of $2+\Delta f$
  - A number computed from the Kaelble modified WLF
- where $n$ is the number of data points in isotherm pair - or - $\Delta f$ (the number of decades of frequency - or time).
This gives a shift factor for each successive pair which are then summed from the lower temperature to obtain all shift factors from the lowest temperature
Using the relationship between shift factor and temperature the shift to the $T_{ref}$ is then determined and all other shift factors re-expressed in relation to this shift factor
SHIFT FACTORS

• For asphalt materials – best shift factor is “modified Kealble”
  • WLF – will not model/fit area below or close to $T_g$
  • Arrhenius – will not fit full range, only works well close to $T_g$
  • Kealble – as originally formatted has to have $T_{ref}$ as $T_g$
  • Others – polynomial – not scientifically founded, poor extrapolation

• Modified Kealble
  • Allows definition of $T_{ref}$ as a separate parameter to $T_g$ (or defining temperature)
  • Based on an adjustment to WLF – scientific basis
  • Models full range of temperatures seen in a asphalt pavement
• A small vertical adjustment to the isotherms is justified before shifting takes place to account for the different densities that are obtained at the various test temperatures.
• This adjusts the measured modulus values to the value associated with the $T_{\text{ref}}$ used in the shifting.
• Justification provided by Rouse (1953) through consideration that stiffness and density of materials are coupled.
• Need to know what the binder density is and the coefficient of linear expansion is to compute change in the density as a function of temperature.
  • For asphalt binders the coefficient of linear expansion is essentially a constant value.

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

Error % = 0.3688 [$\Delta(T-T_{\text{ref}})$]

After density adjustment $G^*$ is greater at values below reference temperature and smaller at higher temperatures.
RESULT OF ANALYSIS  ➔ MASTER CURVE

A standard binder master curve – two parts – a frequency/time dependency plot ... and ... a temperature dependency plot

Fitted relationships allow us to move to different times/frequencies/temperatures
DESCRIPTION OF STIFFNESS MASTER CURVE SHAPE

- Two possibilities
  - Algebraic models
    - Christensen-Anderson (CA) Model
    - Sigmoid forms – Richards, Witczak, etc.
    - Others
  - Mechanical element
    - Relaxation/retardation spectra (also called Prony series)
    - Others – e.g. – 2S2P1D, etc.

- All choices have limitations/advantages
ALGEBRAIC MODELS

- CA Model
  - Limited to data >1e5 Pa – this is the high stiffness part of the master curve
  - Liquid behavior
- Sigmoid formats
  - Can deal with PmB and filled systems better
  - Solid type behavior
    - Does this exist??
MECHANICAL ELEMENT MODELS

- Relaxation/retardation spectra (also called Prony series) most often applied
  - Can model linear visco-elastic solid or liquid behavior
  - Good for interpolation
  - Poor for extrapolation

![Relaxation Spectra Model](image1)

![Retardation Spectra Model](image2)
FEATURES OF DATA

- What are the features ...
  - Moduli
  - Viscosities
  - Specification parameters
  - Etc.
- The properties can be applied to all our failure modes that we are interested in ...
  - Thermal cracking
  - Durability cracking
  - Fatigue cracking
  - Permanent deformation
  - Processing

\[ G^* \]
\[ G^* \cdot \sin \delta \]
\[ G^* \cdot \sin \delta \]
\[ \frac{1}{\eta''} = \frac{G^*}{\sin \delta} \]
\[ T_{VET} \quad \Delta T_c \quad G' \quad G'' \quad \eta^*, \eta', \eta'' \]

\[ G^*_c \quad T_{cr} \]
THERMAL CRACKING

- From 4mm DSR data we can extract $G(t)$ and $m(t)$
- Glover-Rowe at Cold Temperature Criteria (0.0167 rads/sec at climate temperature)
- Can use data to compute thermal stresses
  - Need $E(t)$ master curve – which can be obtained from analysis of DSR data
- $T_d$ in Kealble fit is approximated to $T_g$
- Peak in $G''$ approximated to $T_g$
DURABILITY AND FATIGUE CRACKING

- Durability
  - $\Delta T_c$ from $G(t)$ and $m(t)$ analysis
  - $\Delta T_c$ computed from CA fit
  - $G$-$R$ from DS fit of master curve

- Fatigue
  - $G^* \sin \delta$ from DS fit
  - $G$-$R$ from DS fit of master curve

- Other Linear Visco-elastic parameters may be of interest
  - $G_c$, $T_{VET}$, etc.
PERMANENT DEFORMATION

• Comparison of viscosity data with Jnr
• Viscosity information
• $1/J''$ or more commonly $G^*/\sin\delta$
• ZSV
EXAMPLES

Example 1 – a 4mm data set
Example 2 – a Pmb data set using BBR, DSR 8mm and DSR 25mm
EXAMPLE 1, 4mm DATA

- Typical 4mm data collected by MTE
- Isotherms from -24 to +41 C
- Analysis – what we can get from this
  - Discrete spectra
  - $T_g$ estimation
  - $G(t), m(t)$
4mm MASTER CURVE

- Master curve of G* and phase lag – showing discrete spectra fit
- Shift factor plot showing Kaelble fit
- Data reasonable for interpolation of parameters using interconversion using discrete spectra/Prony series math
In the first plot the data has been computed as \( G(t) \) (with \( T_{\text{ref}} = -12^\circ\text{C} \)) against time.

In the second plot we have the data with \( G(t=60\text{s}) \) plotted against temperature.

In this example:
- \( G(60\text{s}) = 327 \text{ MPa} \)
- \( m(60\text{s}) = 0.188 \)
4mm MASTER CURVE TO ESTIMATE $T_g$ FROM $G''$

- The peak in a plot of $G''$ provides an estimation of the $T_g$ of an asphalt binder
  - Use 0.1 rad/sec – based on Reinke, 2001 AAPT Publication, gives $T_g \approx -20^\circ C$
  - The result is frequency dependent as shown
- Inflection (or defining) temperature, $T_d$, from Kealble is $-6^\circ C$
4mm MASTER CURVE TO ESTIMATE G-R (DURABILITY PARAMETER) AND G'' (SHRP FATIGUE CRACKING PARAMETER)

- **Durability parameter**
  - G-R Parameter -- $G^\ast (\cos \delta^2)/\sin \delta$
  - $15^\circ C$, 0.005 rads/sec
  - $\leq 600$ kPa

- **SHRP Fatigue cracking parameter**
  - $G^\ast . \sin \delta = G'' \leq 5,000$ kPa

- In this case this binder is recovered from a badly cracked core!!
EXAMPLE 2, A PmB DATA SET

- Data set from PmB testing with BBR, 8 and 25mm PP DSR
- Reasonable mastercurve
  - Visco-elastic liquid behavior
  - Transitions clear in data
  - BBR used to define cold temperature/high stiffness performance
EXAMPLE 2, $G^* / \sin \delta$ & ZSV/SSV

- $G^* / \sin \delta$ can be computed at any temperature of interest within range measured.
- Steady state viscosity (zero shear viscosity) can be estimated from discrete spectra fit.
EXAMPLE 2, UNDERSTANDING VISCOSITY AND Jnr

- Dynamic and complex viscosity can be inspected with frequency
- Can compare to other measures – Brookfield, Jnr, etc.
  - Note $\eta_{\text{Jnr}} \text{ Pa.s} \approx 1000/\text{Jnr} (1/\text{kPa})$
EXAMPLE 2, CROSS OVER PROPERTIES

- Definition of cross-over modulus, $G^*_{c}$, $G^*_{VET}$ and cross-over temperature, $T_c$, $T_{VET}$ (defined as VET in UK – visco-elastic transition).
  - $T_c$, $T_{VET}$ – are frequency dependent, $G^*_{c}$ and $G^*_{VET}$ are material properties.

If $G_{\text{glassy}} = 1e9$ – then,

.... $R = 9 - \log G^*_c$

R – is rheological index in CA model.

Why these two frequencies ....

Early work in UK followed van der Poel’s (1954) suggestion that PEN corresponded to approximately 0.4Hz (1.57 rads). They used this value to compare to PEN. Recently, UK has been considering 10rads to be consistent with USA specifications.
This presentation shows items that need to be included in the development of master curves.

- Can be accomplished with software and/or spreadsheets
- Important to be aware of differences in methods
  - Free shifting is best for understanding material properties
  - Keable shift factor model is superior
- Need to account for temperature effects on density changes
- Need to understand limitations of models
  - Algebraic – only cover limited range (for example Christensen- Anderson Model and Sigmoid formats)
Master curves provide a tool for detailed assessment of binder performance

- Can provide estimation of all rheological parameters used in specifications
- Helps to understand polymer network structures
- Provides data on cracking and relaxation performance
- Provides a means for combination of BBR and DSR data in same analysis
Thankyou for your attention!

Questions, Comments