Development of Standard Techniques for the Calculation of Master Curves for Linear-Visco Elastic Materials

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Software Objectives

• Master Curve Production
• Discrete Relaxation and Retardation Spectra Calculation
• Conversions - time to frequency and vice-versa
• Advanced graphing and ease of use to perform complex calculations
Why master curves?

- Powerful tool to understand how asphalt type and chemical makeup affects the visco-elastic behavior of binders
- Enables easy interpolation of properties and avenue for extrapolation
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 being taken as the minimum value between number of the augment n+1, where n is the number of data points - or - $\Delta f$ (the number of decades of frequency - or time).
Normalized for density - vertical shift

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

\[ G(T_R, t) = \frac{T_R}{T} \frac{\rho(T_R)}{\rho(T)} G \left( T, \frac{t}{a_T} \right) \]
Spectra Calculations

*Baumgaertel and Winter (1989)*

- Relaxation and Retardation Spectra Calculated
  - for example

\[
G'(\omega) = G_o + \sum_{i=1}^{\infty} \frac{G_i (\omega \tau_i)^2}{1 + (\omega \tau_i)^2}
\]

\[
G''(\omega) = \sum_{i=1}^{\infty} \frac{G_i \omega \tau_i}{1 + (\omega \tau_i)^2}
\]

- Enables conversion of time to frequency (and vice-versa) and yields information about molecular structure (Rouse)
Basic Visco-Elastic Model - The Maxwell Model
Relaxation Spectra Model

Retardation Spectra Model
Typical Results from Different Equipment

Two example used

1. BBR
2. DSR
BBR
1. Bending Beam Rheometer - Typical Data Set

1. Raw Data - 5 isotherms

2. Stiffness Master Curve, S(t)

3. Compliance Master Curve, D(t)

4. Computed E', E" from spectra calculations
1. Raw Data - 5 isotherms

Sample ID: 145

Apparent Stiffness Isotherms

Legend

- Observed Data Points
  - $\bullet$ = Apparent Stiffness

-23°C

-20°C

-17°C

-14°C

-11°C

$t$, sec

$S(t)$, MPa

$10^1$ $10^2$ $10^3$ $10^4$
Sample ID: 145

Apparent Stiffness Mastercurve D-S. Rms Err 0.42%

Tref = -17

2. Stiffness Master Curve, S(t)
3. Compliance Master Curve, $D(t)$
4. Computed $E'$, $E''$
from spectra calculations
DSR
2. Dynamic Shear Rheometer - Typical Data Set
Sample ID: ac30_30%tl4_orginal

Storage Modulus and Loss Modulus Isotherms

Legend:
- Observed Data Points
- Red circles = Storage Modulus
- Blue squares = Loss Modulus

1. Raw Data - 8 isotherms

Frequency, Hz

G', G'', Pa
Dynamic Mastercurve $T_{ref} = 25^\circ C$

2. Stiffness Master Curve, $G', G''$

Legend:
- Observed Data Points
- Computed Discrete Spectrum
- $\times = (g_i, 1/\lambda_i)$
- $\bullet =$ Storage Modulus
- $\blacksquare =$ Loss Modulus
- $\text{Fitted Storage Modulus}$
- $\text{Fitted Loss Modulus}$
3. Master Curve, $G^*$, $\delta$
4. Master Curve, $G^*$ versus $\delta$
3 formats for master curve

- $G'$, $G''$ versus frequency
- $G^*$, $\delta$ versus frequency
- $G^*$ versus $\delta$ (Black space)
Error
Typical Error

Typical error -

BBR - new spec - < 1.25%
Other DSR etc < 5%

Error need to be determined for various applications. Fit needs to consider “noise” and goodness of fit.
Error Criteria

- Root mean square error

\[
Error = \frac{(S(t) - S(t)_{\text{fitted}})}{S(t)}
\]

\[
rms(\%) = 100 \sqrt{\frac{SSRE}{12}}
\]
Sample ID: ac30_30%tla_orginal

Black's Space, Tref = 25°C

Data points removed from analysis

ERROR 19.63 to 4.01%
Polymer modified binders

Dynamic Mastercurve $T_{ref} = 25^\circ C$

Legend:
- Observed Data Points
- Complex Modulus
- Phase Angle
- Computed Discrete Spectrum
- $g_i$, $1/\lambda_i$
- Fitted Complex Modulus
- Fitted Phase Angle

$G^*$, Pa

Frequency, rad/sec

Phase Angle, deg.
Black space

Black's Space, Tref = 25°C

Phase Angle, deg.

\( G^* \), Pa
Sample ID: shell_mc

Black's Space, Tref = 25 C
Conclusions

• Software developed for rapid production of master curves
  – Shifting based on Gordon and Shaw
  – Inter-conversions enabled
  – Interpolation rapid and easy to perform
  – Graphs in different formats allows understanding of data
  – RMS error criteria - a measure of goodness of fit
  – Works well with modified binders and mixtures