Historical and Current Rheological Binder Characterization vs. Binder Performance

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Why Characterize Binder Rheology With Mathematical Models?

➤ Provide mathematical formula that can be manipulated for purpose of calculation
➤ Provide quantitative parameters that can be used to characterize rheology and changes in rheology
➤ Provide rational basis for specification criteria
➤ Provide link between binder and mixture
**Models – What Is Needed?**

- Needs vary with application
- From binder perspective binder need model that:
  - Captures changes in binder rheology caused by long-term aging
    - Must be compatible with molecular/structure changes at molecular level
  - Links binder and mixture properties
  - Is related to binder “quality” – a forgotten issue
  - Many possibilities – focus on CA model

**Explicit Models – Pre SHRP**

- 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
Models – Christensen-Anderson

- Developed during SHRP
- Genesis was the need to describe relaxation modulus
  - All other rheological functions can be generated from relaxation modulus
- Christensen recognized that relaxation modulus is skewed, not symmetric
  - Concluded that skewed function was needed

CA Model

- Christensen-Anderson - CA model (1993)
  - Relates $G^*(\omega)$ to $G_g$, $\omega_c$ and $R$
Weibul Function to Model Relaxation Spectrum

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

\( F(x) \) = Probability density function
\( m \) = Skewness parameter
\( x \) = Independent parameter
\( b \) = Scale parameter
\( a \) = Location parameter

Cumulative Weibull Function

Integrate to obtain cumulative function:

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

or:

\[ 1 - P(x) = \left[ 1 + \left( \frac{x-a}{b} \right) \right]^{-m} \]
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
$R$ = Rheological Index (shape factor)
$\omega$ = Test frequency
$\omega_c$ = Crossover frequency (location parameter)

CA Model for $\delta(\omega)$

- 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
Temperature Dependency

- WLF based on free volume concepts
  - Good results above $T_g$
- Arrhenius based on rate theory
  - Necessary below glass transition temperature
- Polynomial
  - Useful over small temperature range only
  - Works well with BBR data

R and Delayed Elastic Response

\[
\frac{1}{G^*(\omega)} = \frac{1}{G_E} + \frac{1}{G_{DE}(\omega)} + \frac{1}{G_V(\omega)}
\]

\[
\frac{1}{G_{DE}(\omega)} = \frac{1}{G^*(\omega)} - \frac{1}{G_E} - \frac{1}{G_V(\omega)}
\]

Measured at some $T$ and $\omega$

\[
\frac{1}{G_g}, \quad \frac{1}{(\omega \eta_0)}
\]
Estimate for Rheological Index

- Model can be rewritten as:
  \[ \log G^*(\omega) = \log G_g + \left(\frac{R}{\log 2}\right) \log \left[ 1 - \frac{\delta(\omega)}{90} \right] \]

- \( G^*(\omega) \) versus \( \log[1 - \frac{\delta(\omega)}{90}] \)
  - slope \( \frac{R}{\log 2} \)
  - Can be estimated from a single DSR measurement

- Relationship works well when:
  \[ 10^\circ < \delta(\omega) < 70^\circ \]

Estimation of \( \eta_0 \) and \( \omega_c \)

- Similar shortcuts
- Full mastercurve is not needed to estimate model [parameters
- Useful in following aging studies
Other Models – van der Poel

- Predicts stiffness from Pen and vis
- Recognized hyperbolic relationship \( S \) vs. \( T \)
- Model implicit in development of nomograph
  - Viscous asymptote
  - Elastic asymptote

Mix models - Witczak

- Basic symmetric sigmoid function
- Basis of Witczak model for asphalt mixture \( E^* \) data
Witczak model

\[
\log(E^*) = \delta + \frac{\alpha}{1 + e^{\beta + \gamma (\log t_p)}}
\]

- Two asymptotes and the central/inflection point of the sigmoid
- Model is limited in shape to a symmetrical sigmoid

Temperature Susceptibility Parameters

- \( PI_{R&B} \) (Pfeiffer and van Doormaal, 1936)
  - Ring and ball and pen
- \( PI_{\log Pen} \) (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
Comments - Temperature Susceptibility Parameters

- Based on measurements at two temperatures
- Shear rates not same at multiple temperatures
- Confound time and temperature effects
- Studies show that different indices are not equivalent and vary differently with aging
  - Indices reflect time and temperature susceptibility

Temperature Susceptibility

- In old specifications captures via PI, PVN etc
- How do we capture this in the newer specifications/testing
- Example – five data sets from Lamont Road
BBR data using CAM Model

- Analysis of 5 data examples from Lamont test road
- Master curve construction using AASHTO PP42
  - CAM model

BBR data

- Five sections considered
- Typical example of data
- Used all data available
Master Curve Construction

_used AASHTO PP42 to construct master curves_

Shift factors

_shift factors obtained in Arrhenius form_

Arrhenius Fit: $R^2 = 0.9852$

$\ln(aT) = -28797.3 \cdot (1/T - 1/T_r)$
Temperature susceptibility

- The temperature susceptibility is captured in the slope of the shift factor.
- The better $r^2$ results from the data obtained to compute the empirical parameter closest to the rheological measurements.

Temperature intervals

- Similar to US absolute grade (PG)
- Used in Europe – particularly UK
PI can be related to temp interval

Penetration Index from DSR Data
Model Parameter Changes with Aging
R and $\omega_c$ May Both Change

- Changes in $R$ reflect changes in relaxation Modulus
  - Shape of mastercurve
- Changes in Infinite number of combinations $\omega_c$ reflect hardening
  - Location of mastercurve

Closing Comments

- Many different models are available for characterizing rheological properties of binders
  - Model selected depends on application
- Skewed function is needed to model mastercurve
- Shortcut methods can be used to generate CA model parameters
- Temperature Susceptibility parameters can be related to CA model parameters
- $R$ and or $\omega_c$ can change with aging
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