Continuous Models for Characterizing Linear Viscoelastic Behavior of Asphalt Binders

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Why Model Rheological Behavior?

- Provide rational parameters that can be used to:
  - Explain and understand behavior of bitumen
  - Describe and/or predict the aging process
  - Provide rational parameters for use in the development of specifications
  - Link binder and mixture behavior
- Different applications may justify different model
Historical - Application to Specifications

- $PI_{R&B}$ (Pfeiffer and van Doormaal, 1936)
  - Ring and ball and pen

- $PI_{logPen}$ (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
What Was Lacking in These Models?

- Provided point measurements
  - Did not provide mechanism for interpolation
  - Based on empirical measurements
  - Confounded time and temperature effects
- Significant but under appreciated development
  - Van der Poel’s nomograph
  - Based on empirical measurements
  - Lacking in accuracy
  - Model never given in explicit form
Discrete Models

- Based on springs, dashpots, sliders, and other mechanical analogs
- Examples range from simple Maxwell model to multi-element Prony series
- Mathematically elegant and relatively easy to manipulate but
  - Elements/models lack a sense of intuitiveness
  - Such models are poor candidates for predicting aging or relating to composition
Continuous Models

- Continuous function that defines the mastercurve and contains:
  - Minimal number of model parameters
  - Parameters that have a rational explanation
  - Parameters that can be related to binder composition and a molecular model
  - Parameters that can be related to the aging process
  - Parameters that are useful in specification development
- Number of early examples in literature
Early Continuous Models

- 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
Christensen-Anderson LVE Model

- Original motive was to provide SHRP specification criteria for unmodified asphalt binders
  - Approach was discontinued in favor of point parameters such as $G^*/\sin\delta$, $S(60s)$, etc.
- Based on the observation that the relaxation spectrum is a skewed function of time
  - Skewed logistic function gave best “fit”
- All other rheological functions can be generated from relaxation spectrum
Skewed Logistic Function

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

\[F(x)\] = Probability density function

\[m\] = Skewness parameter

\[x\] = Independent parameter

\[b\] = Scale parameter

\[a\] = Location parameter

Through integration obtain cumulative distribution function

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

$$\delta(\omega) = 90 / \left[ 1 + \left\{ \frac{\omega}{\omega_c} \right\}^{(\log 2) / R} \right]$$

$\delta(\omega) = \text{Measured phase angle}$
Time-Temperature Dependency

- Dependency above and below $T_g$ must be characterized with different algorithms.
- WLF gives good results above $T_g$:
  - Based on free volume concepts.
- WLF is not applicable below $T_g$ due to physical hardening:
  - Free volume is changing with time.
  - Arrhenius gives better results.
- Time-temperature dependency must consider $T_g$. 
Short-cut Estimation of $R$ and $\omega_c$

- Full mastercurve is not needed to estimate model parameters
  - Shortcuts are especially useful in following aging studies where resources for full generation of mastercurve is impractical
$\eta^* \text{ vs. } (1 - \delta/90^\circ)^{1.5}$ gives $\eta_0$

Extrapolation to determine $\eta_0$
Log $\omega$ vs. log tan$\delta$ gives $\omega_c$
Log log $G_g/G^*$ vs. Log tan $\delta$
$|G^*| \text{ and } \delta \text{ Interrelation}
Changes in $R$ and $\omega_c$ with Aging

- Change in $R$ reflects change in time dependency and relaxation spectrum
  - Mastercurve flattens with aging
  - $R$ increases

- Change in $\omega_c$ reflects change in position of mastercurve
  - Mastercurve shifts to longer times or smaller frequencies
  - Reflects increase in $\eta_0$
Change in Mastercurve with Aging

Complex Modulus, Pa

Frequency, rad/s

Tank

PAV Aged

Recovered
Should In-Service Changes in S and m Be Indicative of Performance?

- Crossover frequency
- $R$ - value
- Mastercurve shape as function of PI
Does It Work? Qualified Yes!

- Model was developed for unmodified binders
  - Model works well for unmodified binders if phase angle is less than approximately 70°
  - Need modification to better describe MC as approach 90°
- Model breaks down for modified binders at upper range of application temperatures
  - Elasticity of elastomeric modifiers disrupts shape of mastercurve
  - Need modification for modified materials
CA Model - Discussion

- CA model based on the assumption that the relaxation spectrum is a logistic function
- The model provides simple expressions for $|G^*|$ and $\delta$

\[ |G^*(\omega)| = G_g \left[ 1 + \left( \frac{\omega_c}{\omega} \right)^{(\log 2)/R} \right]^{-R/(\log 2)} \]

\[ \delta(\omega) = \frac{90}{\left[ 1 + \left( \frac{\omega_c}{\omega} \right)^{(\log 2)/R} \right]} \]
**$|G^*|$ and $\delta$ Interrelation**

- Booij and Thoone demonstrated that the real and imaginary parts are inter-related according to Kramers-Kronig functions; when applied to viscoelastic materials, under certain conditions, the Kramers-Kronig functions can be approximated by the following simple equations:

\[
G'(\omega) \approx \frac{\pi}{2} \left( \frac{d G''(u)}{d \ln(u)} \right)_{u=\omega}
\]

(1)

\[
G'(\omega) - G'(0) \approx -\frac{\omega \pi}{2} \left( \frac{d [G''(u) / u]}{d \ln(u)} \right)_{u=\omega}
\]

(2)

\[
\delta(\omega) \approx \frac{\pi}{2} \left( \frac{d \ln |G^*(u)|}{d \ln(u)} \right)_{u=\omega}
\]

(3)
According to Williams and Ferry, the relaxation spectrum can be approximated as follows:

\[
H(\tau) \approx \frac{\sin m\pi/2}{m\pi/2} \left[ G' \left( \frac{d \ln G'}{d \ln \omega} \right) \right]_{\omega=1/\tau} (5)
\]

where \( G' \) is the storage modulus and \( m \) is the estimated negative slope of \( H(\tau) \) on a double logarithmic plot.

Booij and Palmen applied equation 4 to equation 5 and obtained the following approximate expression

\[
H(\tau) = \frac{\sin 2\delta}{2\delta} |G^*| \left[ \frac{2\delta}{\pi} + \frac{d \ln \cos \delta}{d \ln \omega} \right]_{\omega=1/\tau}
\]
Relaxation Spectrum Approximation

This can be further approximated to:

\[
H(\tau) \approx \frac{1}{\pi} \left[ |G^*| \sin 2\delta \right]_{\omega=1/\tau}
\]
CAM Model

- CA model modified to improve fitting in the lower and higher zones of the frequency range
  - Authors applied Havriliak and Negami model to the $|G^*|$ resulting in the following expression:

$$
|G^*(\omega)| = G_g \left[ 1 + \left( \frac{\omega_c}{\omega} \right)^v \right]^{\frac{w}{v}}
$$

$$
\delta(\omega) = 90 \frac{w}{[1 + (\omega_c / \omega)^v]}
$$

- New parameter $w$ describes how fast or how slow the phase angle data converge to the two asymptotes as frequency goes to zero or to infinity
- E.g., as frequency approaches zero, $w > 1$ characteristic of bitumen that reaches 90 degrees asymptote faster than a bitumen with $w < 1$
CAM Model
CAM Model

- Note that Leuseur used Havriliak and Negami model to represent the complex viscosity of bitumens.
- By plotting data in Black space, he showed that not all bitumens are thermorheologically simple.
  - This was noted previously where vertical shift factors were used in conjunction with the CA model and the vertical shift factors were related to wax content.
  - This was also noted when using CAM model.
    - Many models fit $G''$ and $G''$ simultaneously.
A linear viscoelastic material is thermorheologically simple if all characteristic functions (retardation, relaxation spectra, etc) meet the same time-temperature dependency.

Further developed by Ferry based on two assumptions:

- Moduli are proportional to the product of temperature and density.
- Relaxation times depend on a single monomeric friction coefficient.

First condition implies that $G''/G'$, which represents the tangent of the phase angle, is independent of temperature and density.
Accordingly, the proper technique for generating master curves is to first superimpose the phase angle data to generate a set of horizontal shift factors. |G*| data is then shifted with these horizontal shift factors and the vertical shift factors, if any, are determined by obtaining a smooth |G*| master curve.
Using Models to Obtain Mixture Properties from Binder Properties (and vice-versa)

**Semi-empirical model**

- Christensen *et al.* (2003) proposed semi-empirical model to estimate extensional and shear dynamic modulus

\[
E_{\text{mix}} = Pc\left[ E_{\text{agg}}V_{\text{agg}} + E_{\text{binder}}V_{\text{binder}} \right] + \left(1 - Pc\right)\left[ \frac{V_{\text{agg}}}{E_{\text{agg}}} + \frac{(1 - V_{\text{agg}})^2}{E_{\text{binder}}V_{\text{binder}}} \right]^{-1}
\]

\[
Pc = \left( \frac{P_0 + \frac{VFA \cdot E_{\text{binder}}}{VMA}}{P_2 + \left( \frac{VFA \cdot E_{\text{binder}}}{VMA} \right)_{P_1}} \right)^{P_1}
\]

- Pc-contact volume
- \(P_0, P_1, P_2\)-constants
- VFA-voids fill with asphalt
- VMA-voids between aggregate

**Zofka (2007)** proposed modification of \(Pc\):

\[
Pc = \left( \frac{E_{\text{binder}}}{\phi} \right) + 0.609
\]
Forward Problem - Hirsch Model

Hirsch model for PG 58-34 M1 mixtures T=-24°C
2S2P1D Model (Olard and Di Benedetto, 2003)

\[ E^*(i\omega\tau) = E_0 + \frac{E_\infty - E_0}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h} + (i\omega\beta\tau)^{-1}} \]

- \( E^* \): complex modulus,
- \( E_\infty \): glassy modulus, \( \omega\tau \to \infty \)
- \( E_0 \): static modulus, \( \omega\tau \to 0 \)
- \( h, k \): exponents such that \( 0 < k < h < 1 \)
- \( \delta \): dimensionless constant,
- \( \beta \): dimensionless parameter for the linear dashpot
- \( \omega \): \( 2\pi \) frequency,
- \( \tau \): characteristic time varying with temperature
- \( t \): time

No analytical expression for creep compliance in the time domain for this model.
Analogical Models

- **2S2P1D Model (Olard and Di Benedetto, 2003)**
- Each mixture had the same parameters $\delta$, $k$, $h$ and $\beta$ of the associated binder while only the static and glassy modulus ($E_0$ and $E_\infty$) and $\tau_0$ seemed to be binder and mixtures specific.
- The values of $E_0$ and $E_\infty$ for the mixtures were in the range of 250 to 1050MPa and 41500 to 45400MPa respectively.
- Simple regression of the characteristic time of the mixture on the characteristic time of the corresponding binder at the reference temperature in log scale the authors found that:

$$\tau_{mix}(T) = 10^\alpha \tau_{binder}(T)$$

$\alpha$ regression coefficient depending on mixture and aging.
Analogical Models

- **2S2P1D Model (Olard and Di Benedetto, 2003)**

- From the 2S2P1D model a relationship between the binder and the mix complex moduli was proposed. The expression is independent of the rheological model used to construct it.

\[ E^{*}_{\text{mix}}(\omega, T) = E_{0\text{mix}} + \left[ E^{*}_{\text{binder}}(10^\alpha \omega, T) - E_{0\text{binder}} \right] \frac{E_{\infty\text{mix}} - E_{0\text{mix}}}{E_{\infty\text{binder}} - E_{0\text{binder}}} \]

- \( E^{*}_{\text{mix}} \): complex modulus of the mixture,
- \( E^{*}_{\text{binder}} \): complex modulus of the binder,
- \( E_{\infty\text{mix}} \): glassy modulus of the mixture,
- \( E_{0\text{mix}} \): static modulus of the mixture,
- \( E_{\infty\text{binder}} \): glassy modulus of the binder,
- \( E_{0\text{binder}} \): static modulus of the binder,
- \( T \): temperature,
- \( \omega \): \( 2\pi \times \) frequency,
- \( \alpha \): regression coefficient depending on mixture and aging.
Huet Model ((Huet, 1963))

\[ D(t) = \frac{1}{E_\infty} \left( 1 + \delta \frac{(t/\tau)^k}{\Gamma(k+1)} + \frac{(t/\tau)^h}{\Gamma(h+1)} \right) \]

\[ E^*(i\omega\tau) = \frac{E_\infty}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h}} \]

- \( D(t) \): creep function
- \( E^* \): complex modulus,
- \( E_\infty \): glassy modulus,
- \( h, k \): exponents such that 0 < k < h < 1
- \( \delta \): dimensionless constant,
- \( \omega \): \( 2\pi \) frequency,
- \( \tau \): characteristic time varying with temperature
- \( t \): time
- \( \Gamma \): gamma function:
Forward Problem - Huet Model

Granite

Limestone

Huet model for PG 58-34 M1 mixtures T=-24°C
Forward Problem - Huet Model

Huet model parameters for four binder and corresponding granite mixture

<table>
<thead>
<tr>
<th>Material</th>
<th>δ</th>
<th>k</th>
<th>h</th>
<th>E∞ (MPa)</th>
<th>Log(τ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>58-34:M1</td>
<td>2.42</td>
<td>0.18</td>
<td>0.60</td>
<td>3000</td>
<td>0.251</td>
</tr>
<tr>
<td>58-34:M2</td>
<td>4.18</td>
<td>0.22</td>
<td>0.62</td>
<td>3000</td>
<td>0.497</td>
</tr>
<tr>
<td>64-34:M1</td>
<td>3.50</td>
<td>0.21</td>
<td>0.64</td>
<td>3000</td>
<td>0.387</td>
</tr>
<tr>
<td>64-34:M2</td>
<td>3.99</td>
<td>0.23</td>
<td>0.64</td>
<td>3000</td>
<td>0.328</td>
</tr>
<tr>
<td>Mixtures</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>58-34:M1:GR</td>
<td>2.42</td>
<td>0.18</td>
<td>0.60</td>
<td>28000</td>
<td>3.420</td>
</tr>
<tr>
<td>58-34:M2:GR</td>
<td>4.18</td>
<td>0.22</td>
<td>0.62</td>
<td>30000</td>
<td>3.675</td>
</tr>
<tr>
<td>64-34:M1:GR</td>
<td>3.50</td>
<td>0.21</td>
<td>0.64</td>
<td>30000</td>
<td>3.547</td>
</tr>
<tr>
<td>64-34:M2:GR</td>
<td>3.99</td>
<td>0.23</td>
<td>0.64</td>
<td>29001</td>
<td>3.523</td>
</tr>
</tbody>
</table>

\[
D_{\text{binder}} (t) = \frac{1}{E_{\infty \_binder}} \left( 1 + \delta \left( \frac{t}{\tau_{\text{binder}}} \right)^k + \left( \frac{t}{\tau_{\text{binder}}} \right)^h \right) \frac{1}{\Gamma(k+1)} + \frac{1}{\Gamma(h+1)}
\]

\[
D_{\text{mix}} (t) = \frac{1}{E_{\infty \_mix}} \left( 1 + \delta \left( \frac{t}{\tau_{\text{mix}}} \right)^k + \left( \frac{t}{\tau_{\text{mix}}} \right)^h \right) \frac{1}{\Gamma(k+1)} + \frac{1}{\Gamma(h+1)}
\]
Forward Problem - Huet Model

- Based on the strong linear correlation found ($R^2=0.98-0.99$ for all the binders-mixtures), the following expression can be written to relate the characteristic time of the binders and corresponding mixtures with similar mix designs:

$$\tau_{mix} = 10^\alpha \tau_{binder}$$

- $\tau_{binder}$: characteristic time of binder,
- $\tau_{mix}$: characteristic time of mixture,
- $\alpha$: regression parameter, may depend on mix design
Forward Problem - Huet Model

\[ D_{\text{mix}}(t) = D_{\text{binder}}(t/10^{\alpha}) \frac{E_{\infty \text{ binder}}}{E_{\infty \text{ mix}}} \]

\[ S_{\text{mix}}(t) = S_{\text{binder}}(t/10^{\alpha}) \frac{E_{\infty \text{ mix}}}{E_{\infty \text{ binder}}} \]

- \(D_{\text{mix}}(t)\): creep compliance of mixture,
- \(D_{\text{binder}}(t)\): creep compliance of binder,
- \(S_{\text{mix}}(t)\): creep stiffness of mixture,
- \(S_{\text{binder}}(t)\): creep stiffness of binder,
- \(E_{\infty \text{ mix}}\): glassy modulus of mixture,
- \(E_{\infty \text{ binder}}\): glassy modulus of binder,
- \(\alpha\): regression parameter which may depend on mix design,
- \(t\): time
Inverse Problem- Hirsch Model

Hirsch model for PG 58-34 M1 mixtures $T=-24^\circ C$
Inverse Problem - Huet Model

Based on the findings of Forward Problem:

\[ \tau_{binder} = 10^{-\alpha} \tau_{mix} \]

\[ S_{binder}(t) = S_{mix}(t / 10^{-\alpha}) \frac{E_{\infty \_binder}}{E_{\infty \_mix}} \]

- \( S_{mix}(t) \): creep stiffness of mixture,
- \( S_{binder}(t) \): creep stiffness of binder,
- \( E_{\infty \_mix} \): glassy modulus of mixture,
- \( E_{\infty \_binder} \): glassy modulus of binder,
- \( \alpha \): regression parameter which may depend on mix design,
- \( \tau_{binder} \): characteristic time of binder,
- \( \tau_{mix} \): characteristic time of mixture,
- \( t \): time.
Inverse Problem - Huet Model

Granite

Limestone

Huet model for PG 58-34 M1 mixtures T=-24°C
Acknowledgements

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