Application of Rheological Models to Modified Binders

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Objectives

- To review types of models applied to modified binders
  - Discuss models
  - How shifting is done
  - Treatment of temperature
  - Treatment of BBR data
  - Shifting of DSR
- Review some changes in material properties
  - To explain what we are working on with regard to model development
  - To discuss how this applies to modified binders
  - What information may be obtained
  - How does our model fit work – limits
- Summary
Models is a “work in progress”

- No perfect model
- No answer that works well for all binders
- Contributions from many workers still needed
Types of rheological models

- Models to describe master-curves can generally be considered as:
  - functional forms (or equation)
  - mechanical element
Mechanical element models

- 1963 Huet Model
- 1967 Huet–Sayegh Model
- 1980’s Relaxation or retardation spectra/Prony series
- 1987 The 2S2P1D Model
- 2001 Di Benedetto and Neifar (DBN) Model

+ others

If constructed well forms a basis for computations in software etc
Functional forms and mechanical element models

- Functional forms and mechanical element models have “parameters” that are relatable to structural features used in numerical analysis methods.
  - For example:
    - MEPDG – E* model
    - CAM model – used in the assessment of critical cracking temperature of binder (AASHTO PP42/ASTM 6816)
    - Power law – low temperature cracking calculation of mix with IDT
Functional forms

- These generally offer a continuous models
- Can describe the properties over a very wide range of temperatures and frequencies
- The fitted functions can also be used to smooth and extend results thus providing better data for the subsequent fitting of mechanical models
## Functional forms – some examples

### Binders
- 1969: Jongepier and Kuilman’s
- 1969/72: Dobson’s Model
- 1974: Dickinson and Witt’s
- 1992: Christensen and Anderson (CA)
- 1999: Christensen, Anderson and Marasteanu (CAM)
- 2002: Matching Function - Al-Qadi and co-workers

### Mixes
- 1981-2005: Sigmoidal Model (Witczak)
- 2000: Hirsch model (Asphalt mixes)

### Both binder/mix
- 2001: NCHRP Report 429 (Bahia et al.)
- 2009: Generalized Logistic Sigmoidal Sigmoid (RBS)

+ others
Time-temperature superposition

- While a model might describe properties well at a single temperature we need a robust method to describe the time temperature shift parameters.
Time-temperature superposition

- Free or model shifting
- Descriptive shift functions
  - Arrhenius
  - WLF
  - Polynomial
  - A+VTS
  - Kaelble
Shifting

- Free
- Functional form
- Functional form with descriptive shift function
- Shift function
Approach

- Use free shifting
- Adopt functional form approach
  - Descriptive information for sigmoid shape
    - $G_e$ tends to zero for visco-elastic liquids
    - non-symmetrical
  - Sigmoid form for shift factor function
    - Inflection point similar to definition of $T_d$ in SHRP A-369 report
- Use “Rouse” density adjustment
Rouse temperature adjustment

- What is this?
Normalized for density - vertical shift

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

\[ G(T_R, t) = \frac{T_R}{T} \frac{\rho(T_R)}{\rho(T)} G\left(T, \frac{t}{a_T}\right) \]
Effect of density adjustment on $G^*$
Effect of density adjustment on $G^*$

- Difference looks insignificant on log scale.
- If a 50°C shift is considered from the reference temperature then the error is -18.5% which equates to a temperature difference of approximately 1.14°C.
- Density correction is significant in our work with binder master curves.

After density adjustment $G^*$ is greater at values below reference temperature and smaller at higher temperatures.
Just a word on other sigmoid methods

- Various other sigmoid forms used
  - MEPDG
  - NCHRP Report 429
  - Hirsch

- Problem with sigmoid fits is that they have some limited capability
  - Limits, symmetric, etc.

- Sigmoid only describe a sigmoid
  - Binders often have more complex behavior – ultimately we still need better models?!
What are characteristics

- Solid type behavior
- Phase angle will peak
- Two asymptotes – equilibrium modulus and glassy modulus
- Two crossover frequencies
Non-symmetric sigmoid

\[ \log G^* = \delta + \frac{\alpha}{1 + \lambda e^{(\beta+\gamma(\log \omega_r))}}^{1/\lambda} \]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E^*)</td>
<td>complex extensional modulus</td>
</tr>
<tr>
<td>(\omega_r)</td>
<td>reduced frequency in rads/sec</td>
</tr>
<tr>
<td>(\delta)</td>
<td>log equilibrium modulus, (\log G_e)</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>(\log G_e - \log G_g)</td>
</tr>
<tr>
<td>(G_g)</td>
<td>glassy modulus</td>
</tr>
<tr>
<td>(\lambda, \beta, \gamma)</td>
<td>fitting parameters</td>
</tr>
</tbody>
</table>

\(10^{-\beta/\gamma}\) inflection point/frequency
\(\lambda\) controls height of inflection point
Non-symmetric sigmoid, $\lambda$

- When $\lambda = 1$ equation becomes standard logistic.
- When $\lambda$ tends to 0 – then equation becomes Gompertz which is minimum value of inflection $y=1/e$ – or 36.8% of relative height.
- $\lambda$ must be positive for analysis.

Typical range in inflection values:
- $\lambda = -0.5$
- $\lambda = 0.0$ Gompertz
- $\lambda = 0.6$
- $\lambda = 1.0$ Logistic
- $\lambda = 2.0$

When $\lambda$ tends to 0 – then equation becomes Gompertz which is minimum value of inflection $y=1/e$ – or 36.8% of relative height.

$\lambda$ must be positive for analysis.
Example with high modification

- Data files
  - BBR -12, -18, -24°C
  - DSR 0, 15, 3, 45, 60, 75, 90, 105, 120 and 135°C
- BBR data converted to $G'$, $G''$
- Combined data then shifted
  - Free shifting
  - Used complex modulus shift
BBR data

Sample ID: BBR 125-30-0

Apparent Stiffness Isotherms

-24°C
-18°C
-12°C

Legend
Observed Data Points
- = Apparent Stiffness
BBR $S(t)$ to $G’G”$ conversion (1)

- Fit the BBR data is fitted with the CA, CAS and CAM model and determine the fit with the lowest error. This master-curve is adopted.
  - If material is a filled product then fit will most likely be CAS – enables higher glassy modulus
  - For most neat binders fit most likely will be CAM
- Hopkins and Hamming method is used to convert the master curve to the relaxation modulus $E(t)$. 
BBR $S(t)$ to $G'G''$ conversion (2)

- The Hopkins and Hamming algorithm provides a numerical solution to the convolution integral required to convert BBR creep stiffness (compliance, $D_\xi$, is first computed using model parameters, $D_\xi = 1/ S_{\text{BBR}}(\xi)$) to relaxation modulus.
- The convolution integral is:

$$\int_0^t E(\xi) D(t - \xi) d\xi = t$$
BBR $S(t)$ to $G’G”$ conversion (3)

Hopkins and Hamming – numerical solution

$$E(t_{n+\frac{1}{2}}) = \frac{t_{n+1} - \sum_{i=0}^{n-1} E(t_{i+\frac{1}{2}})[f(t_{n+1} - t_i) - f(t_{n+1} - t_{i+1})]}{f(t_{n+1} - t_n)}$$

$$f(t_{n+1}) = f(t_n) + \frac{1}{2} [D(t_{n+1}) + D(t_n)][t_{n+1} - t_n]$$

The initial value $f(t)$ at zero time is set as zero.
BBR S(t) to G’G” conversion (4)

- If E(t) is just taken as 1/D(t) then some significant errors can be introduced.
- Example is PIB
BBR S(t) to G’G” conversion (5)

- Fit the E(t) data with a CAM model using the Glassy modulus determined from the previous fitting. This gives a function which describes a E(t) fit and essentially allows for a different glassy modulus if considered necessary from the earlier step.
- Calculate the discrete spectra for the E(t) fitted function.
- The reciprocal of the observed times are the substituted into the function to estimate the E', E'' data points.
BBR S(t) to G’G” conversion (6)

- The data points are shifted using the original shift values obtained along with a reverse density correction (Rouse) to obtain dynamic isotherms corresponding to the original data.

- Shear data is then obtained by converting to G’, G” with a Poisson's ratio of 0.5.
  - This basically assumes no volume change which is reasonable for a liquid binder.
BBR S(t) to G’G” conversion (7)

- Process is implemented in software since it is quite numerically intensive
- RESULT ➔
- Can now merge this with other dynamic data
Shifting of DSR data

- Shift on $G'$, $G''$ – or $G^*$
  - Often $G^*$ numerically similar – even in software tools
  - Produces compromise – since both $G'$ and $G''$ are contained within $G^*$
  - Sometime $\delta$ is compromised by testing or phase changes within material
  - We used complex modulus shift
Crossover frequency (1) – to 90°C

Typically two cross-over frequencies will occur before significant phase change which can be modeled by a sigmoid.
Typically three cross-over frequencies will occur if data is included beyond a “phase change”
Complex modulus Pairwise shift
Complex modulus fit

Sample ID: 125-30-0_c
Dynamic Mastercurve Tref = 25°C

Legend
- Observed Data Points
- Complex Modulus
- Phase Angle
- Fitted Complex Modulus
- Fitted Phase Angle

Computed Discrete Spectrum
- \( g_1, 1/\lambda_1 \)

\[ G^* \text{, Pa} \]

Phase Angle, deg.

Frequency, rad/sec

\[ 10^0, 10^1, 10^2, 10^3, 10^4, 10^5, 10^6 \]

\[ 10^{-8}, 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} \]
Solid versus liquid model

○ Solid model will only apply when evidence of solid type behavior
  ● Plateau zone – $G'$, $G''$
  ● Phase angle starts to reduce

○ If material transitions then liquid model re-applies – but no functional form
Solid versus liquid model

If data between 105 to 135°C is excluded – the model is VE solid.

$G^*$, rad/sec

$E^*$, -30 to 90°C

$E^*$, 105 to 135°C

$\delta$, Model fit

$\delta$, all data

$T_{ref}=25^\circ$C
Model fit

○ Fitted VE solid model

\[ \log G^* = \delta + \frac{\alpha}{1 + \lambda e^{(\beta + \gamma (\log \omega_r))^{1/\lambda}}} \]

○ If no solid fit
  ● CAM type model

\[ G^*(\omega_r) = G_x [1 + (\omega_c / \omega_r)^\beta]^{-\kappa/\beta} \]

○ Used Kaelble shift

\[ \log a_T = -C_1 \left( \frac{T - T_d}{C_2 + |T - T_d|} - \frac{T_r - T_d}{C_2 + |T_r - T_d|} \right) \]

○ Considered what is happening with cross-over frequency
  ● Looked at that occurring at higher frequency since more likely to be dependent on binder

○ Shape of model
Materials evaluated

<table>
<thead>
<tr>
<th>Material designation</th>
<th>Asphalt</th>
<th>SBS Content</th>
<th>SBS Type</th>
<th>Filler</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Vacuum Distilled Asphalt</td>
<td>61.25%</td>
<td>Radial</td>
<td>30% Calcium Carbonate Filler</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.75%</td>
<td></td>
<td>30% Calcium Carbonate Filler 10.5% Flame Retardant Filler</td>
<td>1.26</td>
</tr>
<tr>
<td>B</td>
<td>Vacuum Distilled Asphalt</td>
<td>56.87%</td>
<td>Radial</td>
<td>35% Calcium Carbonate Filler</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.13%</td>
<td></td>
<td>35% Calcium Carbonate Filler</td>
<td>1.31</td>
</tr>
<tr>
<td>C</td>
<td>Vacuum Distilled Asphalt</td>
<td>61.25%</td>
<td>Radial</td>
<td>35% Calcium Carbonate Filler</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.38%</td>
<td>Radial</td>
<td>35% Calcium Carbonate Filler</td>
<td>1.31</td>
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<tr>
<td></td>
<td>Polyphosphoric Acid</td>
<td>60%</td>
<td>Linear</td>
<td>40% Calcium Carbonate Filler</td>
<td>1.37</td>
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<tr>
<td></td>
<td>Catalytically Air Blown</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Asphalt (100°C SP/35 pen)</td>
<td>4.37%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Type IV Straight Air Blown</td>
<td>60%</td>
<td>Linear</td>
<td>40% Calcium Carbonate Filler</td>
<td>1.37</td>
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<tr>
<td></td>
<td>Asphalt, No Filler</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td>1.02</td>
</tr>
</tbody>
</table>
Aging

- Aging – 4 conditions
  - dark oven aging of 2 mm thick films aged in a dry, dark, forced draft oven at 80°C
    - 0 – no ageing
    - 1 – one month
    - 2 – two months
    - 3 – three months
Effect of aging on $G^*$ master curve, A

- Need to quantify the effects
  - Look at cross-over
  - Shape
  - Temperature susceptibility
  - Etc.
Cross over frequency

- Crossover frequency reduces as material ages
- Consistent with expectations
- Two of the products showed much larger increases – both air blown products
Effect of aging on $G^*$ master curve, E
Change to $G_e$

- VE solid behavior cannot be modeled with some materials after aging has occurred – $G_e \to$ tends to zero
- Materials A, B, C and D – VE solid at 0 aging
  - VE liquid at 2 and 3 months
Temperature susceptibility

- Degree of shift changes between isotherms as material ages
- In all cases C2 increases – controls slope of WLF or Kaelble relationships
Temperature susceptibility

- Can consider three parameters for description of temperature susceptibility from rheology
  - $\beta$ and $R$ (CA model) linked via simple relationship
    - $R = \log_2/\beta$
  - C1 parameter in WLF/Kaelble sets location
  - Note C1 and C2 are not constant values but depend upon material

\begin{align*}
  y &= 0.2622e^{0.0061x} \\
  R^2 &= 0.9248 \\
  y &= 1.1482e^{0.0061x} \\
  R^2 &= 0.9248
\end{align*}
Temperature susceptibility

- What about our old parameters
  - Measured Pen, 25 and 50°C and ring & ball softening point
  - Calculated Penetration Index, PI
  - PI with SP provided best correlation with observed behavior
Temperature susceptibility

- Compare against old measures, for example = PI
- PI reduces for SBS modified materials as solid structure is lost with age
- May increase if further aged!!??
- For non-SBS in study PI increases with aging time
Temperature susceptibility

- With age
  - C2 increases
  - R-value increases
  - Beta reduces
  - PI - can go either way
    - PI reduces as solid structure is lost
    - Increases as liquid structure hardens
Deformation/flow potential

Simulated repeated creep – 3200 Pa

- 1.088% - solid
- 6.600% - liquid (forced)

<table>
<thead>
<tr>
<th>G*/sin(β), kPa @ 64°C</th>
<th>B-0</th>
<th>B-1</th>
<th>B-2</th>
<th>B-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>46.6</td>
<td>233.3</td>
<td>369.1</td>
<td>595.1</td>
<td></td>
</tr>
</tbody>
</table>

- 9.963%
  - Increased deformation, loss of network

- 5.704%
  - Deformation reduces and material becomes stiffer

- 4.548%
  - Reduced deformation, further stiffening
Summary 1

- Can use a non-symmetric sigmoid to describe behavior
  - Shifting – standards need to be very specific on assumptions
  - Many ways to develop data
- Liquid behavior – CAM type model does a reasonable job
  - Must use variable $G_g$ modulus with modified materials
  - $\beta$ and R-value – in various model forms related by $R=\log2/\beta$
- $\beta$, R and C2 all related to temperature sensibility
- Temperature correction is important in the development of master curves
A model format VE solid is discussed the properties of many highly-modified products to be modeled effectively between -40 and +90°C.

The six products evaluated can be described either by the VE solid model (RBS) or the VE liquid model (CAM).

For the SBS modified materials considered in this analysis the polymer network degrades with age resulting in a solid model being no longer applicable to define the rheology of the materials.

- The aged materials are behaving like stiff visco-elastic liquids

The cross-over frequency is significantly affected as the material ages as is the \( \beta \) parameter that defines the rheological type of the binder.

- Both of these changes are anticipated
Summary 3

- The temperature susceptibility as defined by the shift factors needed to produce master curves changes significantly with aging
- Shape and position of master curves change
- Work in progress.....
The end

- Thanks for listening!

Greetings from all of us too!