Roofing Asphalt Characterization:

John Casola
Malvern Panalytical

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Roofing asphalt characterization: simplified testing using intelligent rheology

› This presentation will review some alternate testing techniques which relate to several commonly performed roofing asphalt tests. These methods will be discussed along with actual data presented from automated DSR determination of softening point, penetration, capillary and rotational viscosity. When implemented for quality control, intelligent software will be used for logical decision making which can be used for determination of pass/fail criteria, report generation and escalation decisions for out of spec materials to company procedures.

› Other techniques to investigate adhesive pull off, prediction of sag, as well as, high shear to simulate processing conditions will also be presented.
Data Presented

› 10 Samples of various roofing products
  ▪ Flux
  ▪ Highly Polymer Modified
  ▪ Oxidized
  ▪ Highly Mineral Filled

› Broad range of Applications
  ▪ Mopping
  ▪ Shingles
  ▪ Adhesives
  ▪ Etc...

› Broad range of Customer Requirements
  ▪ Most products used internally. Internal QC/QA
  ▪ Some products are provided to other Manufacturers. External QA & Specific Testing

› Broad range of Material Properties
  ▪ We will focus on basic, common tests
The Goal

› Managing a broad range of products with a broad range of testing conditions
  - Temperature
  - Pass/Fail Limits
  - Viscosity
  - Etc...

› Making the testing easy, reliable and highly reproducible
  - Standard Operation Procedures (SOP) driven to ensure exact procedure is performed
  - Test set up automatically by product
  - Improving statistical accuracy

› Providing immediate feedback with next step solutions
  - Logical decision making based on results to provide operator ‘what next’ to policy
Tests Performed For This Presentation

› Viscosity
› Penetration
› Softening Point
› Pull-Off

› Notes on Units:
› While many manufacturers use Imperial (CGS) units, such as, Fahrenheit, Poise and Inches, I’ve chosen to present most thing in SI units.

› Temperature in Celsius.
› Viscosity will be in Pas
› Frequency in Hertz
Tests Performed

› Viscosity, at various specified temperatures & acceptance limits
  ▪ 204°C, 190°C, 177°C, 163°C, 149°C, 125°C & 0°C

› Penetration at 25°C & 0°C

› Softening Point
  ▪ Measured with static force loading
  ▪ Measured with dynamic force loading

› Pull-Off
  ▪ 0.1 inch/min
  ▪ 1.0 inch/min
  ▪ 12 inch/min

› High Shear Viscosity for discussion
Rotational Viscosity

› Very common test measurement

› Performed at a single rotation rate

› Performed at a single temperature

› Performed of a specific period of time

› Question: What does it really tell us about the product?
Sample H; 1012mPas @ 163C
DSR Shear Viscosity

Initiate Pumping/Sag & Leveling

Pouring

Mopping/Spreading

Pumping

Viscometer

A

B

C

D

E

F
DSR Shear Viscosity
Tuminello & Shaw for polymer MW & MWD
Krieger Dougherty & Einstein Equation PS & PSD

MWD & PSD Controlled

MW & Concentration Controlled
Static Load to Monitor Softening

w/ repeat
Static Determination of Softening Point

Sample A: SP = 124°C
w/ repeat
Oxidized Roofing Asphalt using Static Load ~2009
Dynamic Determination of Softening Point

Modulus and Temperature Vs Time

- 5°C/min
- 25°C
Comparison of Effort to Flow; Interesting Behavior?
Viscosity* to Reported Softening Point (poor fit)

$R^2 = 0.48$
Modulus to Reported Softening Point
Loss Modulus (G’’)
to Reported Softening Point

<table>
<thead>
<tr>
<th>Sample</th>
<th>SP</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>110</td>
</tr>
<tr>
<td>B</td>
<td>107</td>
</tr>
<tr>
<td>C</td>
<td>104</td>
</tr>
<tr>
<td>D</td>
<td>110</td>
</tr>
<tr>
<td>E</td>
<td>112</td>
</tr>
<tr>
<td>F</td>
<td>124</td>
</tr>
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</table>
Loss Modulus (G") to Reported SP

<table>
<thead>
<tr>
<th>Sample</th>
<th>SP</th>
<th>G&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>110</td>
<td>671.15</td>
</tr>
<tr>
<td>B</td>
<td>107</td>
<td>581.78</td>
</tr>
<tr>
<td>C</td>
<td>104</td>
<td>421.87</td>
</tr>
<tr>
<td>D</td>
<td>110</td>
<td>596.60</td>
</tr>
<tr>
<td>E</td>
<td>112</td>
<td>597.23</td>
</tr>
<tr>
<td>F</td>
<td>124</td>
<td>334.05</td>
</tr>
</tbody>
</table>

Modulus and Temperature Vs Time

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Modulus to Softening Point Direct Correlation (poor fit)

R² = 0.481

DSR Modulus (@ SP) vs. Softening Point (Reported)

G''

Linear (G'')
Loss Modulus (G") to Reported Softening Point
Adjust SP to Equal Modulus

$G''$ is an EXCELLENT FIT

<table>
<thead>
<tr>
<th>Sample</th>
<th>SP</th>
<th>$G''$</th>
<th>Diff</th>
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<tbody>
<tr>
<td>A</td>
<td>110</td>
<td>112</td>
<td>2</td>
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<tr>
<td>B</td>
<td>107</td>
<td>107</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>104</td>
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<td>D</td>
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<td>E</td>
<td>112</td>
<td>111</td>
<td>-1</td>
</tr>
<tr>
<td>F</td>
<td>124</td>
<td>122</td>
<td>-2</td>
</tr>
</tbody>
</table>
Sample C w/ Repeat; Results within 1%
DSR Correlation to Softening Point

\[ R^2 = 0.99 \]

**Softening Point (Reported)**

**SP for Equi-Modulus**

- **G''**
- Linear (G'')
Line of Equality +/-2°C

G” to Report SP an alternate approach

SP for Equi-Modulus to 600Pa (measured) vs SP (Reported)
DSR vs. SP
combined dynamic & static loading

Softening Point Correlation

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DSR Viscosity* to Reported Penetration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pen</th>
<th>$n^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>28</td>
<td>9.18E+05</td>
</tr>
<tr>
<td>Sample B</td>
<td>39</td>
<td>6.76E+05</td>
</tr>
<tr>
<td>Sample C</td>
<td>48</td>
<td>3.96E+05</td>
</tr>
<tr>
<td>Sample D</td>
<td>144</td>
<td>1.13E+03</td>
</tr>
<tr>
<td>Sample E</td>
<td>110</td>
<td>1.49E+04</td>
</tr>
<tr>
<td>Sample F</td>
<td>35</td>
<td>1.66E+05</td>
</tr>
</tbody>
</table>

*Viscosity values are measured using DSR (Dynamic Shear Rheometer) and converted to reported penetration values.
Relationship of Viscosity to Pen

![Graph showing the relationship between Pen and Viscosity (n*)](image)

- **Viscosity (n*)**
- **Pen**
- **n**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pen</th>
<th>n*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>28</td>
<td>9.18E+05</td>
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<td>39</td>
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<td>144</td>
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<tr>
<td>E</td>
<td>110</td>
<td>1.49E+04</td>
</tr>
<tr>
<td>F</td>
<td>35</td>
<td>1.66E+05</td>
</tr>
</tbody>
</table>

- **R² = 0.9408**

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Let’s Look at Static Load to Penetration
Relationship of Creep Strain at 5s
Static Loading to Penetration

Rheometer Correlation

\[ R^2 = 0.9976 \]

<table>
<thead>
<tr>
<th></th>
<th>Pen @ 25C</th>
<th>Strain @ 25C</th>
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<tbody>
<tr>
<td>Sample A</td>
<td>28</td>
<td>4.91572</td>
</tr>
<tr>
<td>Sample B</td>
<td>39</td>
<td>8.99743</td>
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<td>Sample C</td>
<td>48</td>
<td>16.4315</td>
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<td>Sample D</td>
<td>144</td>
<td>1.19E+03</td>
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<tr>
<td>Sample E</td>
<td>110</td>
<td>297.965</td>
</tr>
<tr>
<td>Sample F</td>
<td>35</td>
<td>7.95222</td>
</tr>
</tbody>
</table>
Adhesion & Cohesion

Select the Pull Rate

What do you want to do?

- 0.1 inch per minute
- 1 inch per minute
- 12 inch per minute
- User Enterable Rate
Adhesion & Cohesion: Pull rate 1 inch/min
1.0 inch/min
1.0 inch/min: Force vs. Gap
<table>
<thead>
<tr>
<th>Index</th>
<th>Samp. Description</th>
<th>Actn.</th>
<th>T(°C)</th>
<th>t(s)</th>
<th>F(N)</th>
<th>g(mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>493</td>
<td>Sample A Pull off 0.1 inch</td>
<td>1.0 inch/min</td>
<td>59.95</td>
<td>4.930</td>
<td>-0.9610</td>
<td>4.0614</td>
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<tr>
<td>494</td>
<td>Sample A Pull off 0.1 inch</td>
<td>1.0 inch/min</td>
<td>59.95</td>
<td>4.940</td>
<td>-0.9599</td>
<td>4.0656</td>
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<tr>
<td>495</td>
<td>Sample A Pull off 0.1 inch</td>
<td>1.0 inch/min</td>
<td>59.95</td>
<td>4.950</td>
<td>-0.9587</td>
<td>4.0698</td>
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<td>496</td>
<td>Sample A Pull off 0.1 inch</td>
<td>1.0 inch/min</td>
<td>59.95</td>
<td>4.960</td>
<td>-0.9580</td>
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<td>497</td>
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<td>1.0 inch/min</td>
<td>59.95</td>
<td>4.970</td>
<td>-0.9569</td>
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<td>498</td>
<td>Sample A Pull off 0.1 inch</td>
<td>1.0 inch/min</td>
<td>59.95</td>
<td>4.980</td>
<td>-0.9551</td>
<td>4.0824</td>
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<td>499</td>
<td>Sample A Pull off 0.1 inch</td>
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<td>4.990</td>
<td>-0.9549</td>
<td>4.0866</td>
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<tr>
<td>500</td>
<td>Sample A Pull off 0.1 inch</td>
<td>1.0 inch/min</td>
<td>59.95</td>
<td>5.000</td>
<td>-0.9541</td>
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<td>501</td>
<td>Sample A Pull off 0.1 inch</td>
<td>1.0 inch/min</td>
<td>59.95</td>
<td>5.010</td>
<td>-0.9532</td>
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<tr>
<td>502</td>
<td>Sample A Pull off 0.1 inch</td>
<td>1.0 inch/min</td>
<td>59.95</td>
<td>5.020</td>
<td>-0.9522</td>
<td>4.0992</td>
</tr>
</tbody>
</table>

**Point Index**: 1  
**Sample Description**: Sample A Pull off 1.0 inch  
**Action Name**: Area calculation  
**Table Name**: Result data (F(N) vs t(s))  
**Area result**: 67.08  
**Point Notes**
1.0 inch/min w/ repeat

<table>
<thead>
<tr>
<th>Point Index</th>
<th>1</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Description</td>
<td>Sample A Pull off 1.0 inch</td>
<td>Sample A Pull off 1.0 inch</td>
</tr>
<tr>
<td>Action Name</td>
<td>Area calculation</td>
<td>Area calculation</td>
</tr>
<tr>
<td>Table Name</td>
<td>Result data (F(N) vs t(s))</td>
<td>Result data (F(N) vs t(s))</td>
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<tr>
<td>Area result</td>
<td>66.23</td>
<td>67.08</td>
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</tbody>
</table>

Graph showing force (F(N)) vs displacement (g (nm))
1.0 inch/min: Force & Gap vs. Time

Graph showing Gap and Normal force Vs Experiment time.
Adhesion & Cohesion: Pull rate 12 inch/min
12 inch/min     Sample A
12 vs 1.0 inch/min Comparison: Sample A
12 vs. 1.0 inch/min Comparison: Sample F
12.0, 1.0, 0.1 inch/min comparison Sample A
Sample A vs. F 1 inch/min Comparison

<table>
<thead>
<tr>
<th>Point Index</th>
<th>1</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Description</td>
<td>Sample F Pull off 1.0 inch</td>
<td>Sample A Pull off 1.0 inch</td>
</tr>
<tr>
<td>Action Name</td>
<td>Area calculation</td>
<td>Area calculation</td>
</tr>
<tr>
<td>Table Name</td>
<td>Result data (F(N) vs t(s))</td>
<td>Result data (F(N) vs t(s))</td>
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<tr>
<td>Area result</td>
<td>17.61</td>
<td>71.92</td>
</tr>
<tr>
<td>Point Notes</td>
<td></td>
<td></td>
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</table>

Graph showing a comparison between Sample A and Sample F with data points and a table detailing the comparisons.
Differing Filler Volume Fractions Shingle Asphalt

High Shear Capillary Testing on Diff. filler levels @ 350 F

- Sample A1-350F
- Sample B-1 - 350F
- Sample C1-350F
Filled Shingle Asphalt; Differing Processing Temperatures

Shear rate (1/s)

Shear viscosity (Pa.s)

-176.7
-190.6
-204.4
-218.3
-232.2
Abstract
This sequence runs a logarithmic table of shear rates and measures the viscosity. It prompts the user for appropriate information before starting.

This sequence requires a sample to be loaded in a specific way when prompted. Simply follow the on screen instructions.

Category Squeeze flow

When might I use this sequence?
This an alternative method for measuring the shear viscosity of a material over a range of shear rates. It is particularly useful for highly filled yield stress type samples which show power law type flow behavior as these samples tend to be challenging to measuring under standard rotational shear, these sample types tend to slip and fracture (even with roughened plates) which makes measurements problematic. However, these same properties are perfect for squeeze flow where the sample needs to slip across the surface of the plates.

The algorithm is based on a technique described in J. Non-Newtonian Fluid Mech., 81 (1999) 1-15 "Analytical solutions for squeeze flow with partial wall slip" by H.M. Laun, M. Rady, O. Hassager

As with all methods which approximate the shear flow behavior of a non-Newtonian sample, the deformation may not follow the prescribed profile. Therefore, this method should be validated with the samples type of interest before considering the viscosity values to be the same as those recorded under standard conditions.
Squeeze Flow
Sample G at 150C
Squeeze Flow Method
Keys to Automated QC Testing

Manage Sample History and Quality of the Measurement

› How do we manage sample history?
  ▪ Understanding the sample!
  ▪ Loading to minimize stress
  ▪ Precondition to establish sample time zero
  ▪ Time to permit sample to relax before testing or between testing
  ▪ Standard Operating Procedures

› Measurement Quality
  ▪ Monitor normal force; indicator of internal sample stress
  ▪ Monitor approach to steady state (m-Value); tells us when the sample’s at equilibrium
  ▪ Monitor % harmonic distortion; provides a measure of the quality of oscillation data
  ▪ Automatically determine LVER; optimizes the measurement

› Using the Instrument to improve the quality and reproducibility of the measurements
Logical Decision Making

› Know your product & know your plan of attack

› Establish acceptance criteria
  - Life’s great when everything passes!

› What to do when it fails?
  - Can the data lead to the next appropriate step?
    • Add more of something?
    • Let down?
    • Process differently?
    • Specify differently?

› Let’s use the instrument to provide positive feedback.
Customizable Escalation Procedures

Fail Procedure

1. Verify Temperature
2. Test a new sample
3. Get a fresh sample from Production
4. Ensure the sample is properly loaded
5. Call Jas 87
6. When all else fails, Notify Plant Manager
How many tests were used to collect all the data?

2 for DSR

- 2 sample loadings
- 1 - test to perform Pen, Softening Point and Viscosity on same sample. 25mm plates
  - Could just as easily add additional non-destructive tests, for example: Frequency sweeps for Master curve generation
- 1 - test to perform sample Pull-Off. 8mm plates

1 for Capillary

- High shear viscosity
Materials Data Base (bi-directional)

› Set up by Product, Project, Customer, Application...
  ▪ Min – Max Softening Point Temperature Limits
  ▪ Min-Max Viscosity Limits
  ▪ Min – Max Pen Limits
  ▪ Softening Point Temperature
  ▪ Temperature for Viscosity
  ▪ Temperature for Penetration
  ▪ Modulus at Softening Point
  ▪ Penetration Value
  ▪ Pull Off Energy
  ▪ Strain & Stress for LVER Testing
  ▪ Particle size, shape & distribution
  ▪ Sample Loading Temperature
  ▪ Clean Up Temperature
  ▪ And, any other property or parameter…
Thank you for your interest!

Questions?