Emulsions: Recovery, Aging, and Rheological Testing

Fundamental Properties of Asphalts and Modified Asphalts III Product: FP 18

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EMULSIONS

SUMMARY

This Emulsions study was not a single, codified piece of research. Rather, this subtask is a collection of four smaller projects (Phases) performed in support of work being conducted within the FHWA’s Asphalt Research Consortium (ARC) and the Emulsion Task Force (ETF). The knowledge gained from the elements in this subtask contributes to a Draft AASHTO Method (Appendix) titled Recovering Residue from Emulsified Asphalt Using the Universal Simple Aging Test (USAT) Low Temperature Evaporative Technique.

STATEMENT OF PROBLEM

Recovery of asphalt binders from emulsions is the subject of much discussion. Conventional binder recovery temperatures may destroy latex and other emulsion structures, whereas, lower recovery temperatures are particularly time consuming. This activity focuses on the use of small samples for characterizing performance properties of emulsion residues as well as determining an optimum temperature and system for recovering these binders. Dynamic Shear Rheometry using 4-mm parallel plates affords the opportunity to greatly reduce the amount of sample needed to characterize the low and intermediate [Sui et al. 2010].

SUPPORT OF FHWA STRATEGIC GOALS

The primary goal of this study is to characterize the low temperature rheological properties of small quantities of asphalt binders recovered from emulsions using a dynamic shear rheometer that has been fitted with 4-mm parallel plates. Additionally, this study was created to support the efforts of the FHWA Emulsion Task Force as needs would arise.

The work conducted in this study supports the FHWA strategic goals to optimize pavement performance and increase environmental stewardship through the rejuvenation of existing pavements.

EXPERIMENTAL

Background - Dynamic Shear Rheometry using 4-mm Diameter Parallel Platens

A dispute concerning the modulus of glycerol in the glassy regime ($G_g$) led Schröter et al. [2006] to develop a method to correct for the compliance of a dynamic shear rheometer, and its tools and platens. Sui et al. [2010] applied this compliance correction method to asphalt low temperature dynamic shear measurements (~ 5°C to -40°C) using 4-mm diameter parallel plates and a 1.7 mm gap (the technique is referred to here as simply “4-mm DSR”). The effect of the compliance correction is demonstrated in figure 1. At low frequency (high temperature) the
bitumen is compliant and the effect of the instrument compliance correction negligible. However, at high frequency (low temperature) the bitumen is no longer as compliant. The compliance correction adjusts the DSR measurements to reveal the true magnitude of the bitumen glassy modulus.

![Diagram showing master curves of the complex shear modulus](image)

Figure 1. Master curves of the complex shear modulus from corrected and uncorrected data for aged bitumen as a function of reduced frequency at a reference temperature of 25°C measured using 4-mm DSR.

The test method requires only 25 mg of material (in practice about 100 mg is necessary in order to allow sample trimming, etc.), which is several orders of magnitude less than the amount required to fabricate a bending beam rheometer (BBR) beam. Also, no specimen pre-molding is needed, and a relatively low temperature (60 ~ 70°C) is required to load the samples into the rheometer.

BBR m-value and creep stiffness S(t) are estimated through a correlation with 4-mm DSR developed by Sui et al. [2011]. In the Sui et al. method, the slope and magnitude of the shear stress relaxation modulus G(t) master curve at 2 hours and at the true low PG grading temperature are correlated with the corresponding S(t) and m-values at 60 seconds and 10°C above the true low PG grading temperature from BBR measurements. The Sui et al. method was modified by measuring G(t) slope and magnitude at 60 seconds and at 10°C warmer that the PG grading temperature.

Asphalt binder samples recovered from emulsions are analyzed using frequency sweep DSR at several temperatures in order to construct master curves of asphalt properties. One hundred milligrams of each sample is a sufficient amount of material using the 4-mm parallel plate
geometry with a nominal 1.75 mm gap. The samples are run on a Dynamic Shear Rheometer (DSR) at temperatures from -40°C to 60°C in 10°C increments. Data are collected using the frequency sweep mode from 0.1 to 100 rad/s at most temperatures.

The WRI protocol is to heat the samples to about 70°C for 20 minutes to get the necessary fluidity for transferring a small amount (less than 50 mg) to the preheated (50°C) rheometer. Once transferred, the gap is set to about 1.75 mm and the sample is neatly trimmed. The oven is then closed and the rheometer is kept at 50°C for about 5 minutes to insure adhesion of the sample to the plates. The rheometer is then cooled to 30°C and held there for 20 minutes to let the sample equilibrate prior to collecting data over the frequency range. The rheometer can then be cooled to 20°C and held for 20 minutes prior to data collection over the frequency range. This procedure is repeated at 10 or 15 degree increments to a minimum of -40°C. The temperature is then increased to a higher temperature (40°C or 45°C) and held for 20 minutes prior to data collection over the frequency range. The frequency sweeps are then performed up to 60°C, or until the sample fails due to low viscosity. The gap is adjusted appropriately for each temperature decrease to maintain the desired sample bulge. The linear viscoelastic range has been predetermined for asphalt at each temperature and the strain is set within that limit. The elastic and viscous components of the modulus ($G'$ and $G''$) are determined at each temperature and frequency. All other rheological properties can be determined based on these data.

**Phase 1**

Four-mm DSR data were collected on 8 samples previously recovered from asphalt emulsions labeled CRS-2, HFRS-2, HFRS-2P, HFRS-2P latex. Several binder residues were PAV aged and analyzed as well. The aged samples were CRS-2, CRS-2P, HFRS-2, and HFRS-2P. ‘P’ indicates polymer-modified asphalts. To investigate low temperature properties, master curves were built from isotherms in a temperature range from 20°C to -40°C. The effects of polymer modification and aging on the CAM model [Marasteanu and Anderson 1999] fitting parameters (glassy modulus $G_g$, crossover frequency $\omega_c$, and rheological index R) and relaxation behavior of asphalt residues are discussed in this work. Also, we compared the low temperature performance determined from both BBR and DSR for 4 PAV aged materials. In addition, the low limiting temperatures were determined from both stress relaxation modulus $G(t)$ and relaxation rate $m_r$.

**Phase 2**

A comparison between 4-mm DSR low temperature data from Western Research Institute (WRI) and 8-mm DSR intermediate temperature data from University of Wisconsin-Madison (UW-Madison) along with BBR measured data was performed.

Bending beam rheometer (BBR) data on four PAV aged emulsion residues (CRS-2, CRS-2P, HFRS-2, and HFRS-2P) were provided by UW-Madison. Along with the BBR data, UW-Madison also provided the BBR test results (m-value and creep stiffness) at -12°C using 8-mm intermediate temperature dynamic shear rheometer (DSR) data. The measured BBR values are compared with the m-value and creep stiffness values obtained using 4-mm DSR.
The linear correlations developed for hot mix asphalts by Sui et al. [2011] were used here to predict BBR creep stiffness $S(60\ s)$ and $m(60\ s)$ value from the 4-mm DSR data. The linear correlations between BBR and DSR are shown in the following equations:

\[
S(60\ s)(\text{at } T) = 2.14 \times 10^7 + 1.71769 \times G(7200\ s)(\text{at } T - 10^\circ C)
\]  

\[
m_c(60\ s)(\text{at } T) = -0.11495 + 0.70751 \times m_r(7200\ s)(\text{at } T - 10^\circ C)
\]

where $S(60\ s)$ and $m_c(60\ s)$ are the creep stiffness and its slope at 60 s and testing temperature $T$, and $G(7200\ s)$ and $m_r(7200\ s)$ are the relaxation modulus and its slope at 7200 s and 10°C below $T$.

**Phase 3**

Three emulsion samples were sent for analysis to WRI by PRI Asphalt Technologies of Tampa, FL, at the request of Dr. Gayle King of the FHWA Emulsion Task Force. These emulsions were poured into the wells in the aluminum plates used for the Universal Simple Aging Test (USAT) [Farrar et al. 2013]. The emulsion residue was then recovered by placing the plates in a force draft oven for 6 hours at 60°C. The goal of this residue recovery is to determine the asphalt/water ratio so that in subsequent tests, the proper amount of emulsion will be added to the wells to recover a 300 micron film which will be utilized for further testing. It was discovered that, for each of the three emulsions, the asphalt/water ratio was 65:35. Once the asphalt/water ratio was known the amount of emulsion required was determined. USAT plates were again used to recover residues from the samples from these samples.

Additionally, the binder residue was recovered from the same three samples by PRI. These unaged residues, along with binder residues recovered at WRI from the same three emulsions using the USAT and the same USAT recovered binders after PAV aging, were evaluated using 4-mm DSR to measure and compare Superpave low temperature properties.

**Background – Universal Simple Aging Test (USAT) Applied to Emulsion Residue Recovery and Aging**

Development of the USAT is reported elsewhere [Farrar et al. 2012], however the following provides a brief description of the USAT and how it was used in this study.

Figure 2 illustrates the USAT plate used by WRI to recover and age the emulsion residues. There are three slots on the plate to allow recovery and aging of three separate films. Each slot requires 1.00 g of asphalt, which produces a film thickness of about 300 μm. In order to achieve a 300 μm film of emulsion residue in each slot after drying, the asphalt/water ratio of the emulsions was determined. All three emulsions appeared to consist of approximately 65 percent asphalt and 35 percent water by mass. Using this ratio, 1.67 g of emulsion was placed in each slot which resulted in an approximate film thickness of 300 um after drying. A total of three plates were prepared, one for each emulsion. Figure 3 illustrates how the emulsions were poured into the slots on the plates. The emulsions were sufficiently fluid to spread out evenly and cover the entire surface of the slot.
The plates with emulsion were placed in a forced draft oven at 60°C for 6 hours to recover the emulsion residue. The plates were then removed from the oven, allowed to cool to room temperature, and the residue from one slot from each plate was removed and tested using 4-mm DSR. The plates were then placed in a standard pressure aging vessel (PAV) for 8 hours at 20 atm and 100°C. Aging the 300 µm film in a PAV at 20 atm and 100°C for 8 hours is equivalent to the level of aging of the standard PAV using a standard PAV pan 1/8” thickness [Farrar et al. 2012]. The recovery and aging scheme are illustrated in figure 4.
The test matrix resulted in a total of nine 4-mm DSR tests:

(3) 4-mm DSR tests (emulsion residues CRS-2P, CQS HP, LMCQS-h)
(3) 4-mm DSR tests (USAT emulsion residues CRS-2P, CQS HP, LMCQS-h)
(3) 4-mm DSR tests (USAT PAV aged emulsion residues, CRS-2P, CQS HP, LMCQS-h)

The standard 4-mm DSR test matrix was successfully carried out except in a few cases where there was insufficient torque generated during the 45°C and/or 60°C frequency sweeps due to the sample being too soft to measure in a 4 mm x 1.75 mm configuration. These sweeps were discarded. Also, on several occasions the low temperature frequency sweeps at (-30°C) displayed anomalous behavior (sample slippage/breakage) and were discarded.

In order to determine the continuous low temperature performance grade where the -30°C frequency sweep was not used due to slippage or breakage (this happened on only two occasions) or the low temperature continuous grade was below -30°C, the low temperature portion of the master curves were extrapolated using the Christensen Anderson (CA) model [Christensen and Anderson 1992]. Typically, the extrapolation was only for a few degrees Celsius.

The CA model relates the frequency dependence of the complex modulus to the glassy modulus ($G_g$), the cross-over frequency ($\omega_c$) and the rheological index ($R$). The form of the mathematical function is seen in equation 3.
\[ G^*(\omega) = G \left[ 1 + \left( \frac{\omega_c}{\omega} \right)^{\log_2 R} \right]^{-\frac{R}{\log 2}} \] (3)

**Phase 4**

Western Research Institute (WRI) provided technical assistance and support to a national study titled “Evaluation of Emulsified Asphalt Surface Treatments,” which was being performed by the National Center for Pavement Preservation. The study involves two main areas of research: (1) provide technical assistance to the FHWA Pavement Preservation Emulsion Task Force for development of a specification for chip seal and microsurfacing emulsified asphalt, and (2) provide recommendations to the FHWA Federal Lands Highway Division (FLH) for improvements to their standard specifications for chip sealing and microsurfacing.

A paper on the Death Valley National Park site chip seal was published in 2014 [Farrar et al. 2014].

As part of our preparation for the sample collection of chip seal residue from the National Park sites, we collected residue from several chip seals near Laramie, WY that were of a comparable age to the Death Valley site. Note the sampling (described below) involves removing a very small patch (roughly 6” by 6”) of chips and emulsion, typically near the edge of the travel way.

**Background – In-Service Emulsion Residue Sampling and Evaluation**

The field chip seal study involved several steps outlined below:

**Sample Collection**

Chip seal emulsion residue can be collected from the pavement surface using a variety of scraping tools, provided that the pavement surface temperature is sufficiently high. On a warm, sunny day where pavement surface temperatures are 50°C or above, sample collection is relatively simple and can be accomplished using a stiff putty knife or other scraper-type tool. The tool’s cutting edge is forced through the chip layer by rocking the blade back and forth a bit to work the edge down to the original pavement surface and under the emulsion layer. Once the edge is in contact with the underlying pavement surface, the tool edge can be slid across the old surface to cleanly remove the emulsion residue layer. Researchers successfully used the various scraping tools shown in figure 5 (tile scraper, putty-knife, and reciprocating saw with tile scraper blade) for emulsion residue collection at several field sites.
Extractions

Standard extraction and recovery methods such as AASHTO T 319 are generally appropriate for the recovery of asphalt binder from unmodified or polymer modified hot or warm mix asphalt. However, there are some unique aspects to be considered when extracting field chip seal samples of unmodified or polymer modified emulsion residue—particularly in the case of SBR latex modified emulsion residue, where there is a concern that the polymer structure that forms during emulsion curing may be significantly disrupted by the extraction solvent or the high heat involved during the recovery phase of the process.

Takamura [2000, 2003] has shown that when water starts to evaporate from SBR latex modified asphalt emulsion, dispersed latex particles in the emulsion migrate together and form a honeycomb structure surrounding the asphalt droplets. Takamura [2003] further suggests and shows some evidence that this SBR honeycomb structure imparts elastic properties to the residue, allowing high strain from external stresses even at low temperature without causing major fracture.

In regard to laboratory recovery of emulsion residue, Hazlett [2007] asked: “How do we get emulsion residue representative of in-service binder?” The present study addressed the question: “How do we extract and recover emulsion residue from chip seal field samples representative of the in-service binder?”

The Death Valley chip seal was constructed using an SBR latex modified emulsion, so the first step in evaluating the question was to confirm that there was in fact a honeycomb structure.
present in the emulsion residue field samples. Researchers considered and tried several methods to acquire an image of the honeycomb structure: atomic force microscopy (AFM), epifluorescence, and scanning electron microscopy (SEM). Along with these methods, also tried were different treatments to the emulsion residue to draw out the polymer structure. After several preliminary experiments, it appeared that the best method, along the lines proposed by Wolfe et al. [1986], was to use SEM after dissolution of the asphalt with methyl ethyl ketone (MEK), which is a poor solvent for SBR. Gold or platinum coating was not necessary, as researchers used a backscatter electron detector that required only minimal sample preparation. Figure 6 displays the apparent honeycomb observed in the Death Valley emulsion residue using SEM and MEK treatment.

![SEM image](image_url)

Figure 6. SEM image: Death Valley MP 50.5 original scraping soaked in MEK before imaging.

To evaluate whether or not the structure shown in figure 6 is the honeycomb or perhaps an artifact, researchers recovered emulsion residue from an SBR latex modified emulsion provided by the Utah DOT using the universal simple aging test (USAT) method [Farrar et al. 2012]. The USAT emulsion residue recovery method is comparable to AASHTO PP 72-11, Method B (method B) which utilizes a forced draft oven at 60°C for 6 hours. Figure 7 shows the SEM image of the USAT-recovered emulsion with a honeycomb structure comparable to that in figure 6.
Figure 7. SEM image: CRS-2L (SBR latex modified emulsion) recovered in the lab using the USAT method, soaked in MEK before imaging.

Figure 8 shows an image of the USAT-recovered material after dissolution in dichloromethane (DCM) and then removal of DCM under vacuum at 80°C. In this figure, there is a complete absence of the honeycomb structure.

Figure 8. SEM image: CRS-2L (SBR latex modified emulsion) lab-recovered, dissolved in DCM, then DCM removed with vacuum at 80°C, soaked in MEK before imaging.
**Infrared Analysis**

Researchers acquired IR spectra of the top and bottom of the emulsion residue using a “solvent wash” method. The samples used for this analysis were collected with the reciprocating tile blade equipment shown in figure 5 and were essentially intact with an area of roughly 3 square inches. The surfaces were washed with carbon disulfide as shown in figure 9. The liquid was centrifuged to eliminate very fine aggregate particles before the asphalt was recovered using a vacuum oven at 60°C. After drying, ATR single-bounce diamond IR spectra were collected.

![Surface wash technique with carbon disulfide.](image)

The key to obtaining the low temperature rheology was application of 4-mm DSR. The test method requires only 25 mg of material (in practice about 100 mg is necessary in order to allow sample trimming, etc), which is several orders of magnitude less than the amount required to fabricate a BBR beam. Also, no specimen pre-molding is needed and a relatively low temperature (60 ~ 70°C) is required to load the samples into the rheometer. This low temperature should allow the structure of SBR latex polymer to be retained in the specimen.

**RESULTS AND DISCUSSION**

**Phase 1 Results**

**CAM Model Fitting Parameters, Relaxation Modulus G(t), and Apparent Relaxation Rate m_r at 2 Hours at a Temperature of ~28°C**

To observe the effects of polymer modification and aging on CAM fitting parameters and relaxation behavior, the glassy modulus G_g, crossover frequency \( \omega_c \), and rheological index \( R \) were calculated using Rhea® software and are listed in table 1. Table 1 also lists relaxation modulus G(t) and apparent relaxation rate m_r at two hours at a temperature of -28°C.

As seen in table 1, the magnitude of the crossover frequencies for unaged and PAV aged materials are in the order of \( 10^{-6} \) and \( 10^{-9} \) respectively. The unaged CRS-2 is an outlier. This
might be due to the specific material properties. Looking at G(t) and m_r at 2 hours listed in table 1, it is clear that the polymer modification softens the pure asphalt for the cases studied here, although the types of polymers used for modifying the asphalts are unknown. Comparing to the unmodified asphalts CRS-2 and HFRS-2, the relaxation modulus G(t) of CRS-2P and HFRS-2P at 2 hours at the same temperature decreases for both unaged and PAV aged materials. Conversely, the apparent relaxation rates of the polymer-modified materials increase in three out of 4 pairs, compared to those of unmodified asphalts. The changes of both G(t) and m_r indicate that the polymer modification softens the pure asphalts for most cases studied in this work.

Interestingly, the addition of latex to HFRS-2P stiffens HFRS-2P slightly, and the resulting values of HFRS-2P latex lie between HFRS-2 and HFRS-2P. As reported previously by Farrar et al. [2013], the rheological index, R, of asphalt materials increases and crossover frequencies decrease upon aging. The same phenomena were observed here by looking at R of unaged CRS-2, HFRS-2, HFRS-2P and their PAV age materials. Surprisingly, unlike the aging, the polymer modification affects the rheological index, R, the opposite way. Rather than decreasing R due to the apparent softening which took place by adding polymer, R increases as seen in the pairs of unaged HFRS-2 and HFRS-2P, PAV aged CRS-2 and CRS-2P, and HFRS-2 and HFRS-2P in table 1. This also can be seen from the pair of HFRS-2P and HFRS-2P latex residues. The stiffening effect from adding latex to HFRS-2 decreases R for HFRS-2 latex instead of causing R to increase. This interesting finding needs to be confirmed by looking at more polymer-modified emulsion residues with different types of polymers.

Table 1. CAM model fitting parameters as well as G(t) and m_r at 2 hours at a temperature of -28°C.

<table>
<thead>
<tr>
<th>Materials</th>
<th>G_0 x 10^9 Pa</th>
<th>( \omega_c ), rad/s</th>
<th>R</th>
<th>G(t) x 10^8 Pa at 2 hr</th>
<th>m_r at 2 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRS-2</td>
<td>1.16</td>
<td>2.16 \times 10^{-5}</td>
<td>1.77</td>
<td>0.27</td>
<td>0.477</td>
</tr>
<tr>
<td>HFRS-2</td>
<td>1.25</td>
<td>2.19 \times 10^{-6}</td>
<td>1.99</td>
<td>0.50</td>
<td>0.395</td>
</tr>
<tr>
<td>HFRS-2P</td>
<td>1.47</td>
<td>2.30 \times 10^{-6}</td>
<td>2.29</td>
<td>0.29</td>
<td>0.413</td>
</tr>
<tr>
<td>HFRS-2P latex</td>
<td>1.17</td>
<td>2.22 \times 10^{-6}</td>
<td>2.06</td>
<td>0.39</td>
<td>0.398</td>
</tr>
<tr>
<td>CRS-2</td>
<td>1.65</td>
<td>5.14 \times 10^{-6}</td>
<td>2.53</td>
<td>1.55</td>
<td>0.259</td>
</tr>
<tr>
<td>CRS-2P</td>
<td>1.62</td>
<td>3.18 \times 10^{-9}</td>
<td>2.76</td>
<td>1.14</td>
<td>0.261</td>
</tr>
<tr>
<td>HFRS-2</td>
<td>1.29</td>
<td>8.41 \times 10^{-9}</td>
<td>2.27</td>
<td>1.75</td>
<td>0.249</td>
</tr>
<tr>
<td>HFRS-2P</td>
<td>1.29</td>
<td>8.01 \times 10^{-9}</td>
<td>2.53</td>
<td>1.10</td>
<td>0.264</td>
</tr>
</tbody>
</table>

Comparison of Low Temperature Performance between BBR and DSR

To compare low temperature performance determined from both BBR and DSR, the G(t) and m_r at two hours and -28°C for four PAV aged materials listed in table 1 were plotted along with the creep stiffness S(60 s) and apparent creep stiffness relaxation rate m_c(60 s) at 60 s and -18°C from BBR data [Bahia et al. 2010] as shown in figures 10 and 11. In figure 10, BBR creep stiffness shows the same trend as the DSR relaxation modulus. In another words, the stiffness ranking from both BBR and DSR for four PAV aged materials is the same: HFRS-2 > CRS-2 >
CRS-2P > HFRS-2P. However, the trend for relaxation rate from both BBR and DSR is not exactly the same, although three of four materials show the same order. The order of relaxation rate from BBR is HFRS-2P > CRS-2 > CRS-2P > HFRS-2, which is not the same as that from DSR: HFRS-2P > CRS-2P > CRS-2 > HFRS-2 (see data listed in table 1). Generally, the stiffer the material, the slower it relaxes, and this is the trend seen in the the DSR data reported here.

Figure 10. BBR $S(60\text{ s})$ at reference temperature of -18°C [Bahia et al. 2010] and $G(2\text{ hr})$ at reference temperature of -28°C determined from DSR for 4 PAV aged emulsion residues.

Figure 11. $m_c(60\text{ s})$ from BBR at reference temperature of -18°C [Bahia et al. 2010] and $m_r(2\text{ hr})$ at reference temperature of -28°C determined from DSR for 4 PAV aged emulsion residues.
Although the relaxation rate rankings for four asphalt materials from BBR are not exactly the same to that of DSR, overall they exhibit a similar trend in stiffness and relaxation rate from both BBR and DSR. While these correlations are for PAV aged hot mixed asphalt extracted binders, it is expected that emulsion residues should correlate similarly. To observe the correlations for emulsion residues, in figure 12, the BBR creep stiffness is plotted against shear stress relaxation modulus. In figure 13, the apparent creep stiffness relaxation rate is plotted against the apparent shear stress relaxation rate. Good linear correlations between BBR and DSR data were observed from both stiffness and apparent relaxation rate as seen in figures 12 and 13 with \( R^2 \) values of 0.936 and 0.951 respectively in these figures. Using this approach it was found that \( G(2 \text{ hr}) = 168 \text{ MPa} \) is equivalent to \( S(60 \text{ s}) = 300 \text{ MPa} \) at a \( 10^\circ \text{C} \) lower temperature. Similarly, it was found that \( m_i(2 \text{ hr}) = 0.249 \) is equivalent to \( m_c = 0.3 \) at a \( 10^\circ \text{C} \) lower temperature. These correlations are almost identical to those found for asphalt binders [Sui et al. 2011]. To be safe, we applied the Superpave criteria found for asphalt binders [\( G(t) \leq 160 \text{ MPa} \) and \( m_r \geq 0.26 \), as low temperature performance grading specifications]. The low limiting temperatures determined from these specifications are listed in table 2.

![Figure 12. Correlation between BBR creep stiffness and DSR stress relaxation modulus.](image)

**Linear Regression:**

\[
S(t) = A + B \times G(t)
\]

- \( A = 4.50782 \)
- \( B = 1.75175 \)
- \( R = 0.93636 \)
Figure 13. Correlation between BBR creep stiffness relaxation rate and DSR stress relaxation modulus relaxation rate.

Low Limiting Temperatures Determined from DSR

Table 2 lists the low limiting temperatures from both G(t) at 160 MPa and m_r at 0.26. As shown in the table, the low limiting temperatures determined from both stiffness and relaxation rates are similar.

Table 2. Low limiting temperatures determined from DSR for 10 unaged and PAV aged emulsion residues.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Limiting Temp from G(t) at 160 MPa (°C)</th>
<th>Limiting Temp from m_r at 0.26 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRS-2 unaged</td>
<td>-35.5</td>
<td>-37.0</td>
</tr>
<tr>
<td>HFRS-2 unaged</td>
<td>-34.3</td>
<td>-35.3</td>
</tr>
<tr>
<td>HFRS-2P unaged</td>
<td>-37.8</td>
<td>-38.6</td>
</tr>
<tr>
<td>HFRS-2P latex</td>
<td>-36.9</td>
<td>-36.7</td>
</tr>
<tr>
<td>CRS-2 PAV</td>
<td>-28.5</td>
<td>-27.9</td>
</tr>
<tr>
<td>CRS-2P PAV</td>
<td>-31.4</td>
<td>-28.1</td>
</tr>
<tr>
<td>HFRS-2 PAV</td>
<td>-27.5</td>
<td>-27.2</td>
</tr>
<tr>
<td>HFRS-2P PAV</td>
<td>-30.5</td>
<td>-28.3</td>
</tr>
</tbody>
</table>
Phase 2 Results

From the DSR low temperature data, \( G(7200 \text{ s}) \) and \( m_r(7200 \text{ s}) \) at reference temperature of -22°C were calculated as listed in table 3. Using the linear correlations shown in equations 1 and 2, the BBR \( S(60 \text{ s}) \) and \( m_r(60 \text{ s}) \) at -12°C can be predicted from 4-mm DSR data by substituting the calculated \( G(7200 \text{ s}) \) and \( m_r(7200 \text{ s}) \) into the equations. The predicted BBR data at -12°C from 4-mm low temperature DSR data (WRI) are listed in table 4.

<table>
<thead>
<tr>
<th>Material</th>
<th>( G(7200 \text{ s}), \text{MPa} )</th>
<th>( m_r(7200 \text{ s}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRS-2</td>
<td>66.0</td>
<td>0.333</td>
</tr>
<tr>
<td>CRS-2P</td>
<td>52.3</td>
<td>0.328</td>
</tr>
<tr>
<td>HFRS-2</td>
<td>73.4</td>
<td>0.335</td>
</tr>
<tr>
<td>HFRS-2P</td>
<td>33.5</td>
<td>0.368</td>
</tr>
</tbody>
</table>

The method used for predicting BBR data from 8-mm intermediate temperature DSR data developed by Hanz and Bahia [2010] calculates the equivalent frequency \( \omega \) at a given dynamic testing temperature as shown in equation 4.

\[
T_d \approx \left( \frac{1}{T_s + 273} - \frac{2.303R \log(t_s \omega)}{250000} \right)^{-1} - 273
\]  

where:
- \( T_d \) = test temperature for dynamic testing at frequency \( \omega \), °C
- \( T_s \) = specified temperature for creep testing, °C
- \( R \) = ideal gas constant, 8.31 J/K.mol
- \( t_s \) = specified creep loading time, s
- \( \omega \) = dynamic testing frequency, rad/s

Substituting \( T_d = 10°C \), \( T_s = -12°C \), and \( t_s = 60 \text{ s} \) into equation 3, the equivalent frequency at 10°C is obtained, \( \omega = 129.62 \text{ rad/s} \).

With the calculated equivalent frequency, the creep stiffness at 60 s and -12°C was then predicted using equation 5.

\[
S(t) = \frac{3G^*(\omega)}{1 + 0.2 \sin(2\delta)}
\]

where:
- \( S(t) \) = creep stiffness at time \( t \), Pa
- \( G^*(\omega) \) = complex modulus at frequency \( \omega \), Pa
- \( \delta \) = phase angle at frequency \( \omega \)
m(60) was predicted using equation 6 [Ferry 1980] from the 8-mm DSR data.

\[
m = \frac{d \left[ \log G^*(\omega) \right]}{d (\log \omega)}
\]  

(6)

where \( m = \) slope of \( \log G^*(\omega) \) vs. \( \log \omega \) plot at a given frequency

**Comparison between Measured and Predicted BBR Data**

Using the methods introduced above, the measured BBR values and the predicted BBR values from both 4-mm and 8-mm DSR are listed in table 4. As seen in the table, 4-mm low temperature DSR provided better predictions of \( m \) values for all four asphalts. For creep stiffness, the predictions from 4-mm data are more accurate than those from 8-mm data for samples CRS-2 and HFRS-2. To have a good sense of comparison between BBR predictions from 4-mm low temperature and 8-mm intermediate temperature DSR data, the data listed in table 4 are plotted in figures 14 and 15.

<table>
<thead>
<tr>
<th>Materials</th>
<th>S(60), ( \times 10^6 ) Pa</th>
<th>m(60)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBR Measured</td>
<td>4-mm DSR</td>
<td>8-mm DSR</td>
</tr>
<tr>
<td>CRS-2</td>
<td>135</td>
<td>135</td>
</tr>
<tr>
<td>CRS-2P</td>
<td>135</td>
<td>111</td>
</tr>
<tr>
<td>HFRS-2</td>
<td>168</td>
<td>148</td>
</tr>
<tr>
<td>HFRS-2P</td>
<td>72.2</td>
<td>76</td>
</tr>
</tbody>
</table>
Figure 14. Comparison of $S(60\ s)$ data between BBR measured and DSR predicted at temperature of $-12^\circ\text{C}$.

Figure 15. Comparison of $m(60\ s)$ data between BBR measured and DSR predicted at temperature of $-12^\circ\text{C}$. 
Phase 3 Results

Low Temperature Mechanical Properties

Mechanical measurements on asphalt binders to determine the continuous low temperature specification performance grade are currently carried out using a bending beam rheometer (BBR). The BBR test (AASHTO T313) provides a measure of low temperature stiffness and relaxation properties of asphalt binders after field aging and extraction or after RTFOT/PAV conditioning.

The BBR test requires approximately 15 grams of asphalt binder per beam. This relatively large amount of asphalt binder limits its application with emulsion residues. For this report, the low temperature properties are not measured with the BBR but are instead measured with 4-mm plate rheometry and BBR m-value and creep stiffness S(t) are estimated through a correlation developed by Sui et al. [2011]. The continuous low temperature performance grades of the unaged emulsion residues obtained by PRI using method B and by WRI using the USAT and WRI USAT PAV aged emulsion residues are shown in figure 16. PAV aging the residue reduces the continuous low temperature grade by roughly 5 to 20 percent.

![Figure 16. Continuous low temperature performance grade.](image)

The m value is the slope of the creep stiffness curve at the performance grade temperature plus 10°C at 60 seconds. The m value of an asphalt binder provides an indication of the asphalt’s
ability to relax stress. A minimum m value of 0.3 is typically specified for laboratory rolling thin film oven/pressure aging vessel RTFO/PAV aged asphalts. Creep stiffness is used to evaluate the potential for high thermal stress development. The m values at a temperature of -28°C for the three emulsion residues are shown in figure 17.

Figure 17 includes the AASHTO T313-08 multilaboratory precision limit (d2s%) for m-value. The multilaboratory precision limit represents tests on duplicate samples by different operators, using different rheometers, in different labs. It was used here to compare the m-value results of recovered emulsion by PRI using method B and by WRI using the USAT method rather than single operator precision limits because, although the residues were tested in the same laboratory, they were recovered in different laboratories. The m-value results for the LMCQS-h residues are within the d2s% limit and the CRS-2P and CQS-1hP are only slightly outside the limit. PAV aging of these emulsions results in a decrease in m-value by roughly 10 to 20 percent.

![Figure 17. Emulsion residue: m-value at -28°C.](image)

**Phase 4 Results**

The extent of aging can be assessed by comparing the limiting m-value temperature of lab and field recovered residues. An example of the results from the Death Valley site are shown in figure 18.
Figure 18. Death Valley National Park chip seals. Comparison of residue recovered from the original emulsion used on the project to the field recovered residue.

The solvent wash spectrum shown in figure 19 represents the top and bottom of the emulsion residue layer. The extent of oxidation at the top surface compared to the bottom of the emulsion layer can be observed by comparing the height and broadness of the carbonyl absorbance bands centered at ~1700 cm\(^{-1}\) and the sulfoxide bands centered at ~1030 cm\(^{-1}\). The extent of polymer degradation at the surface and bottom can be assessed by comparing the bands at either 966 cm\(^{-1}\) and at 699 cm\(^{-1}\). The 966 cm\(^{-1}\) band corresponds to the SBR C-H out of plane bending of transalkene (present in the polymerized butadiene), and the 699 cm\(^{-1}\) band corresponds to the SBR C-H out of plane bending in monoalkylated aromatics (styrene) [Nösl er et al. 2008]. Here we evaluate the bands at 966 cm\(^{-1}\) due to difficulty in interpreting the spectrum in the 699 cm\(^{-1}\) region.

Figure 19 shows that there is more carbonyl at the top surface compared to the bottom, which was expected. The difference is not large and suggests a relatively limited oxidative gradient. In terms of polymer degradation, there appears to be a slight gradient from the top to bottom based on the 966 cm\(^{-1}\) band. Thermooxidative reactions in styrene butadiene occur at unsaturated bonds of the polybutadiene segments, causing not only chain scission but also macrophase separation between polystyrene-rich and polybutadiene phases [Kyu and Fan 2001]; no oxidation of the polystyrene segments is expected.
CONCLUSIONS

This study demonstrates the application of 4-mm DSR for measuring the low and intermediate rheological properties of unaged and aged emulsion residues. Good linear correlations between BBR and DSR data were observed for both stiffness and apparent relaxation rate.

Overall, 4-mm parallel-plate low temperature DSR data provides better predictions for BBR data than 8-mm intermediate temperature DSR data for m value.

The USAT was used to recover and age the emulsion residues. The mechanical properties of the residua obtained by PRI using the method B and USAT recovered emulsion residues were compared. One of the emulsion residues was within the AASHTO multilaboratory precision (d2s%) for m-value and G* sin δ. The other two residues were slightly outside their respective multilaboratory precision statements. Interestingly, the USAT recovered residues were slightly softer (in terms of m-value and continuous low temperature grade) at low temperature than the PRI generated residues. residues.

PAV aging stiffens the USAT recovered residues bringing them closer to possible embrittlement failure. It’s an open question as to the extent of aging of an emulsion residue in-service several years after placement, and if the particular USAT PAV protocol used here simulates the aging that would typically occurs. Also, it is interesting to note that there are significant differences between the different types of emulsion residues in terms of the extent of oxidative aging using the USAT PAV protocol.
ACKNOWLEDGEMENTS

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DISCLAIMER

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REFERENCES


APPENDIX

Standard Method of Test for

Recovering Residue from Emulsified Asphalt Using the Universal Simple Aging Test (USAT) Low Temperature Evaporative Technique

AASHTO Designation: T XXX-13
Standard Method of Test for

Recovering Residue from Emulsified Asphalt Using the Universal Simple Aging Test (USAT) Low Temperature Evaporative Technique

AASHTO Designation: T XXX-13

1. SCOPE

1.1. This practice covers a method for recovering the residue from emulsified asphalts using a low temperature evaporative technique that is similar to pavement conditions. The recovered residue can be used for further testing as required using test methods such as those specified in M 140 and M 208.

1.2. The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3. *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.*

2. REFERENCED DOCUMENTS

2.1. *AASHTO Standards:*

- T 59 Emulsified Asphalts
- M 208, Cationic Emulsified Asphalt
- M 140, Emulsified Asphalt
- R 28, Accelerated Aging of Asphalt Binder

2.2. *ASTM Standards*

- D977 Specification for Emulsified Asphalt
- D2397 Specification for Cationic Emulsified Asphalt
- D6934 Test Method for Residue by Evaporation of Emulsified Asphalt
- D6997 Test Method for Distillation of Emulsified Asphalt
- E 145 Standard Specifications for Gravity-Convection and Forced-Ventilation Ovens

2.3. *Other Standard:*

- NF EN 13074 Recovery of Binder from Bitumen Emulsions by Evaporation.

*Note 1*—The EN 13074 Standard is published and distributed through AFNOR (French Standard Institute) and is available online at [www.afnor.fr](http://www.afnor.fr).

3. TERMINOLOGY

3.1. *Definitions:*
3.1.1. **USAT**—Universal Simple Aging Test.

3.1.2. **DSR**—Dynamic Shear Rheometer

### 4. SIGNIFICANCE AND USE

4.1. The procedure described in this practice is used to obtain a residue from an emulsified asphalt that can then be tested in a dynamic shear rheometer (DSR). The lower evaporative temperature (60°C) of this procedure provides conditions that are close to that of actual road application temperatures. This practice should be used in place of recovery techniques such as those of T59, when the high temperature used in that standard would negatively affect the residue. In addition, if desired, the USAT plate with recovered residue can be placed directly in a pressure aging vessel (PAV) to long-term age the residue.

### 5. APPARATUS

5.1. **USAT Plate**—Figure 1 illustrates the USAT plate used to recover and age, if desired, emulsion residue. There are three slots on the plate to allow recovery and aging of three separate films. The plate is a standard 6061 aluminum alloy.

![Figure 1—USAT Plate Dimensions](image)

5.2. **Spatulas**—Palette knife or other suitable material for spreading the emulsified asphalt, and scrapping the recovered emulsified residue from the plate for testing.

5.3. **Glass Stirring Rod**—Stirring rod for testing consistency of emulsion and stirring heated emulsion to establish consistent viscosity.

5.4. **Forced Draft Oven**—Horizontal air flow, mechanical convection oven meeting the requirements of ASTM E 145, Type IIA at 60°C ± 1°C. The racks should be able to be spaced a minimum of 10 cm from the top and bottom of the oven and with a spacing of a minimum of 4 cm between racks with samples. The oven racks must be checked for level, with a bubble level of 250 mm minimum length, from side to side and front to back of the oven.

5.5. **Sample containers**—Metal tins with metal cover 40mm diameter, 15mm height for storing the recovered emulsion residue until testing.

### 6. HAZARDS

6.1. Standard laboratory caution should be used in handling emulsions and preparing test specimens.
7. **PROCEDURE**

7.1. Determine the emulsion asphalt to water ratio.

7.1.1. Method A—Follow AASHTO T 59, Section 6, Emulsion Asphalt Residue by Evaporation.

7.1.2. Method B—USAT Method

7.1.2.1. Record the weight of an empty USAT plate.

7.1.2.2. Pour 1.70 g of emulsion into each slot of the USAT plate following the procedure described in sections 7.2.

7.1.2.3. Record the weight of the USAT plate with emulsion and place into a 60°C forced draft oven for 6 hours.

7.1.2.4. Remove the USAT plate and allow to cool at ambient lab conditions for one hour and record the weight.

7.2. Recover the emulsion residue using a USAT plate.

7.2.1. Gently stir the emulsion with a glass stirring rod. If the emulsion is not a consistent viscosity throughout the container, the emulsion particles may have aggregated and a consistent emulsion should be established by following the procedure described in sections 7.3.

7.2.2. Heat the USAT plate to a temperature of 60°C.

7.2.3. Pour the required amount of emulsion into each slot of the heated USAT plate. For most emulsions, a disposable pipette may be used instead of pouring to more easily achieve the desired quantity of emulsion in each USAT well.

**Note 2**—The required amount of emulsion for each slot is determined by performing Method A or B in Section 7.1 to determine the asphalt to water ratio and then performing the calculations in Section 8.

**Note 3**—During pouring, the emulsion will spread out and cover most of the slot area, to complete the spreading process so all of the slot is covered with emulsion, use a spatula and push the emulsion to the edges of each slot in the USAT plate.

7.2.4. Place the USAT plate with the emulsified asphalt into a 60°C forced draft oven for 6 hours ± 15 minutes.

7.2.5. Remove the USAT plate with the emulsified asphalt residue from the oven and allow to cool at ambient lab conditions for one hour prior to removal of the residue from the plate.

**Note 4**—OPTIONAL - At this point, the USAT plate with emulsion residue may be placed in a PAV under standard R28 conditions and long-term aged to simulate the aging process that occurs on the road over a period of 1 to 3 years depending on the climate and other environmental factors. Also, since the film thickness is 300 µm rather than 3.2 mm as is the case in the standard R28 method, the time in the PAV is reduced from 20 hours to 8 hours [Farrar et al. 2012].

7.2.6. Remove the residue from the plate using a spatula and place the residue in a metal tin for further testing.

**Note 5**—Store the emulsion residue under nitrogen at room temperature prior to testing. Freezing the emulsion residue could damage it.
7.3. Establishing a consistent emulsion

7.3.1. Place sealed vessel containing the emulsion in a forced draft oven at 60°C.

7.3.2. If the quantity of emulsion is less than 1 liter, remove the emulsion from the oven after 1 hour and gently stir with a glass rod until a consistent viscosity is achieved (Typically less than 1 minute).

Note 6—If a consistent emulsion is not achieved after stirring while at 60°C, the emulsion is broken and unsuitable for this AASHTO method.

8. **CALCULATION**

8.1. Calculate the emulsion asphalt to water ratio:

\[
D = \frac{(C-A)}{(B-A)-(C-A)}
\]

Where:

A = weight of empty USAT plate, g
B = weight of USAT plate with emulsion, g
C = weight of USAT plate and residue after oven drying, g
D = asphalt to water ratio

8.2. Calculate the amount of emulsion to place in each slot to achieve a 300 µm film thickness after drying. The weight of emulsion residue after drying should be 1.0 g.

\[
\text{Emulsion (grams)/slot} = 1 + \frac{1}{D}
\]

9. **KEY WORDS**

9.1. Emulsified Asphalt

10. **REFERENCES**
