Recovery and Laboratory Testing of Asphalt Emulsion Residue: Application of the Simple Aging Test (SAT) and 4mm DSR

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ABSTRACT

This study involves application of two new test methods to the recovery of asphalt emulsion residue, long-term oxidative aging of the residue, and mechanical testing of the unaged and aged residue to determine low and intermediate temperature rheological properties. The two new methods are: (1) the simple aging test (SAT) which is a thin-film (300 μm) oxidative aging test, and (2) a dynamic shear rheometry (DSR) technique (commonly referred to as 4mm DSR) that allows testing to -40°C, and requires only ~ 25 mg. Three polymer modified emulsions are recovered by two methods: (1) AASHTO PP 72-11 - Method B, and (2) using a SAT plate. Both methods use the same evaporative technique to recover the residue (6 hours at 60°C in a forced draft oven). The rheological properties (m-value, G* sin δ, and ductility) of the recovered emulsion residues by both methods are reported as well as the rheological properties of the aged emulsion using the SAT. The rheological properties of the unaged emulsion residues recovered by both methods are roughly equivalent. The proposed SAT recovery method and application of 4mm DSR offer significant improvements over Method B and current DSR methodology. The recovery process is simpler with the SAT plate than Method B, and the SAT plate has been designed so that it can be placed directly in a standard PAV for long-term aging and the time required for standard PAV aging is reduced from 20 to 8 hours. There is no extrapolation of intermediate temperature DSR data to low temperature. The error due to instrument compliance at low temperature is corrected in the 4mm DSR procedure.

INTRODUCTION

Over the last several decades a number of asphalt emulsion recovery methods have been developed and many of them involve temperatures well above the temperatures that the emulsion product is exposed to in the field (*1*). In the last several years, the focus has been on residue recovery that simulates field curing, particularly for polymer modified emulsions since the high temperatures involved in distillation and some cases oven evaporation methods can significantly affect the binder's rheological properties (*2*). An example of simulating field curing is European Standard Method EN 13074 (*3*) which simulates the curing process just after the emulsion breaks and the road is reopened to traffic (*1*). The method specifies conditioning at ambient temperature for 24 hours followed by 24 hours at 50°C. The film of residual binder is 1 mm thick. ASTM D7497 Method A (*4*) is similar to EN13074 as it requires 24 hours at 25°C followed by 24 hours at 60°C in a forced draft oven. The initial emulsion film is 2 mm thick.

One issue with both EN 13074 and ASTM D7479 Method A is that they require 48 hours to complete. In response, a recovery method that draws down the emulsion using a wet film applicator on a silicon mat to an approximate film thickness of 380 µm has been provisionally adopted by AASHTO PP 72-11 as Method B (*5*). The 380 µm emulsion film is cured in a forced draft oven for six hours at 60°C. The residue thickness after curing can vary from about 190 to 300 µm depending on the ratio of asphalt to water.

If there is interest in long term aging the recovered residue in accordance with AASHTO R28, then the residue has to be transferred to suitable pan to provide the 3.2 mm film thickness required in R28.

ASTM D7497 Method A can generate sufficient emulsion residue for the Bending Beam Rheometer (BBR) test which requires approximately 15g per beam and typically several beams are required. However, AASHTO Method B produces substantially less residue and it is not practical to test with the BBR. However, Hanz and Bahia (6) have proposed estimating low temperature creep properties form intermediate temperature oscillatory shear measurements with 8 mm diameter parallel plate geometry. The dynamic moduli are interconverted to creep compliance and then the interconverted creep compliance is extrapolated to low temperature.

In the present study, two recently developed test methods are proposed as possible improvements to (1) the current PP 72-11 Method B emulsion residue recovery method, (2) laboratory long-term aging of the residue, and (3) low and intermediate rheological testing of the unaged and aged residue. The two test methods are referred to as the simple aging test (SAT) and 4mm DSR. Both methods are described below.

Applying the SAT and 4mm DSR to emulsion residue recovery, oxidative aging, and rheological testing offers the following advantages:

(1) The SAT method proposed here is simpler than drawing down an emulsion using a wet film applicator on a silicon mat and the SAT method results in a consistent 300 µm film regardless of the emulsion asphalt to water ratio. Of course, this approach then requires an intermediate step to estimate the asphalt to water ratio in order to place the proper amount of emulsion on the SAT plate to generate a 300 µm residue film.

(2) After the emulsion residue has been recovered on the SAT plate (recovery time is the same as Method B, i.e., 6 hours at 60°C in a forced draft oven) the plate has been designed so that it can be placed directly in a standard PAV and aged in accordance with R28. However, because the film thickness is only 300 µm rather than 3.2 mm, the time necessary for residue aging in the PAV is reduced from 20 to 8 hours (*7*).

(3) 4mm DSR only requires 25 mg (in practice 150 mg is needed for loading the sample into the rheometer and trimming). The large amount of sample (50 to 100g) required for BBR is no longer necessary.

(4) 8mm DSR requires about three times as much material as 4mm DSR and 4mm DSR is valid up to about 30°C. Given the limited amount of material produced in Method B, the reduction in material required for intermediate temperature testing is an advantage, albeit not a major advantage.

(5) 4mm DSR allows direct testing of the low temperature rheological properties including the dynamic moduli (G' and G"), and thru interconversion the relaxation modulus G(t) and creep compliance modulus J(t). There is no extrapolation of intermediate temperature data. The error due to instrument compliance at low temperature is corrected in the 4mm DSR procedure so direct testing on the DSR is possible to as low as -40°C.

MATERIALS AND TESTING

The three polymer modified emulsions studied in this investigation are described Table 1. The emulsions were received from PRI Asphalt Technologies, Inc. In addition to the emulsions, the corresponding recovered emulsion residues were also received from PRI. The residues were recovered by PRI in accordance with AASHTO PP-72-11 Method B.

TABLE 1 Emulsions and Emulsion Residues Received from PRI

Emulsion Label	Emulsion Description
CRS-2P	Polymer modified, cationic rapid set
CQS-1hP	Polymer modified, cationic quick set
LMCQS-1h	Latex modified, cationic quick set

The rheological properties of the emulsion residues received from PRI, and emulsion residues recovered and aged using the SAT were measured at WRI using 4 mm diameter parallel plate geometry with a Malvern Kinexus rotational dynamic shear rheometer (DSR). Frequency sweeps were performed at 15°C intervals over a temperature range of -30 to 45°C (in some cases to 60°C) and an angular frequency range of 0.1 to 100 rad/sec.

The first frequency sweep was performed at 30°C after 20 minutes of conditioning at 30°C to insure the specimen was at the test temperature. After performing the frequency sweep at 30°C the temperature was lowered to the next test temperature and again allowed to condition at that temperature for 20 minutes. The process was continued until reaching -30°C. The normal force was monitored continuously during the test and the gap adjusted to keep to keep the normal force at or close to zero. Keeping the normal force at or close to zero is essential to prevent stresses from building in the sample and possible rupture or loss of plate adhesion.

The repeatability of the 4mm DSR test is currently under investigation and is a part of ruggedness and round robin testing that will be performed in the near future under the auspices of the Binder Expert Task Group. However, during the development of the 4mm DSR test good reproducibility was found with data collected on 4, 8 and 25 mm diameter plates by different operators which confirmed that reliable data can be obtained using small 4 mm diameter parallel plates (*8*).

Storage and loss modulus master curves were developed from frequency sweep data using Rhea™ software developed by Abatech Consulting Engineers.

4mm DSR (Dynamic Shear Rheometry Using 4mm Diameter Parallel Plates)

A dispute concerning the modulus of glycerol in the glassy regime (G_g) led Schröter et al. (*9*) to develop a method to correct for the compliance of a dynamic shear rheometer, and its tools and platens. Sui et al. (*8*) applied this compliance correction method to bitumen low temperature dynamic shear measurements (~ 5°C to -40°C) using 4 mm diameter parallel plates and a 1.75 mm gap.

As mentioned above, the test method requires only 25 mg, but in actual practice about 150 mg is required in order to load and trim the sample, which is still about two 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.

BBR m-value and creep stiffness S(t) are estimated through a correlation with 4mm DSR developed by Sui et al. (*10*). 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.

Simple Aging Test (SAT) Applied to Emulsion Residue Recovery and Aging

The emulsion residues were recovered by using the simple aging test (SAT) plates. Development of the SAT is reported elsewhere (*7*), however the following provides a brief description of the SAT and how it was used in this study.

Figure 1 illustrates the SAT plate used 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 to water ratio of the emulsions were determined. All three emulsions appeared to consist of approximately 65% asphalt and 35% 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 μm after drying. A total of three plates were prepared, one for each emulsion. Figure 2 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.

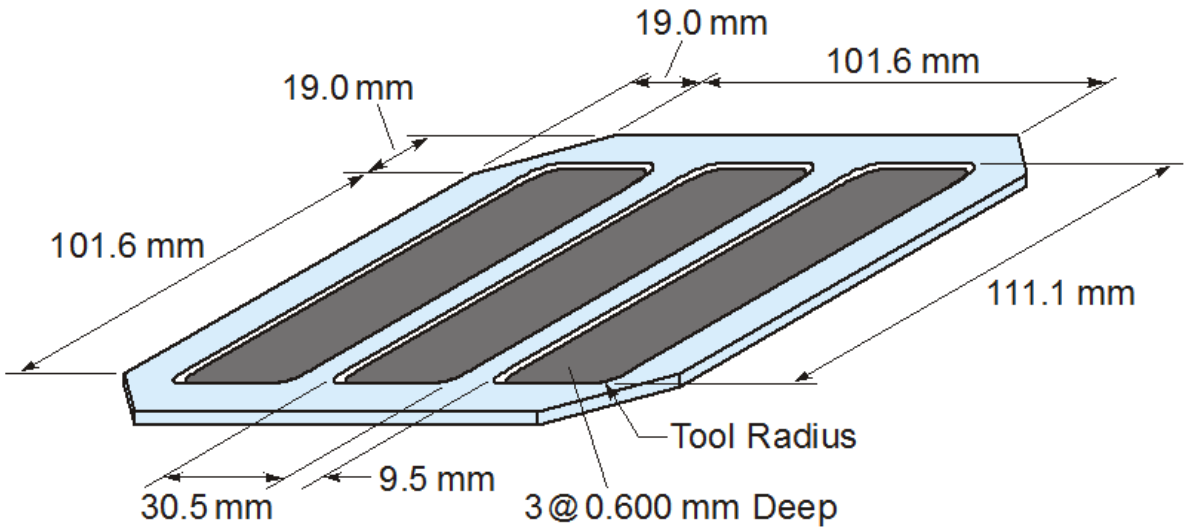

FIGURE 1 SAT plate dimensions.

FIGURE 2 Pouring emulsion residue onto the SAT plate.

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 4mm DSR. The plates were then placed in a standard pressure aging vessel (PAV) for 8 hours at 20 atm. Aging the 300 µm film in a PAV at 20 atm for 8 hours is equivalent to the level of aging of the standard PAV using a standard PAV pan and film thickness (*7*). It should be noted here that this significant savings in time is achieved by reducing the film thickness from 3.2 mm, which is the standard PAV film thickness, to 300 µm. The much thinner film thickness dramatically reduces diffusion effects. The recovery and aging scheme are illustrated in Figure 3.

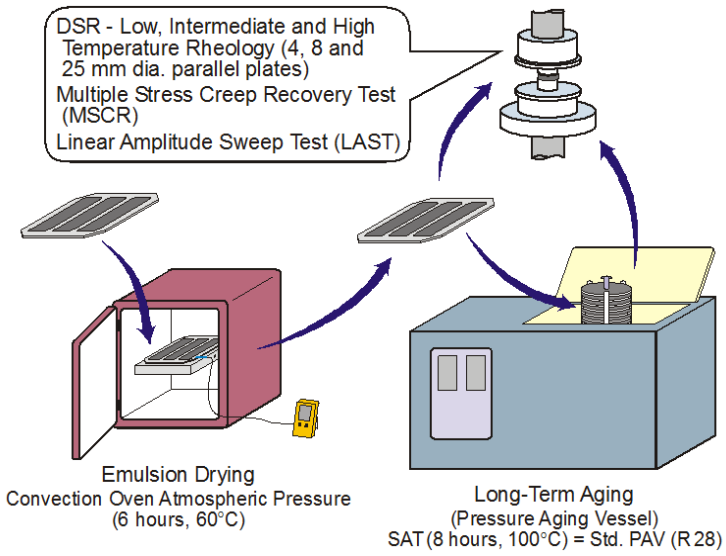

FIGURE 3 Emulsion residue recovery and long term-aging and testing scheme.

The 4 mm DSR test was successfully carried out except in a few cases there was insufficient torque generated during the 45°C and/or 60°C frequency sweeps because of a lack of emulsion residue stiffness under these conditions and these sweeps were discarded. Also, on two 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 available due to slippage or breakage or the low temperature continuous grade was below -30°C, the low temperature portion of the master curves were extrapolated using the Christensen-Anderson-Marasteanu (CAM) model (*11*). Typically, the extrapolation was only for a few degrees Celsius. As mentioned previously, 4mm DSR can go as low as -40°C, so even the very slight extrapolation performed in a few cases for this study would not generally be required.

LOW AND INTERMEDIATE TEMPERATURE MECHANICAL PROPERTIES

Master Curve Comparison

Figure 4 compares the complex shear modulus master curves generated from the available frequency sweeps using the Rhea™ software. The software uses the WLF equation to obtain an initial estimate of the horizontal shift, but the master curve is refined using a pair-wise shifting techniques (*12*). There are three plots in Figure 4, one for each emulsion, comparing the complex modulus of the SAT recovered emulsion, the PRI recovered emulsion, and the PAV aged SAT recovered emulsion.

There is a clear stiffening effect observed from the SAT PAV aging. The unaged SAT and PRI emulsion residues appear similar, but that is difficult to assess on a log-log plot. A better way to assess how well they compare is to compare specific rheological properties, which is performed in the next section.

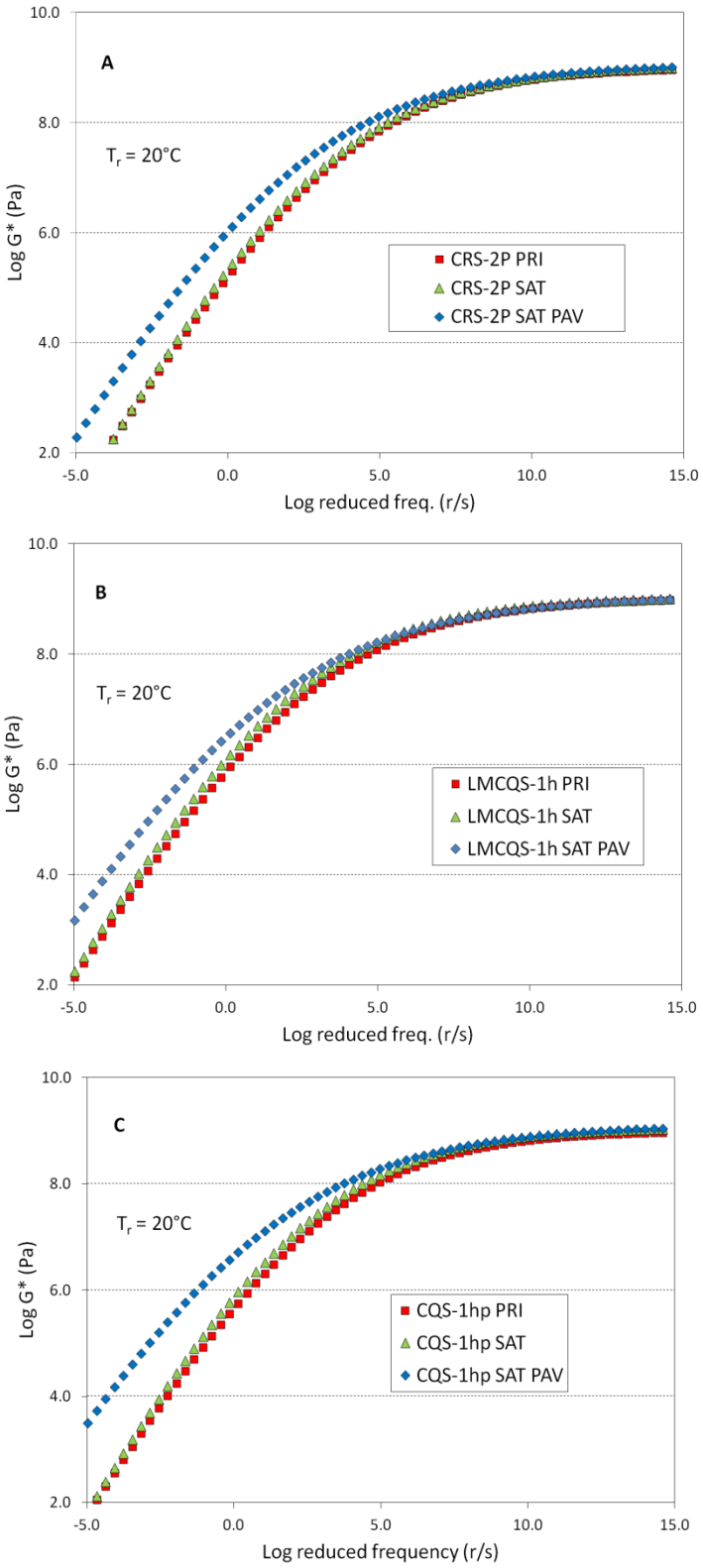

FIGURE 4 Master curves for the emulsion residues and SAT aged emulsions residues listed in Table 1. A: CRS-2P; B: LMCQS-1h; C: CQS-1hP.

Low Temperature Properties

The continuous low temperature performance grades of the unaged emulsion residues and SAT PAV aged emulsion residues are shown in Figure 5. The low temperature performance grade was determined using an iterative procedure to find the temperature at which m-value = 0.3 or S(t) = 300 MPa. PAV aging the residue reduces the continuous low temperature grade in the range of 5 to 20% depending on the particular emulsion residue.

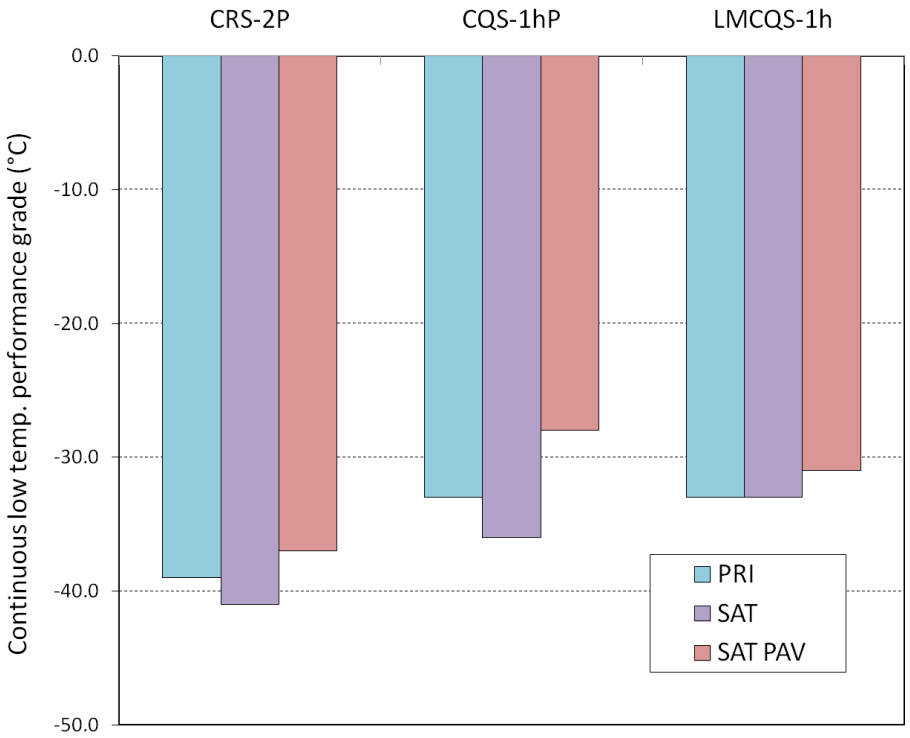

FIGURE 5 Continuous low temperature performance grade.

M-value is the slope of the creep stiffness curve at the performance grade temperature plus 10°C at 60 seconds. 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. M-values at a temperature of -28°C for the three emulsion residues are shown in Figure 6.

Figure 6 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 and by WRI using the SAT 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-1h 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%.

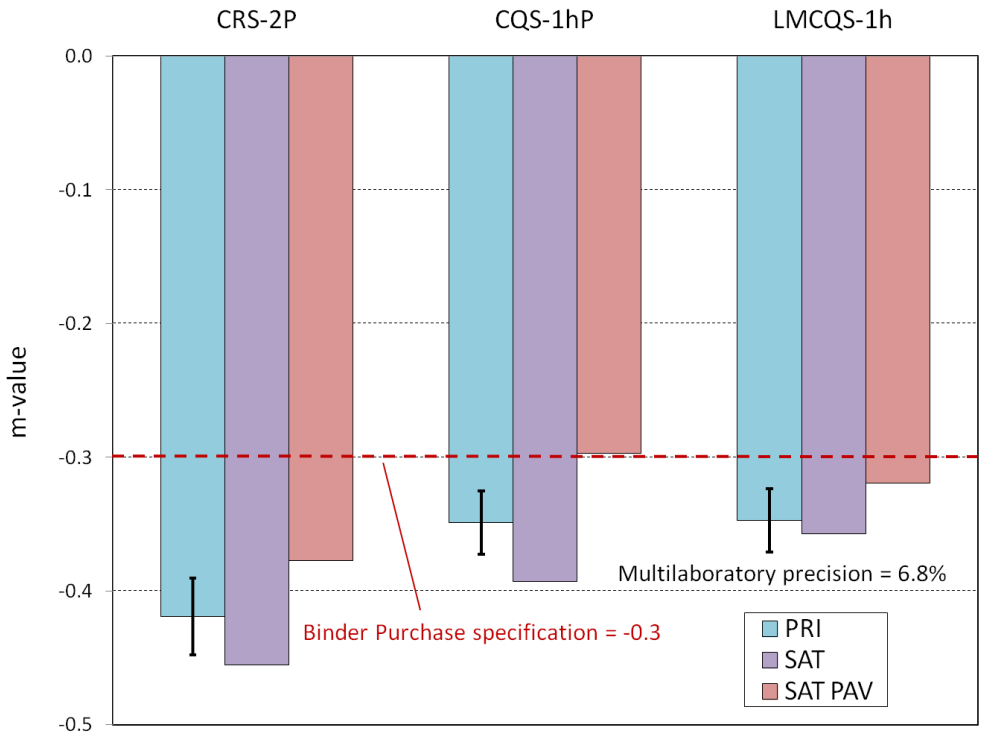

FIGURE 6 Emulsion residue: m-value at -28°C.

Intermediate Temperature Properties

Fatigue cracking resistance of an RTFO/PAV aged asphalt binder is typically evaluated using G* sin δ. G* represents the binder complex shear modulus and δ represents the phase angle. G* can be thought of as representing stiffness, and δ the viscoelastic response of the binder. Binder purchase specifications for hot mix pavement typically require the factor to be less than 5 MPa. The factor is considered a measure of energy dissipation which is related to fatigue damage. The critical temperature range for fatigue damage is near the midpoint between the highest and lowest service temperatures. A test temperature of 19°C was selected for this analysis. Figure 7 shows the G* sin δ results. As in the m-value plot (Figure 6) the multilaboratory precision is included in Figure 7 to allow comparison of the PRI and SAT recovered residues.

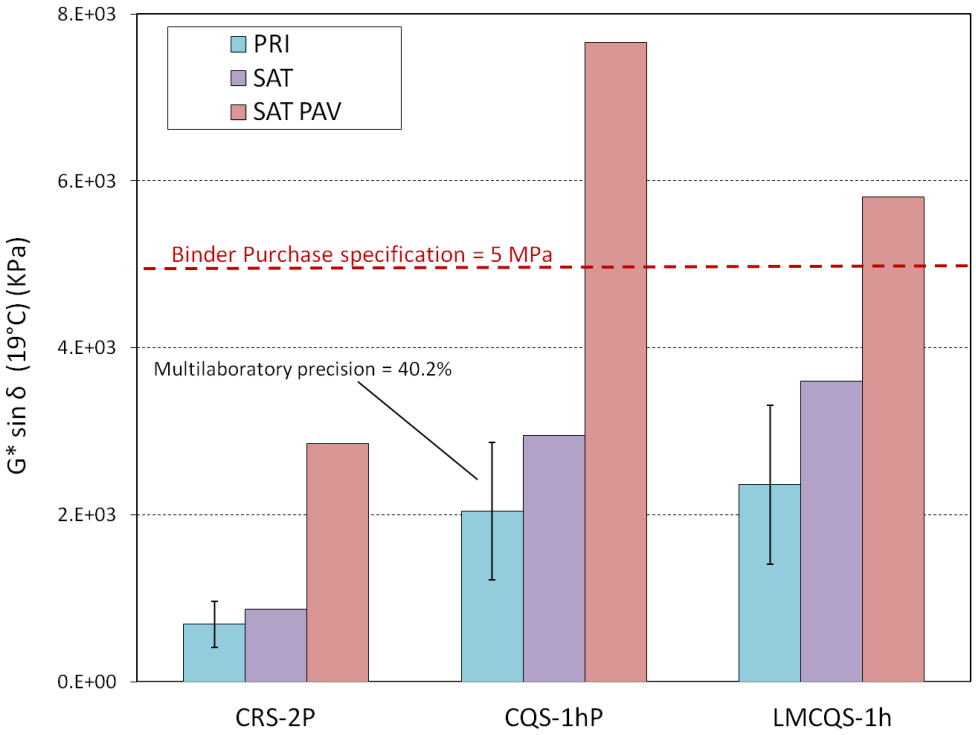

FIGURE 7 Emulsion residue: G* sin δ at 19°C.

Ductility

Ruan et al. (*13*) showed the extensional flow of conventional asphalt binders, as measured by a ductilometer, can be qualitatively described with a simple elongation model using a viscoelastic Maxwell element. The model correlates well with ductility (especially when ductility < 10 cm), and is of the form:

$$\text{Ductility} = 0.23 * \left\{ \frac{G'}{\frac{n'}{G'}} \right\}^{(-0.44)} \quad (1)$$

where ductility is measured in cm at 15°C and an elongation rate of 1 cm/min with a ductilometer and G', and η' are measured with a dynamic shear rheometer at a reference temperature of 15°C and a frequency of 0.005 r/s.

Equation (1) was applied to the 4mm DSR data for the emulsion residues and the calculated ductility is displayed in Figure 8. Based on the work of Ruan et al. the embrittlement threshold is approximately 5 cm.

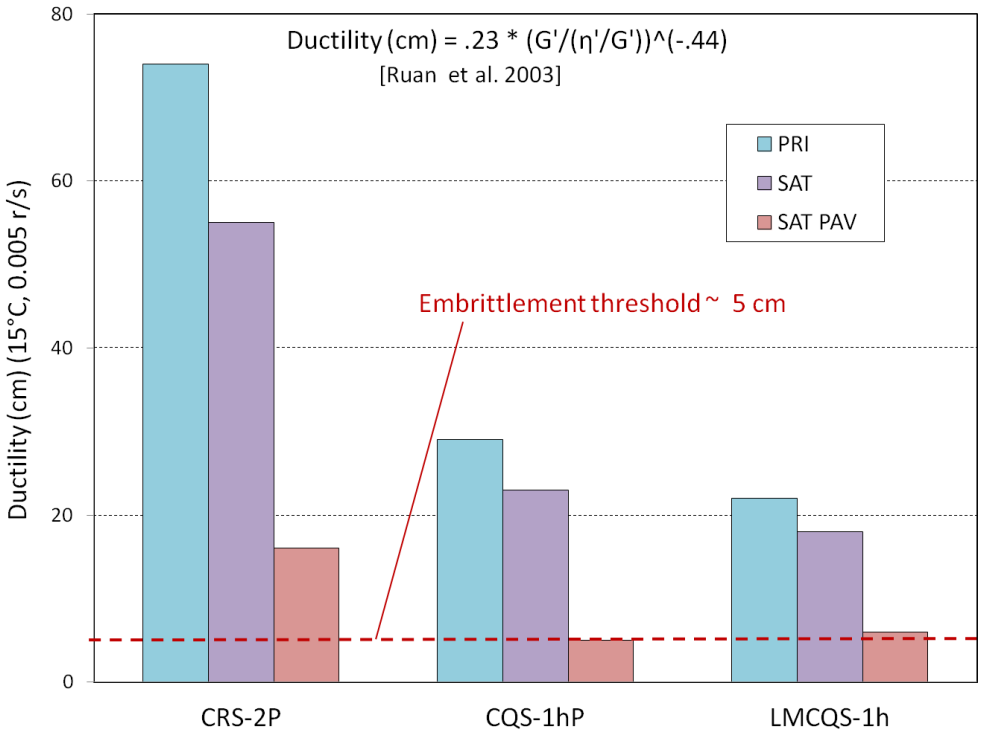

FIGURE 8 Emulsion residue ductility.

High Temperature Properties

The high temperature rheological properties were not investigated for this study. However, it should be noted that the SAT recovery and aging methodology produced sufficient material for 8 and 25 mm DSR parallel plate geometry.

Discussion

The SAT recovered residues were slightly softer (in terms of m-value and continuous low temperature grade) at low temperature than the PRI residues. However, at intermediate temperature, stiffness (in terms of G* sin δ and ductility) was reversed, i.e. the SAT recovered emulsions were slightly stiffer than the PRI emulsions. Of course, it's possible that this change in comparable stiffness is due simply to an anomaly in the data. However, , it could be that the SAT residues were drier than the PRI residues. If that was the case, it is possible that increased residual/entrained water in the PRI residue would act as a plasticizer at intermediate temperature, which would explain why the SAT residue was stiffer at intermediate temperature, but the presence of increased moisture at low temperature may have a stiffening effect on the PRI residue. Moisture levels of the emulsion residues after recovery and long-term aging were not measured in this study.

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 SAT PAV protocol used here simulates the aging that would typically occur. 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 SAT PAV protocol.

The relationship between the reported low and intermediate rheological properties and field performance of the emulsions was not considered since performance data were not provided.

CONCLUSION

This study demonstrates the application of 4mm DSR for measuring the low and intermediate rheological properties of unaged and aged emulsion residues. The simple aging test (SAT) was used to recover and age the emulsion residues. The mechanical properties of the PRI (PRI used AASHTO PP 72-11 – Method B to recover the residue) and SAT recovered unaged 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. Overall, the SAT method appeared to be comparable to Method B in terms of the recovered emulsion residue mechanical properties.

Long-term oxidative aging was performed by simply placing the SAT plates with residue in a standard pressure aging vessel (PAV) for 8 hours at 20 atm. Aging the SAT recovered residue in a PAV at 20 atm for 8 hours is equivalent to the level of aging of the standard PAV using a standard PAV pan and film thickness. The long-term aging was performed to demonstrate the effect of aging on three binder mechanical properties (m-value, G* sin δ, and ductility). All three properties were significantly affected by the aging. PAV aging stiffened the SAT recovered residues bringing them closer to possible embrittlement failure.

It is beyond the scope of this study to comment on the need to perform oxidative aging on laboratory recovered emulsion residues for specification testing. The point being made here is that if it is deemed necessary to age the residue for specification testing, the SAT method is a simple and fast alternative to standard PAV aging.

The proposed SAT recovery method and application of 4mm DSR offers several advantages over Method B and current DSR methodology such as eliminating the silicon mat and wet film applicator. There is no extrapolation of intermediate temperature DSR data to low temperature. The error due to instrument compliance at low temperature is corrected in the 4mm DSR procedure.

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REFERENCES

1. Transportation Research Circular E-C122, Asphalt Emulsion Technology. *Review of Asphalt Emulsion Residue Procedures* Transportation Research Board, Characteristics of Bituminous Materials Committee, October 2007, Washington, D.C.
2. Hanz, A., Z. Arega, and H. Bahia. Rheological Evaluation of Emulsion Residues Recovered Using Newly Proposed Evaporative Techniques, TRB 88th Annual Meeting Compendium of Papers DVD, 2009.
3. European Standard Method EN 13074-1. Bitumen and bituminous binders - Recovery of binder from bituminous emulsion or cut-back or fluxed bituminous binders.
4. ASTM D7497-09, Standard Practice for Recovering Residue from Emulsified Asphalt Using Low Temperature Evaporative Technique.
5. AASHTO PP 72-11 Standard Practice for Recovering Residue from Emulsified Asphalt Using Low-Temperature Evaporative Techniques.
6. Hanz, A., and H. U. Bahia. Initial Evaluation of an Approach to Estimate Low Temperature Creep Stiffness Properties using Intermediate Temperature DSR Testing. White paper submitted to the FHWA Emulsion Task Force, Federal Highway Administration, Washington D.C., 2010.
7. Farrar, M., R. William Grimes, Changping Sui, Jean-Pascal Planche, Shin-Che Huang, Thomas F. Turner, and Ron Glaser. Thin Film Oxidative Aging and Low Temperature Performance Grading Using Small Plate Dynamic Shear Rheometry: An Alternative to Standard RTFO, PAV, and BBR. Submitted to the Eurasphalt & Eurobitume Congress, Istanbul, Turkey, June 13-15 2012.
8. Sui, C., M. J. Farrar, W. H. Tuminello, and T. F. Turner. New Technique for Measuring Low-Temperature Properties of Asphalt Binders with Small Amounts of Material. In *Transportation Research Record: Journal of the Transportation Research Board*, No. 2179, Transportation Research Board of the National Academies, Washington, D.C., 2010, pp. 23-28.
9. Schröter, K., S. A. Hutcheson, X. Shi, A. Mandanici, and G. B. McKenna. Dynamic Shear Modulus of Glycerol: Corrections Due to Instrument Compliance. *Journal of Chemical Physics*, Vol. 125, 2006, 214507.
10. Sui, C., M. J. Farrar, P. M. Harnsberger, W. H. Tuminello, and T. F. Turner. New Low-Temperature Performance-Grading Method Using 4-mm Parallel Plates on a Dynamic Shear Rheometer. In *Transportation Research Record: Journal of the Transportation Research Board*, No. *2207*, Transportation Research Board of the National Academies, Washington, D.C., 2011, pp. 43-48.
11. Marasteanu, M. O., and D. A. Anderson. Improved Model for Bitumen Rheological Characterization. Eurobitume Workshop on Performance Related Properties for Bituminous Binders, Luxembourg, May 1999, paper no.133.
12. Rowe, G. M., and G. L. Baumgardner. Evaluation of the Rheological Properties and Master Curve Development for Bituminous Binders used in Roofing, Session III, Advancing Membrane Roofing, pp. 103-116. In Roofing Research and Standards Development, 6th Volume, W. J. Rossiter, and T. J. Wallace, editors. ASTM Committee D-8 on Roofing Waterproofing, and Bituminous Materials. STP 1504, 2007.

13. Ruan, Y., R. R. Davison, and C. J. Glover. An Investigation of Asphalt Durability: Relationships between Ductility and Rheological Properties for Unmodified Asphalts. *Petroleum Science and Technology*, Vol. 21, No. 1, 2003, pp. 231-254.