Binder performance and testing

Innovations in analysis of rejuvenators in blends using RAP as part of Infravation projects

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Abstract

A new approach to evaluate an aged binder rejuvenation based on both chemical and rheological tests was pioneered as part of Infravation's AlterPave and BioRePavation projects. This paper focuses of results obtained under BioRePavation where blends of bio-rejuvenators with virgin binder and Reclaimed Asphalt Pavement (RAP) were made and evaluated both in the laboratory and in a field Demonstrator at the IFSTTAR accelerated loading facility. The chemical analytical tests of Infrared Spectroscopy (IR) and Saturates Aromatics Resins and Asphaltene Determinator (SAR-AD™) developed by the Western Research Institute (WRI) were performed to evaluate the rejuvenation of the binder blends. Low temperature rheologic tests including ΔTc, a parameter related to binder relaxation, were performed to evaluate possible rejuvenation of the physical properties, using the Dynamic Shear Rheometer. Blends were artificially aged in the lab via RTFO and extended PAV accelerated aging to test the likely longevity of pavements made with these rejuvenator, RAP, and binder combinations. Additionally, a new micro-sampling device and concept also developed by WRI under a contract with the FHWA, was utilized to sample test sections that were made using some of the RAP+Virgin Binder+Rejuvenator blends. The extracted and recovered binder from the field was evaluated via IR and rheology to demonstrate that laboratory blend performance was approximating field performance. Aging severity of the sampled sections was also evaluated.

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1. Introduction

The use of Reclaimed Asphalt Pavement (RAP) is widespread due to its availability, its economics incentive, and the need to reduce both waste and consumption from the construction and maintenance of roads. Additives are becoming more widely used to help rejuvenate RAP and increase compatibility between RAP and Virgin Bitumen (VB), particularly in the case of high RAP content mixes (over 30-40% RAP). Aging propensity of blends of RAP with VB and additives are necessary to evaluate likely service life of new pavements. Also necessary are tests that may highlight the mechanism of rejuvenation or softening by an additive on a VB + RAP and help predict the performance.

The purpose of the work highlighted in this paper is to demonstrate novel and predictive analysis tools of rejuvenator + VB + RAP blends via laboratory aging, rheological, and chemical measurements. These techniques were applied to the BioRePavation project that was part of the Infravation family of projects. Samples or blends were aged in the Rolling Thin Film Oven (RTFO) followed by the Pressure Aging Vessel (PAV) for 40 hrs. Performance Grading (PG) using US Superpave specifications, Infrared Spectroscopy (IR) and Saturates, Aromatics, Resins, and Asphaltene Determinator (SAR-AD) developed by the Western Research Institute (WRI) were measured on the laboratory prepared and aged samples.

In addition to the above tests, field samples of the blends used in the BioRePavation demonstrator project carried out at the IFSTTAR accelerated load facility near Nantes, France, were compared to the lab samples via a novel non-destructive micro-sampling device that allows for collection of small (100g) of powdered asphalt mix from the field and developed by WRI. The bitumen portion of this mix can then be extracted and recovered for laboratory testing.

2. TESTING OF LABORATORY BLENDS

2.1. Materials, Blending, and Aging

The three biomaterials used in this study were Sylvaroad™ RP 1000 performance additive [1] which is referred to as Biomaterial-1 (BM-1) and supplied by Kraton Chemical, epoxidized methyl soyate referred to as BM-3 additive and supplied by the Iowa State University (ISU), and Biophalt® which is a bio-binder containing Styrene Butadiene Styrene (SBS) polymer which is referred to as BM-2 and supplied by Eiffage.

All blends of materials used in this study are listed in Table 1, where VB is virgin bitumen and AB is aged bitumen solvent extracted from RAP. The proportion of each material in the blend was decided from the mix design testing. Field sections were also made with the same binder contents in Table 1. These laboratory blends were aged using the rolling thin film oven (RTFO) technique and both the RTFO and pressure aging vessel (PAV) for 40hrs to simulate short and long term aging, respectively [2,3].

Table 1. List of the blends with the quantity of each ingredient used in the study. VB stands for Virgin Bitumen and AB stands for Aged Bitumen (Bitumen extracted from RAP).

Bitumen Properties	Reference Name
2.26% Sylvaroad + 60.10% VB + 37.64% AB	BM-1 Blend
62.36% Biophalt + 37.64% AB	BM-2 Blend
3.0% EMS + 59.4% VB + 37.6% AB	BM-3 Blend

2.2. Rheology

Rheological results were obtained using dynamic shear rheometry (DSR). Low temperature rheology was measured using 4 mm geometry DSR rather than the traditional bending beam rheometer [4]. Low temperature m-minimum value was measured at 0.28 and S-maximum at 143 MPa. 4mm DSR performance grading (PG) allows much smaller size samples (1.0 g instead of 100 g) and significant time savings.

After RTFO short-term and RTFO/PAV extended long term aging (40 hrs PAV), all solutions improve by lowering both the PG specification intermediate temperature and the crossover temperature when compared to the non-rejuvenated control. While the BM-1 and BM-3 solutions still meet the upper PG spec of 70°C for the virgin bitumen, the BM-2 replacement bitumen decreases the continuous high temp PG spec by 2 degrees to 68°C. Because BM-2 is also highly SBS modified and the classical PG specifications are somewhat insensitive to SBS polymer, the likelihood of rutting being a problem for this replacement bitumen is very low. These results are in Figures 1.

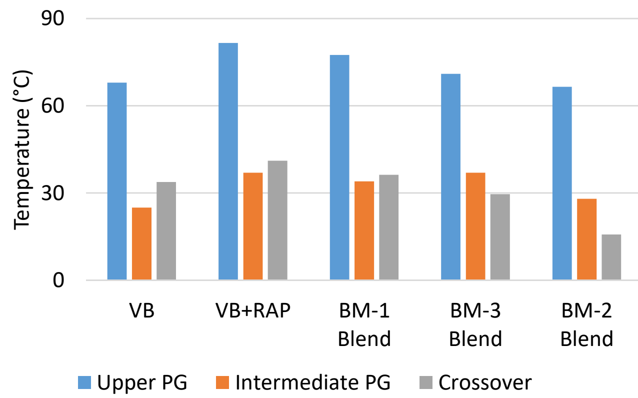

Figure 1. Crossover, upper and middle PG temperatures.

All solutions improved low temperature performance grades and all solutions improved the ΔTc (see Figure 2). ΔTc is the difference T_S-T_m between T_S the critical temperature on stiffness at 300MPa by BBR or 143 MPa by DSR and T_m the critical temperature on m-value at 0.3 (BBR) or 0.28 (DSR). It is related to the bitumen relaxation capability, and has been shown to correlate well with field cracking performance [5]. The less negative the better the cracking resistance, values below -5°C are suspected to lead to cracking failure.

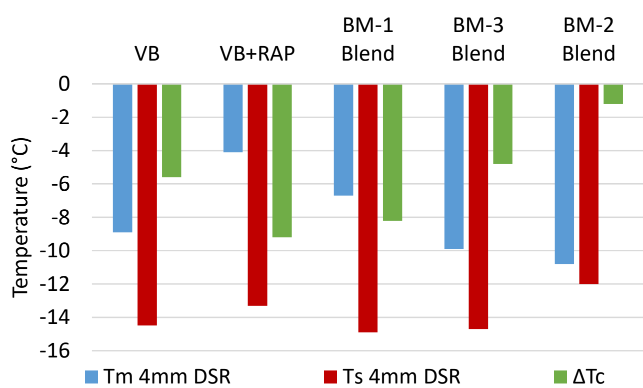

Figure 2. Low temperature passing temperatures for m and S, and ΔTc from 4mm DSR.

2.3 Infrared Spectroscopy (IR)

Liquid cell (CS_2 solvent) IR absorbance spectra including proportional sums of the individual spectra are presented in Figure 3. All absorbance IR spectra were collected by dissolving 50 mg of bitumen or blend in 1.0 ml CS_2 solvent to generate a solution of known concentration. The blend sum of components spectra for Figures 3 were created by adding 2.3% of the BM-1, 60.1% of the VB spectra and 37.6% of the AB spectra, the same proportion of each material that was used to make the physical blend. Because IR absorbance is a linear phenomenon, following Beer's law in the <1.5 absorbance range, this sum of components spectra compared to the 2.3% rejuvenator blend spectra can give an indication of chemical interaction between blend components. For the 2.3% BM-1 blend, the spectra show that the same peaks are present in both the proportional sum spectra (red) and rejuvenator blend spectra (blue), with only a baseline shift, indicating that no significant chemical interactions between components are detected by the IR before or after aging. Possible reactions before aging are the rejuvenator reacting with components from the RAP or base bitumen. Additional possible reactions during or after aging are oxygen reacting with the bitumen or RAP, oxygen reacting with the rejuvenator, the oxidized rejuvenator reacting with the base bitumen or RAP, or oxygen reacting with polymer that may be present.

The small peaks rise at 1170 and 1196 cm^{-1} (Figures 3, 4) in the BM-1 and BM-3 blends are likely caused by esters from long chain fatty acids. These functional groups are usually present in bio-derived oils. There is a peak present at ~1740 cm^{-1} in all the bio-derived oil spectra that is indicative of an aliphatic ester axial deformation from C=O bond. While some of this peak interferes with the carbonyl absorbance with aging (~1700 cm^{-1}), it appears to diminish somewhat in the 2PAV (or PAV for 40 hrs) spectra indicating that a portion of the esters are likely eliminated or reacted with oxidative aging for all of these materials [7-10].

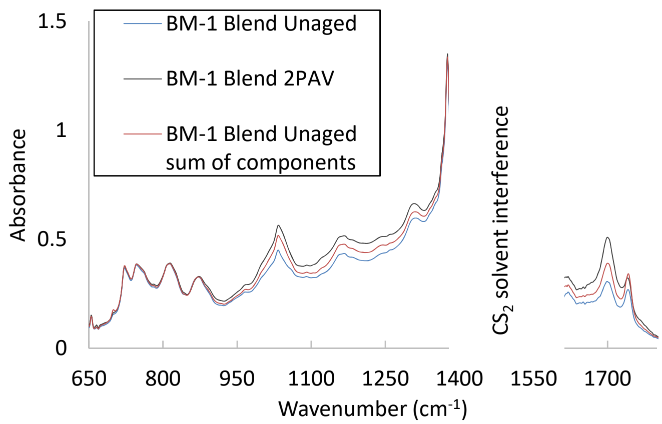

Figure 3. IR spectra of the BM-1 blends.

The IR overlay spectra in Figure 4 shows the sum of components and the BM-3 blend spectra are very similar with no areas of peaks shifting between samples indicating that chemical interaction between the BM-3 rejuvenator and the VB+RAP blend is unlikely. However, upon 2PAV aging, there is a shift in the ~855 cm^{-1} peak to higher wavenumber showing that there is likely either a chemical interaction occurring between the aged blend and the BM-3 material, or the aging of the BM-3 material is responsible for the shift. Assigning these peaks or shifts to particular functionalities has been difficult. The literature shows that oxirane rings (the simplest 3 member epoxide ring) contain two distinct peaks at 825 and 845 cm^{-1} [7-10]. It is possible that different epoxides are shifted up to the 850 - 875 cm^{-1} range and that the shift/decrease in these peaks with aging is the opening of the epoxide rings or interaction of these epoxides with polar functionalities within bitumen. Because there is aged bitumen already present in the unaged BM-3 blend and this shift begins to occur in the RTFO aged BM-3 blend (Figure 5), it is likely that sufficient time at elevated temperature is necessary for either the aging of the BM-3 additive or chemical interactions between the epoxy groups and polar functionalities. Owing to the subtly of the shift, it is more likely that this interaction between the BM-3 and aged bitumen is physical rather than chemical.

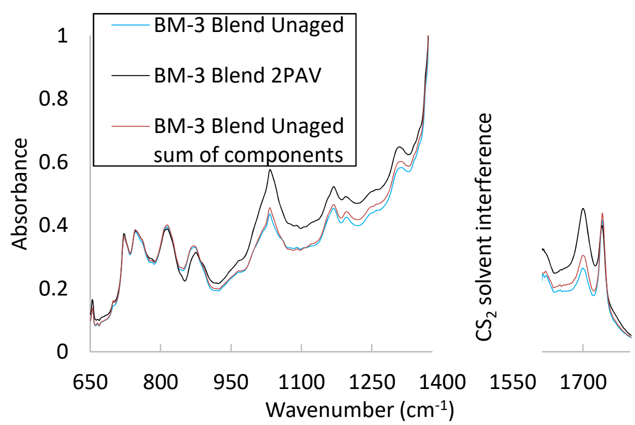

Figure 4. IR spectra of the BM-3 blend.

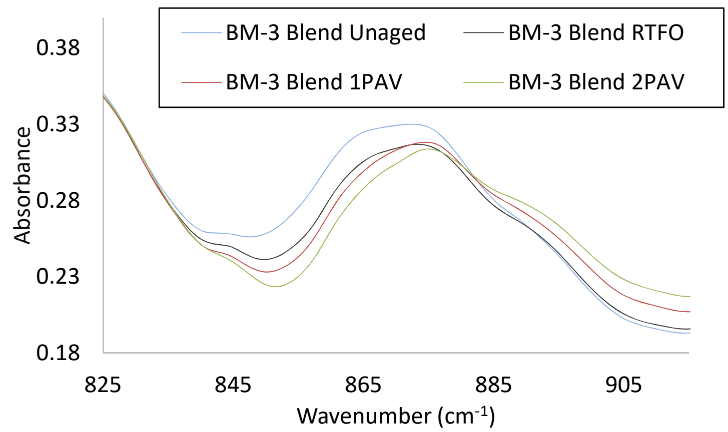

Figure 5. IR spectra of the BM-3 blend aging series.

Overlays of the BM-2 blend, BM-2 blend 2PAV aged and sum of components of IR spectra are displayed in Figure 6. These plots show that all the components peaks present in the real spectra are also present in the sum of components spectra indicating that there is not a chemical interaction between BM-2 and AB that is detectable by IR. The peaks at 965 and 700 cm^{-1} are indicative of SBS polymer and confirms its presence as stated by the BM-2 manufacturer. It is well known that SBS polymer in bitumen oxidatively ages resulting in shorter chain length polymers that significantly impacts the rheology, structure, and performance of modified bitumen [11, 12]. This study shows similar results with some decrease in the polymer peaks after lab aging (Figure 6 blue and black). SBS can also act as a sacrificial oxidant that slows bitumen oxidation. These plots show that many additional peaks are present in the fingerprint region in the BM-2 blend compared to traditional bitumens which is not unusual given that this is a bio-based replacement binder that likely contains many different functionalities that are not present in traditional bitumens. Identification of these peaks were not made.

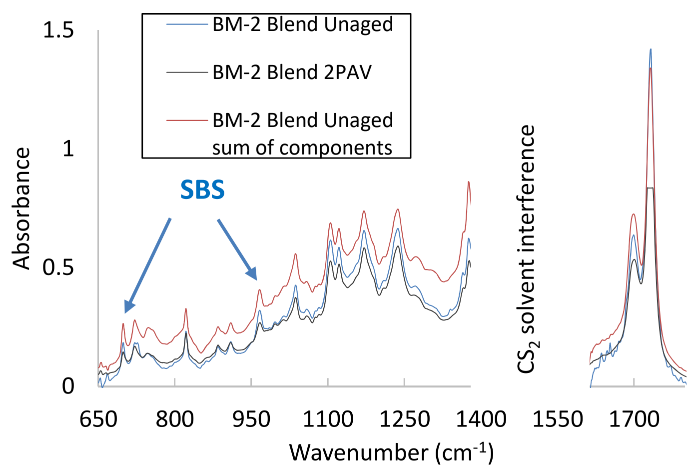

Figure 6. IR spectra of the BM-2 replacement bitumen blend.

2.4 Saturates, Aromatics, Resins, Asphaltene Determinator (SAR-AD)

Some samples were analyzed with the automated Saturates, Aromatics, Resins, and Asphaltene Determinator (SAR-AD™) that couples a liquid chromatography separation with an asphaltene analysis method [13]. This method separates asphalt into several polarity and aromaticity based fractions. The relative quantities of material in each of these fractions is a key step in understanding the links between material make-up and both physical performance and oxidation. Less elaborated methods for these types of separations have been around for decades and help explain the widely accepted asphalt colloidal model [14] (Lesueur, 2009).

In the method, a filtered 20 µL aliquot chlorobenzene solution of a sample is injected, and the combined system generates SAR chromatographic fractions and 3 solubility-defined asphaltene subfractions. Each of the six fractions passes through a 500 nm wavelength optical detector and an evaporative light scattering detector (ELSD). The 500 nm detector determines the concentration of visible light absorbing material that consists of pericondensed aromatic ring structures and aromatic structures with heteroatoms. The ELSD provides approximate weight percent values for all SAR-AD fractions. For the sake of simplicity, only ELSD results are included here.

The SAR-AD results in Figure 7 reveal that unaged VB + AB blend and unaged BM-1 blend have nearly identical quantities of fractions while the VB is enriched in saturates and aromatics by comparison. This indicates that the BM-1 additive does not significantly change the compositional makeup of the blend material. An example of this would be increasing the solubility or compatibility of an asphaltene and allowing it to report to the resins fraction.

The results from Figure 8 are differences between the unaged and aged 40 hrs in the PAV. These indicate that BM-1 additive slightly changes the aging profile with more aromatics oxidizing and fewer resins oxidizing to form asphaltenes in comparison to the VB + AB control. The VB shows more oxidation of the aromatics to form asphaltenes. This is not surprising as the VB contains more aromatics and fewer resins prior to aging.

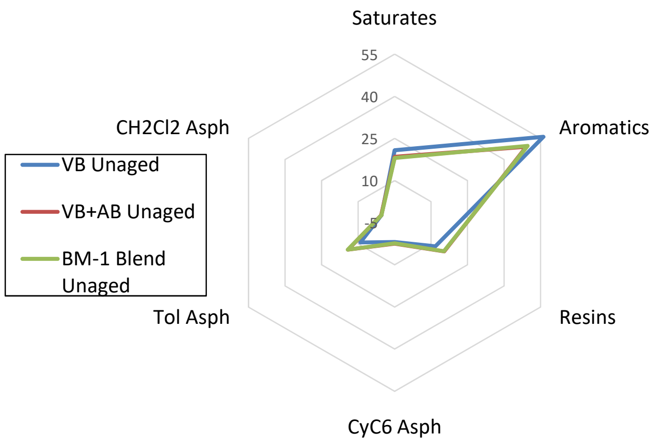

Figure 7. Spider plot showing the SAR-AD fractions measured by the ELSD in unaged BM-1 blend.

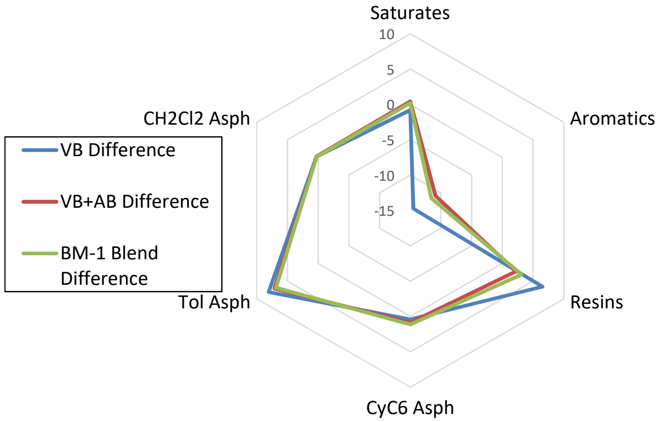

Figure 8. Spider plot showing the change in quantity of SAR-AD factions between unaged and aging 40 hrs in the PAV as measured by the ELSD. Negative numbers mean the fraction decreased with aging.

SAR-AD results in Figure 9 show that the BM-3 blend has nearly identical quantity of SAR-AD fractions as the VB + AB reference blend. This indicates that the BM-3 additive does not interact with the binder to change the compositional makeup of the material. Figure 10 results are the differences between the unaged aged 40 hrs in the PAV and shows that the BM-3 blend loses mostly aromatics and some saturates with aging. These materials become resins, some less polar asphaltenes (CyC_6), and toluene asphaltenes. This aging profile shows much less production of polar material than the reference blends with aging indicating that BM-3 is either an oxidation inhibitor when mixed with a RAP blend or the BM-3 interacts with the polar functionalities making them behave more like resins or aromatics, which is possible given the presence of epoxide rings in its chemical make-up. These epoxides, when interacting with asphaltenes, could help make some asphaltene molecules more compatible or even soluble in the bitumen through chemical modification or solvation.

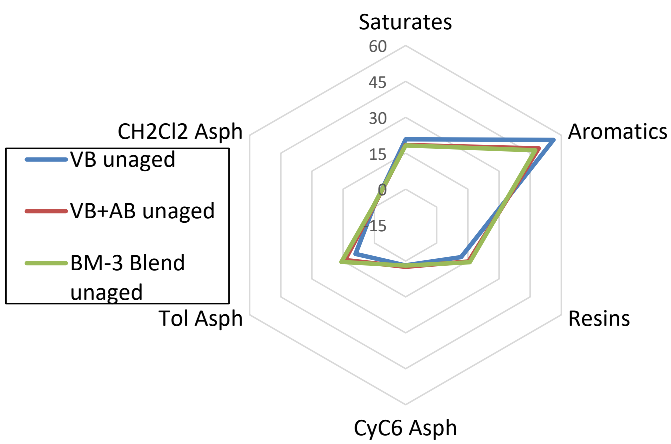

Figure 9. Spider plot showing the quantity of SAR-AD fractions measured by the ELSD in unaged BM-3 blend and reference materials.

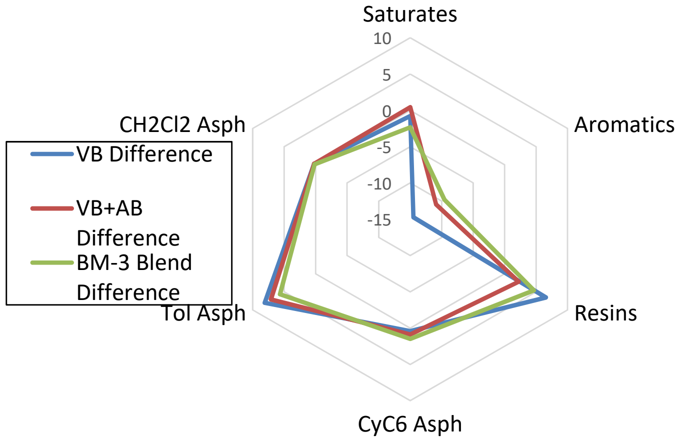

Figure 10. Spider plot showing the change in quantity of SAR-AD factions with aging 40 hrs in the PAV as measured by the ELSD for BM-3 blend and reference materials. Negative numbers indicate the fraction decreased with aging.

The SAR-AD results in Figure 11 indicate that the BM-2 blend is enriched in resins and low in saturates by ~15% compared to both the VB + AB and VB references giving it a markedly different compositional profile in relation to traditional binders. Further, the changes with aging between the unaged and 40 hr PAV aging highlighted in Figure 12 show that the BM-2 blend has a relatively small quantity of aromatics decreasing upon oxidation compared to the traditional binders and blends. The resins also slightly decrease rather than increase with 40 hr PAV aging. These compositional changes are consistent with only minor oxidative aging and confirm that this blend appears to be resistant to aging related changes. It is unclear what fraction the SBS reports to as a non-SBS modified bio-binder was not available for comparison.

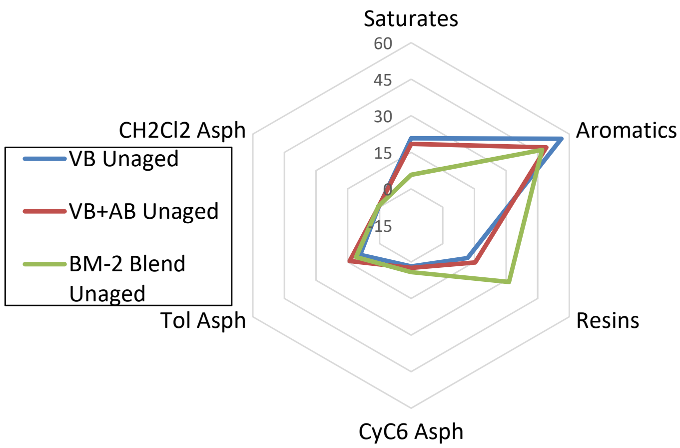

Figure 11. Spider plot showing the quantity of SAR-AD fractions measured by the ELSD in unaged BM-2 blend and reference materials.

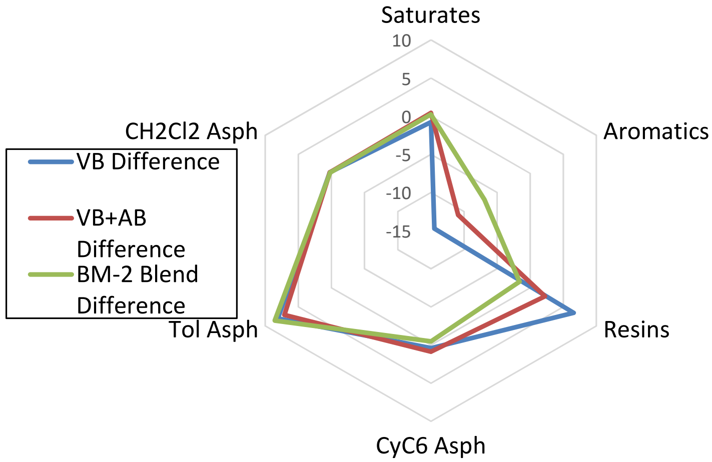

Figure 12. Spider plot showing the change in quantity of SAR-AD factions with aging 40 hrs in the PAV as measured by the ELSD for BM-2 blend and reference materials. Negative numbers mean the fraction decreased with aging.

3. FIELD SAMPLING

3.1 Methods

The in-situ non-destructive micro-sampling concept begins with sampling the pavement using a hammer drill equipped with a 19mm masonry drill bit and vacuum dust collector [16]. For this project, 5 holes were drilled 13 mm deep and the dust from each hole was collected to obtain about 100 g of material. This material constitutes the top of the wearing course where most of the pavement oxidation occurs. The bitumen portion of the drilled dust was extracted from the aggregate/fines portion by washing the samples with toluene:ethanol:water (85:14.25:0.75). IR spectra were measured on the recovered bitumen to ensure that all solvent was removed. Rheology of the recovered bitumens were then measured on a DSR with 4 mm parallel plate geometry and IR spectra were collected. The general concept of this technique is presented in Figure 12.

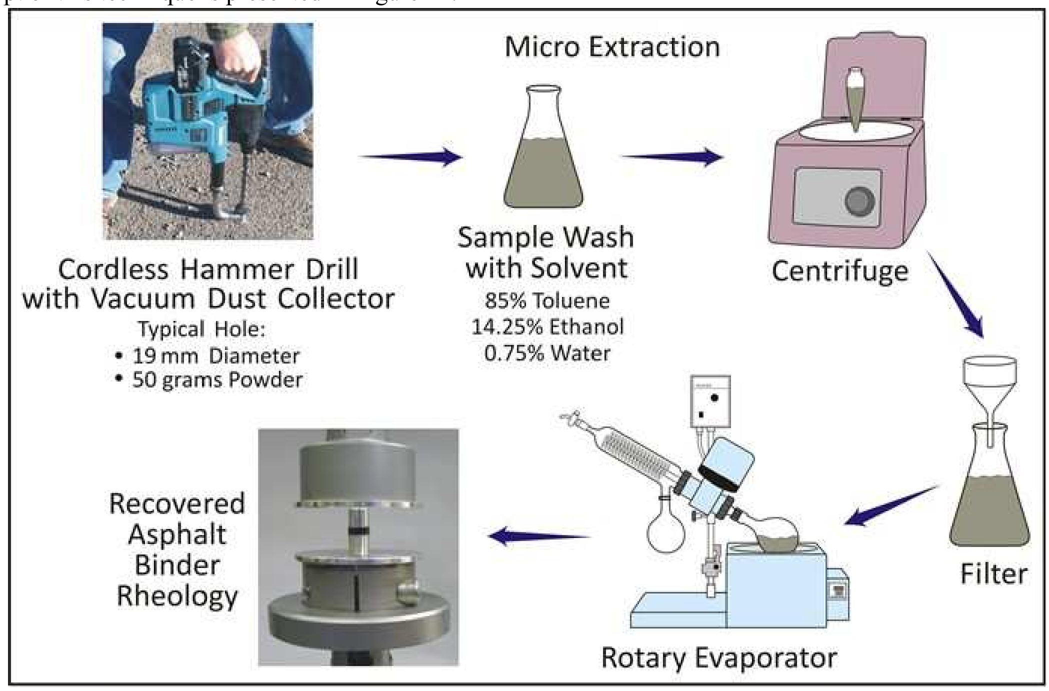

Figure 13. Micro-sampling concept.

3.2 Results

Four different pavement sections were built at IFSTTAR Accelerate Load Facility (ALF) and designed to test surface layer materials. A maximum of 1 million traffic loads (depending on pavement deterioration rate) were applied while monitoring each pavement section. To identify pavement failure mechanisms, comprehensive evaluation of each section was conducted via sampling for lab tests and trenches at the end of the full scale experiment. These test sections and experiments are described in the literature by Blanc, et al [15]. In addition to the classical monitoring, micro-sampling was performed by IFSTTAR using the micro-sampling device. All field data here are from the top 13 mm of pavement after 5 months aging in the field which occurred at the same time as 1,000,000 Equivalent Single Axel Loads (ESAL) of traffic on the test track.

Figure 14 shows the IR spectra of the lab blends and the extracted and recovered lab blends after being in the field for 5 months. The IR spectra of the BM-3 blend in Figure 12 shows the peaks at 1740, 1170, and 1196 cm^{-1} all absent in the field samples. These peaks are indicative of the BM-3 rejuvenator and are missing in these extracted samples because the BM-3 material is volatile enough to co-evaporate with the toluene:ethanol solvent during the recovery of the binder from the solvent. This is consistent with the information supplied by the manufacturer of BM_3. Therefore, the rheology of the extracted and recovered field samples is only a measure of the VB+RAP. Both the BM-1 and BM-3 blend field samples show the same peaks present as the laboratory blends indicating that these modifiers are still present for the rheological testing of the field samples. For the BM-2 spectra, the difference at 1700 cm^{-1} between the unaged lab blend and the sample from 5 months in the field is likely due to oxidation and decrease of the esters and corresponding peak at ~1740 cm^{-1}. This ester peak overlaps with the 1700 cm^{-1} peak causing it to decrease commensurately.

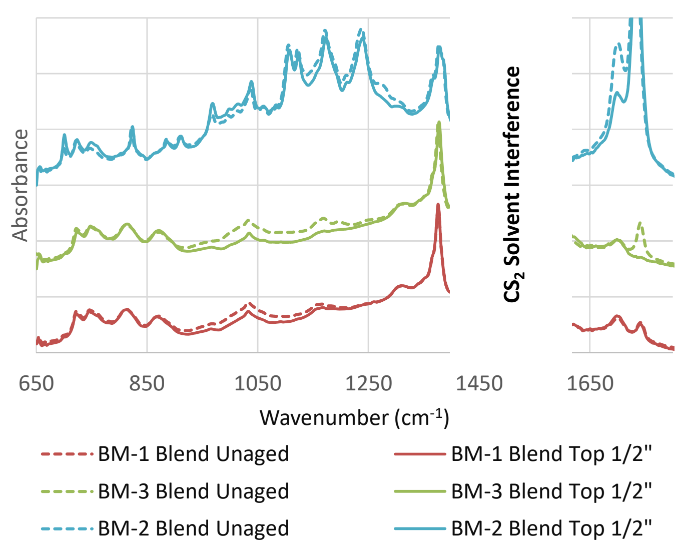

Figure 14. IR spectra of the extracted and recovered asphalt blends and the lab blends.

Rheology results in Figure 15 show the low temperature passing m, S and ΔTc for the field samples at 5 months of service. EME is a reference mix with 20% of RAP. EME2 (stands for "Enrobé à Module Elevé") is considered worldwide as the base course mix having the best mechanical/structural performance and the 20% RAP content was chosen for this reference mix because it is the average level used in mixes in France. These results show that the BM-1 and BM-3 improved both the low-temperature passing m and S values compared to the EME control. While the BM-2 bio-binder showed these metrics to be slightly worse, both the polymer modified nature of BM-2 and the significant improvement in ΔTc indicate that this section should perform better than the control with regard to cracking. ΔTc of both BM-1 and BM-3 sections show improvement compared to the control, even though the BM-3 rheology was tested without the rejuvenator present due to co-evaporation during the extraction and recovery process. This rheology data is consistent with the field performance data in Figure 16 that shows the EME control cracking significantly and BM-3 section cracking slightly after 1.4 million traffic loading cycles including 0.4 million cycles under increased loading to force cracking. The cracking in the BM-3 section was emanating from coring sites which is likely the reason the cracking leveled off after 10% instead of steadily increasing.

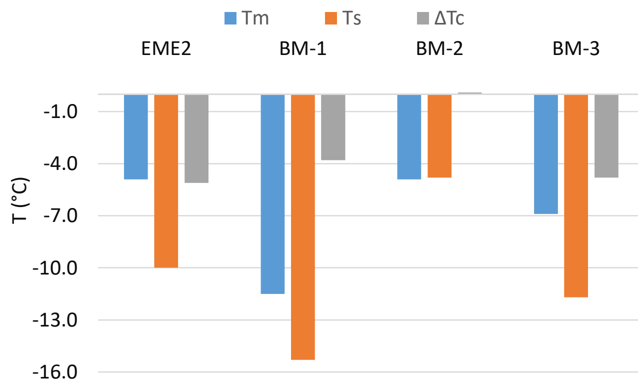

Figure 15. Low temperature passing temperatures for m, S, and ΔTc from 4mm DSR for the surface of the field sections sampled at 5 months after construction.

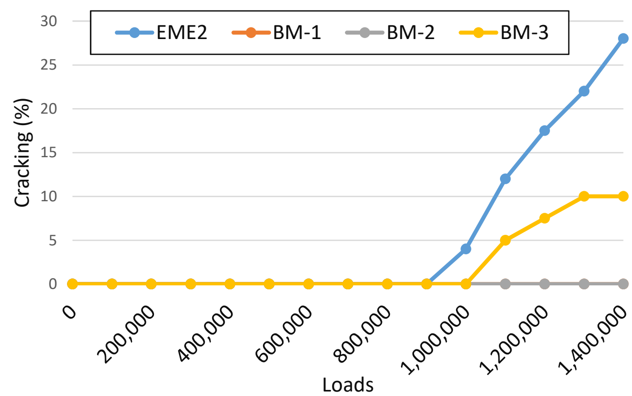

Figure 16. Extent of cracking in % on the 4 sections. This figure is copied from the literature [15].

4. CONCLUSIONS

Laboratory blending and measuring the rheology, IR, and SAR-AD fractions of bitumen blends were shown to be practical tools for evaluating both the effectiveness and mechanism of action of rejuvenators. These tests can also be performed on small quantities of field samples collected using a micro-sampling hammer drill device. Testing of the micro-sampled material from the test sections showed that the bitumen rheological performance parameter of ΔTc correlated with extent of load-related cracking in the pavement.

Additional conclusions can be drawn by applying these tools to the bio-material and RAP blends from the BioRePavation project. If proper lab aging (RTFO/PAV) and rheology (DSR) is performed upfront, the bio-based rejuvenators and materials from this study can be confidently used in recycled paving projects using high amounts of RAP. They can improve the rheological properties compared to the virgin bitumen-RAP blend both before and after aging. While the mechanism of action widely varies based on the biomaterial used, there is nothing from the chemical results that would exclude the use of the 3 products tested in this study as they all improved the rheology of the RAP blends before and after extended aging, and field extraction. IR results indicate that BM-1 does not appear to alter the oxidation of bitumens while BM-3 and BM-2 appear to change the oxidation rate or mechanism.

A follow-up survey of the BioRepavation test sections at IFSTTAR as a function of time on a longer period is recommended. It would provide a unique opportunity to confirm the result trends in terms of product performance as well as rheological and chemical performance parameters.

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