

Understanding improvements to low temperature rheology of stiff binders modified with epoxidized plant derived oil materials through analytical chemistry

Joseph H. Podolsky¹, Mohamed Elkashef¹, Nacu Hernandez², Austin Hohmann², R. Christopher Williams¹, Eric W. Cochran²

(¹ Iowa State University, Civil, Construction and Environmental Engineering Department, 394 Town Engineering, Ames, Iowa, 50011, USA, podolsky@iastate.edu, mkashef@iastate.edu, rwilliam@iastate.edu)

(² Iowa State University, Chemical, and Biological Engineering Department, 2114 Sweeney Hall, Ames, Iowa, 50011, USA, nacu23@iastate.edu, ahohmann@iastate.edu, ecochran@iastate.edu)

ABSTRACT

Through recent work at Iowa State University, great potential was seen from epoxidized plant oil materials, epoxidized benzyl soyate (EBS) and epoxidized methyl soyate (EMS) as fluxes/rejuvenators. This work found that improvement in low temperature performance was greater than improvement in high temperature performance for Solvent De-Asphalting (SDA) and Residuum Oil Super critical Extraction (ROSE) unit bottoms when using either EBS or EMS as compared to results from modified Vacuum Distillation (VD) tower bottoms with EBS and EMS. Based on these results analytical chemistry was done using Fourier Transformed Infrared with Attenuated total reflection (FTIR-ATR) and Ion Mobility Mass Spectrometry equipment. Chemical analysis showed that there is indeed something in the SDA and ROSE binders that is interacting with both EBS and EMS, and making them perform aggressively. The region of interest for future study was identified from ion mobility mass spectrometry to be between m/z 250 and m/z 400 for the SDA and ROSE binders.

Keywords: stiff asphalt binders; epoxidized plant derived oil materials; asphalt binder chemistry; FTIR-ATR; ASAP IM-MS

1. INTRODUCTION

Asphalt binders are steadily becoming stiffer due to the ever-increasing demand for more expensive lighter fraction products and the decreasing supply of lighter crudes. Stiff asphalt binders are residuals produced from upgraded refineries such as Vacuum Distillation (VD), Solvent De-Asphalting (SDA), and Residuum Oil Super critical Extraction (ROSE) units. These units are used to increase the output of more valuable heavy oil components. In a VD unit, heavy gas oils are produced by the vaporization of atmospheric distillation unit residuals in a column under vacuum conditions so the oil will not crack [1, 2]. Further processing of VD unit residuals can take place with use of SDA and ROSE units. Both SDA and ROSE units function by separating fractions based on molecular type using solvents to extract asphalt and catalytic cracking feedstock. Source materials commonly used are heavy vacuum gas oil, atmospheric residue, and vacuum residue. Products are more valuable heavy De-Asphalted Oil (DAO), which are used to make heavy lubricants [3-6]. Straight asphalt binders produced from these refinery units have very limited use as paving binders in hot mix asphalt due to constraints from climatic conditions to meet performance expectations.

1 Materials that are commonly used to soften/repair stiff asphalt binders are known as
 2 fluxes. These materials repair a stiff asphalt binder’s rheological properties to a point at which
 3 the unusable binder can now be used in paving roadways. Another word that is used quite often
 4 in place of flux is rejuvenator. Rejuvenators are used to restore an aged asphalt binder within
 5 Reclaimed Asphalt Pavement (RAP) to a virgin un-aged state [7-9]. Through recent work at
 6 Iowa State University it was found that epoxidized plant oil materials improve low temperature
 7 rheology (performance grade – PG) of SDA and ROSE unit bottoms more than they reduce the
 8 high temperature PG (e.g. not a linear shift in the continuous grade). This was not the case for
 9 the VD tower bottoms, where the high temperature PG is reduced at an almost 2:1 ratio
 10 compared to improvement in the low temperature PG. To better understand what is causing
 11 higher rheological improvements at low temperature for the SDA and ROSE unit bottoms as
 12 compared to the lower rheological improvements at low temperature for the VD tower bottoms
 13 an investigation was initiated focused in analytical chemistry. For this work three control binders
 14 as well as modified control binders with dosages ranging from 8% to 15% of epoxidized plant oil
 15 materials were produced for testing. To better understand why there was higher low temperature
 16 improvement, such techniques as fourier transform infrared – attenuated total reflectance (FTIR-
 17 ATR) spectroscopy, and ion mobility mass spectrometry (IM-MS) through atmospheric solids
 18 analysis probe (ASAP) ionization were utilized.

19 **2. MATERIALS & EXPERIMENTAL METHODS**

20 **2.1 Base Binders, Epoxidized Plant Oil Materials & PGs**

21 Non-food soybean oil derived specialty chemicals such as epoxidized benzyl soyate
 22 (EBS) and epoxidized methyl soyate (EMS), produced by the benzylolysis and methanolysis of
 23 epoxidized soybean oil, and were used as modifiers of the VD, SDA and ROSE binders. EBS
 24 and EMS were blended with the control binders (VD, SDA, and ROSE binders) at $155 \pm 3^\circ\text{C}$ for
 25 one hour at 2,000 rpm with a Silverson shear mill in combination with a digitally controlled heat
 26 mantle. Six binders were produced this way, and then graded according to Superpave standards
 27 as shown in Table 1.

28 **TABLE 1 PGs of Control & Modified Binders**

Group Code	Base Asphalt	Dosage/Material	Critical High Temperature	Critical High Temperature	Critical Low Temperature	PG
			(Unaged) (°C)	(RTFO) (°C)	(PAV) (°C)	
C1	VD	None	89	89.3	-11	88-10
C2	VD	8% EBS	70	70	-24	70-22
C3	VD	8% EMS	67.2	69.6	-23.7	64-22
C4	SDA	None	103.4	106.9	27.2	100+32
C5	SDA	12% EBS	71.8	77.6	-13.8	70-10
C6	SDA	12% EMS	68.9	76.4	-14.8	64-10
C7	ROSE	None	104.7	103.8	28.8	100+32
C8	ROSE	15% EBS	67.5	69.7	-18.6	64-16
C9	ROSE	15% EMS	58.6	62	-21.3	58-16

29

2.2 Experimental Methods

2.2.1 FTIR-ATR

Fourier Transformed Infrared (FTIR) is an analytical chemical characterization technique used to obtain an infrared spectrum of asphalt binders through absorption or emission. Attenuated total reflection (ATR) is a sampling technique used in combination with the FTIR, and allows solid and liquid specimens be tested without initial preparation [10]. In the ATR a beam of light passes through a crystal and reflects off the internal surface of a non-absorbing material holding the specimen. It is this reflection which forms the evanescent wave which produces information such as an infrared spectrum [11]. The specimen is directly placed on the reflecting surface as shown in Figure 1 (b), and absorbs the attenuated light, which penetrates a depth of only a few micrometers. The use of FTIR-ATR increases the sensitivity of measurement because multiple reflections lead to increased absorbance. In past work, the use of FTIR-ATR has been employed to monitor the diffusion rate of the rejuvenator into the asphalt binder [12]. For FTIR-ATR testing a Bruker Tensor 37, Figure 1 (a), was used with a boat shaped ATR device (ATR crystal is germanium) as shown in Figure 1 (b). The following settings were used for testing: resolution – 2cm^{-1} , sample scan time – 16 scans, saved data from 4000 to 855 cm^{-1} , scanner – 5kHz , aperture setting – 6mm , laser wavelength – 15800.36 , and phase resolution – 32 . To prepare specimens for testing three steps were undertaken: 1) Specimens were prepared by pouring heated binder into 8mm dynamic shear rheometer molds, 2) 8mm specimens placed into the boat and mixed with methylene chloride (methylene chloride was used to help dissolve and spread the binder more evenly over the ATR crystal), and 3) the boat was placed in an oven to evaporate methylene chloride at 60°C for 5 minutes. After testing each specimen, cleaning was done with methylene chloride, q-tips and cotton swabs. Due to contamination concerns, the ATR boat device was used to prevent methylene chloride from contaminating the mirrors underneath the crystal.



FIGURE 1 FTIR-ATR (a) FTIR – Bruker Tensor 37, and (b) ATR boat device

2.2.2 ASAP IM-MS

Ion mobility in a spectrometer in which the ions are first separated based on their mobilities, and then separated based on their mass-to-charge ratio. The rotationally averaged collision cross section (CCS) which is a physical property of ions reflecting the shape of the ions can then be measured more accurately, and thus more isomers can be identified. This combination creates a multi-dimensional form of separation. Ion mobility mass spectrometry is mainly used for analyzing complex mixtures based on differing mobilities in an electric field. Ion mobility also enables a much higher peak capacity in mass spectrometry, and thus more compounds can be identified and analyzed. This helps in omics studies where analyzing as many compounds in a single run is required. For the purpose of this work ion mobility coupled with mass spectrometry is being utilized for the analysis of petroleum based products with isomers ranging in size and number from carbon 5 to carbon 100 and 3 to 5929×10^{38} . For ASAP IM-MS

1 testing, a Waters SYNAPT G2-Si High Definition Mass Spectrometer (HDMS) in Figure 2 (a),
2 was used with an ASAP probe as shown in Figure 2 (b). Specimens were prepared as follows: 50
3 mg asphalt binder transferred to a glass vial for accurate weighing; toluene added to prepare
4 stock samples that were 10.0 mg/mL in concentration; an aliquot of stock was diluted with
5 toluene and methanol to form a specimen that was 2 mg/mL in concentration in 90/10 (v/v)
6 toluene/methanol. The experimental parameters are shown below:

- 7 • *Positive Ion ASAP, MS Spectra from $m/z = 50$ to 1200 , Corona Pin Current = $20 \mu A$;*
- 8 • *IMS Wave Velocity = 1200 m/sec, IMS Wave Height = 40 V, Cone Voltage = 40 V; and*
- 9 • *Source = 120 °C, Desolvation Gas Flow = 400 L/hr, and Cone Gas Flow = 75 L/hr.*

10 Before insertion of the ASAP probe with each test specimen, a temperature step ramp from $50^\circ C$
11 to $650^\circ C$ (6 steps, 1st – $50^\circ C$, 2nd – $250^\circ C$, 3rd – $350^\circ C$, 4th – $450^\circ C$, 5th – $550^\circ C$, 6th – $650^\circ C$) was
12 started and lasted for 6 minutes. The probe with each test specimen was inserted at 0.5 minutes
13 during the temperature ramping. For comparison of the results a program called HDMS Compare
14 was used.



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16
17 **FIGURE 2 ASAP IM-MS (a) Waters SYNAPT G2-Si HDMS, and (b) ASAP probe**

18 19 **3. FTIR-ATR RESULTS & ANALYSIS**

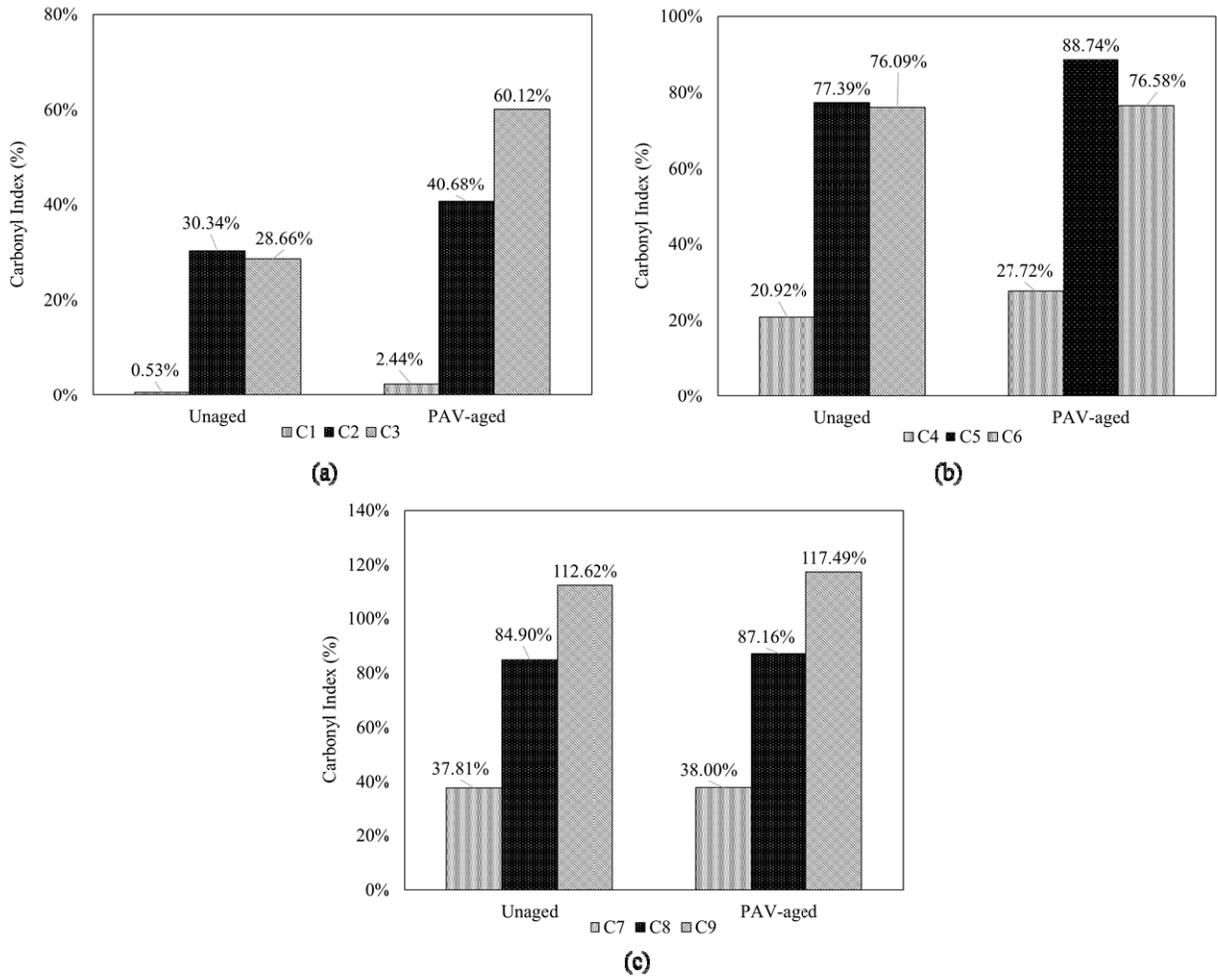
20 The main application of FTIR in asphalt binders is to identify the carbonyl and sulfoxide
21 groups. The rate of increase in these groups serves as an indication of the oxidative aging that
22 takes place with time. The carbonyl peak has shown to correlate better with aging compared to
23 the sulfoxide group which in some cases decompose with aging [13]. The area under the
24 carbonyl peak noted around a wavenumber 1740 cm^{-1} is normalized with respect to the areas of
25 the methyl and ethyl peaks at wavenumbers $\approx 1377 \text{ cm}^{-1}$ and $\approx 1466 \text{ cm}^{-1}$. The carbonyl index is
26 defined as:

$$27 \quad I_{CO} = V_{CO} / V_r \times 100 \quad [1]$$

28 where, I_{CO} : Carbonyl index (%), I_{SO} : V_{CO} : Carbonyl peak area, V_r : Methyl + ethyl peak
29 area. For the purpose of this study, the area of the carbonyl peak was calculated between
30 wavenumbers 1753 cm^{-1} and 1660 cm^{-1} , while the areas of the ethyl and methyl peak areas were
31 calculated as the area under the FTIR spectrum between wavenumbers 1525 cm^{-1} and 1350 cm^{-1} ,
32 as outlined in the French MLPC Method No. 69 [14].

33 The carbonyl indices were calculated for all the studied binders at both the unaged and
34 PAV-aged stages. The results are plotted in Figure 3 (a) through (c) below. The rate of increase
35 of the carbonyl index is similar for both the control and modified binders when using the ROSE
36 binder as shown in Figure 3 (c). In Figure 3 (b) it is shown that the rate of oxidative aging is
37 lower when the SDA binder is modified with EMS than the control SDA binder and the SDA
38 binder modified with EBS. For the control and modified VD binders in Figure 3 (a), both EBS

1 and EMS show lower rates of oxidative aging as compared to the control VD group's rate of
 2 oxidative aging. However, the rates of oxidative aging seen by the modified VD binders with
 3 EBS and EMS are still much higher than the rate of oxidative aging seen for the SDA and ROSE
 4 modified binders with EBS and EMS. These results indicate that EBS and EMS are interacting
 5 with a chemical component or components in all three control binders, but are having a much
 6 greater influence in making the SDA and ROSE binders less susceptible to oxidative aging. This
 7 subject is further discussed in the next section.

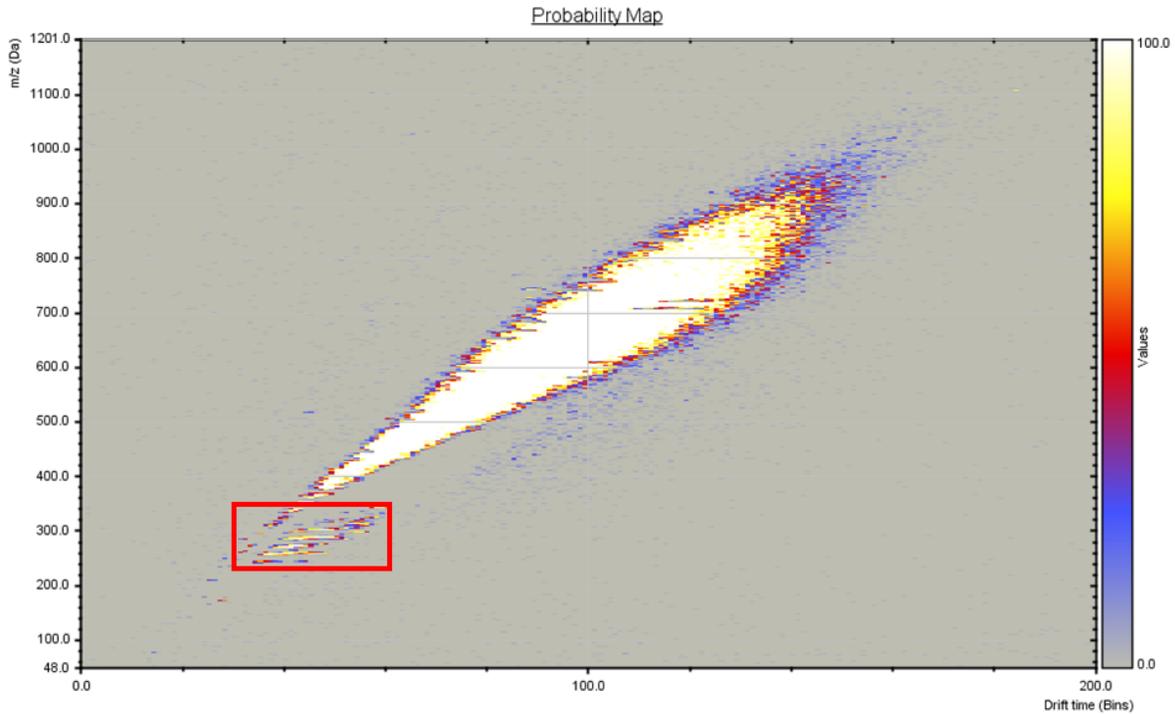


8
 9 **FIGURE 3 Carbonyl index for binders (a) C1, C2, C3, (b) C4, C5, C6, and (c) C7, C8, C9**

10
 11 **4. ASAP IM-MS RESULTS & ANALYSIS**

12 Various comparisons (9 in total) were made for the nine binders (control and modified
 13 binders) using the program HDMS Compare. Each comparison is between two binders. Due to
 14 the fact that there were many visible differences between the control binders and their modified
 15 binders, it was felt that differences and similarities between the control binders themselves
 16 should be examined more thoroughly. For the comparisons of the control binders to one another,
 17 probability maps were used in HDMS Compare. From the probability maps, the majority of the
 18 differences occurred between mass spectrum locations m/z 200 and m/z 500 from 30 to 80 drift
 19 time bins when comparing C1 to C4, and C1 to C7. Of main interest is the identification of
 20 similarities between C4 and C7 that show up as differences between C1 and C4, and C1 and C7.

1 When examining this same region for the comparison between C4 and C7 there are several
2 similarities between C4 and C7 located between drift time bins 30 and 60, and mass spectrum
3 locations m/z 250 and m/z 400 as shown in Figure 4. It is believed the EBS and EMS are more
4 effective at improving the critical low temperature than reducing the critical high temperature for
5 the SDA and ROSE unit binders because of these molecules. Due to the fact that these binders
6 are not commonly produced nor used in asphalt paving, the thought is that by further modifying
7 EBS and EMS through addition of these molecules, more aggressive rejuvenators can be
8 produced for use with RAP and recycled asphalt shingles (RAS). Further analysis is needed to be
9 done in the future on this region of data using a library database for identifications.



10
11 **FIGURE 4 Probability Maps of Differences and Similarities between C4 & C7**

12
13 **5. CONCLUSIONS & FUTURE RECOMMENDATIONS**

14 Based on the chemical analysis it was shown that there is indeed something in the SDA
15 and ROSE binders that is interacting with both EBS and EMS, and making them perform more
16 aggressively. The FTIR-ATR results show that the effect on oxidative aging is not the same
17 between the three binders when modified with EBS and EMS, and that both materials either keep
18 the same level of oxidative aging as the control or decrease the rate of oxidative aging in the
19 SDA and ROSE binders. These results correlate with previous work, where EBS and EMS
20 improved the low temperature more significantly than the high temperature for the SDA and
21 ROSE unit bottoms, whereas for the VD tower bottoms this was not the case. From the ASAP
22 IM-MS work and analysis it was shown that the area of interest for future examination within the
23 base binders, SDA and ROSE, is between m/z 250 and m/z 400. It is believed that the chemical
24 components causing the EBS and EMS to perform more aggressively are within this range of the
25 mass spectrum. It is recommended that further testing take place, both rheological and chemical,
26 especially with the SDA and ROSE unit bottoms controls (C4 and C7) with and without EBS and
27 EMS.

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