Aging Influence on Rheology Properties of Petroleum-Based Asphalt Modified with Biobinder

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Abstract: This paper aims to investigate the viability of using swine waste binder to improve the rheological properties of bituminous asphalt binder. Due to rising bituminous asphalt binder costs, diminishing reserves of crude oil from which asphalt binder is derived, and the gradual paradigm shift toward more environmentally friendly and energy efficient hot-mix asphalt (HMA) mixtures, the asphalt pavement industry is exploring different sustainable alternative binders. Biobinder has the potential to partially or fully replace typical crude-based asphalt. In this paper, biobinder from swine manure is produced by thermochemical liquefaction process at 380°C and 40 MPa (approximately 400 atm) pressure in the absence of oxygen. A Superpave PG 64-22 is then modified with 5% biobinder by total weight of asphalt binder to produce the biobinder. Samples of the base asphalt binder (nonmodified PG 64-22) and samples of asphalt modified with biobinder are characterized by running the Superpave rotational viscosity (RV), dynamic shear rheometer (DSR), and the bending beam rheometer (BBR) tests. Furthermore, Fourier transform infrared (FTIR) spectroscopy investigations were used to validate the chemical bond initiations that caused changes in stiffness and viscosity of the asphalt modified with 5% biobinder from those of base asphalt binder (PG 64-22). The modification resulted in 27% decrease in viscosity of the base binder. The rolling thin film (RTFO)–aged samples of modified binder experienced a 28.9% decrease in average viscosity change when compared with the RTFO-aged samples from the base binder. Additionally, the pressure aging vessel (PAV)–aged samples of modified binder experienced a 62.9% decrease in average viscosity change when compared with the PAV-aged samples of base binder. The rotational viscosity results proved that the addition of biobinder (swine waste asphalt binder) can reduce the viscosity of the asphalt binder. Furthermore, the modified binder had lower complex moduli and phase angles compared with the base binder (based on DSR results). The BBR results indicated that biobinder had the potential to improve the thermal cracking performance of conventional asphalt binders by reducing the creep stiffness and increasing m-value. The BBR results proved that the modification of the PG 64-22 induces a one grade jump on the lower temperature side. The functional groups in typical petroleum-based asphalt binders remained unchanged after the addition of the biobinder to the PG 64-22 binder. Additionally, the FTIR spectra showed that addition of biobinder decreased the stiffness of the PG 64-22 binder through the reduction in molecular carbonyl and sulphoxide bond chains at high temperature. This research investigation provides useful rheological and morphological guidance on the use of swine waste binder as an asphalt binder and mixture modifier. **DOI: 10.1061/(ASCE)MT.1943-5533.0000712.** *© 2014 American Society of Civil Engineers.*

Author keywords: Swine waste binder; Rheological; Bioasphalt; Pyrolysis; Superpave; Rotational viscosity (RV); Dynamic shear rheometer (DSR); Bending beam rheometer (BBR).

Introduction

The dynamics of world resource economics suggest that all industries, including the asphalt pavement industry, should be exploring economically, socially, and environmentally sustainable approaches to development. Rising asphalt binder prices on the world market, diminishing crude oil reserves from which asphalt is derived, and a quest for a more environmentally friendly and energy efficient asphalt binder are key challenges the asphalt pavement industry is facing. One of the most promising ways to address this issue is producing binders from biomass resources. Though, on a limited scale, a number of noteworthy research works are being conducted worldwide on producing biobinders from biological resources such as vegetation and forest waste, yard waste, and sugar cane molasses. In this paper, swine waste manure, a different type of feedstock, is processed into biobinder by a thermochemical process known as liquefaction (Fini et al. 2010). This biobinder is then used as a modifier in typical asphalt binder (PG 64-22); to characterize the effect of this modification on base binder, high-, intermediate-, and low-temperature rheological properties were evaluated in this paper.

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Note. This manuscript was submitted on May 19, 2011; approved on October 9, 2012; published online on October 11, 2012. Discussion period open until July 1, 2014; separate discussions must be submitted for individual papers. This paper is part of the ***Journal of Materials in Civil Engineering***, Vol. 26, No. 2, February 1, 2014. © ASCE, ISSN 0899-1561/2014/2-358-366/$25.00.

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Literature Review

Although research into the development and application of biobinders as a useful sustainable component in asphalt paving is relatively new in the field, a number of research activities are noteworthy in this area. Researchers are beginning to focus on biobinders as a sustainable substitute to crude asphalt and build on earlier developments in the mid-1950s.

Researchers have confirmed that biobinder produced from biomass, specifically swine manure, is a promising candidate to be used as an alternative for asphalt binder (Fini et al. 2011; You et al. 2011). It was found that the addition of biobinder to base binder can improve the base binder's low-temperature properties while improving its workability (Fini et al. 2011). Other alternative asphalt such as asphalt lignin products obtained from bioresources have shown promising industrial applications such as asphalt binders, concrete admixtures, well drilling mud, dust control, vanillin production, and dispersants (Terrel and Rimsritong 1979; Sundstrom and Klei 1982; Sundstrom et al. 1983). Marchessauk et al. (1982) determined that lignin was water insoluble, had average molecular weight of approximately 700, and possessed ultraviolet (UV) and infrared (IR) spectra characteristics similar to those of milled wood lignin. After careful spatula mixing of kraft lignin with conventional asphalt, Terrel and Rimsritong (1979) determined that satisfactory coating, workability, compaction, and fatigue resistance are possible with lignin-asphalt blends containing 30% lignin. Sundstrom et al. (1983) further established that for asphalt binders containing 30% lignin, they could attain maximum stability near 6% total binder content. Research works from another group of researchers show the potential of lignin as a biological polymer in retarding the aging (oxidation) of asphalt pavements (Dizhbite et al. 2004; Bishara et al. 2005; Ouyang et al. 2006; McCready and Williams 2007).

In Australia, bioresources such as lignin and cellulose, sugar and molasses, vinasses, natural tree and gum resins, natural latex rubber and vegetable oils, palm oil waste, coconut waste, peanut oil waste, canola oil waste, and potato, wheat, and rice starches have been developed into a biopolymer alloy adhesive binder (Echopave Australia 2009). Preliminary performance tests indicate, for example, that molasses bioasphalt can potentially resist fatigue, solvent, cracking, rutting, and skidding in asphalt pavements. Efforts are under way between Washington State University (WSU) and a New York–based technology firm to produce bioasphalt from waste cooking oil (Wen et al. 2013). The developed cooking oil–based bioasphalt possesses a faint deep fat fry smell.

In Table 1, a review and comparative analysis of some of the literatures studied on biobinder is provided. Despite some relevant research conducted into using bioresources for bioasphalt, a lot more needs to be done for the asphalt paving industry to fully embrace bioasphalts for use in highway and airport pavement construction. In this paper, bioasphalt is developed from swine manure and its rheological characteristics as an asphalt binder modifier were determined. This further research into bioasphalt development from swine waste will add to the current body of knowledge on the subject in terms of the aging influence on the rheological properties of the swine bioasphalt.

Materials and Experimental Program

Preparation of the Biobinder

The base binder used in this study was a PG 64-22 asphalt binder. The swine-based biobinder was produced through a thermochemical liquefaction process. Past research has shown that the thermochemical process is capable of converting biowaste such as sewage sludge into biooils (Williams and Besler 1992; Zahn et al. (1997); Zhang and Lei 1998; Ocfemia et al. 2006; Appell et al. 1971). Thermochemical liquefaction processing of the swine manure to biooil using a high-pressure batch reactor followed by distillation was conducted based on the approach developed by Fini et al. (2011). A heavy-duty magnetic drive stirrer was installed for the mixing. A type J thermocouple was fitted into the reactor for direct temperature measurements of the reaction media. Furthermore, a

Table 1. Summary of Reviewed Literature on Biooil Use

Researcher(s)	Type of biobinders	Summary of finding(s)
Barth (1962)	Lignin asphalt	• Similar functional group structures to the resin fractions of asphalt binders and mixtures. • Contains significant unsaturated aromatic rings joined by alkyl chains just like traditional asphalt. • Similar adhesive properties to traditional asphalt.
Terrel and Rimsritong (1979)	Lignin asphalt	• Good coating, workability, compaction, and fatigue resistance achieved. • Optimum paving mixture needs more asphalt with lignin-asphalt binders than with asphalt alone.
Dizhbite et al. (2004), Bishara et al. (2005), Ouyang et al. (2006), and McCready and Williams (2007)	Lignin asphalt	• Has antiaging properties in asphalt pavements.
Echopave Australia (2009)	Echopave bioasphalt (biopolymer blend)	• Less soluble in standard laboratory solvents • Better durability and fatigue performance than typical asphalt. • Emissions and mass loss similar to petroleum-based asphalt.
Metwally and Williams (2010)	Oakwood, cornstover, and switch-grass bioasphalt	• Needs heat upgrading before use in asphalt binders and pavements. • Mixing temperature range may be lower than that of petroleum-based binders by approximately 30-40°C. • The rheological properties are improved after addition of modifiers to bioasphalt. • High-temperature performance grade similar to that of traditional asphalt binders. • Low-temperature performance grade varies from typical asphalt binder due to high oxygen content.

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standard pressure gauge was installed on the reactor head. A temperature controller was also used to control the temperature of the reactor (Fini et al. 2011). During the process, swine waste was degraded by heat in the absence of oxygen to provide a complex volatile phase, a carbonaceous char, and the biooil (yielding at 70% conversion efficiency based on dry matter). The biooil was then processed and refined of any physical contaminants to produce biobinder. To achieve this, the biooil was first dissolved in either acetone or acetone and toluene mixtures and filtered to separate biochar (biochar is approximately 10% of biooil by weight). Then it was distilled under vacuum conditions. During the distillation, the biooil's viscosity was measured every 10 min to obtain biobinder with viscosity of 0.5 Pa.s. (500 cP) at 135°C.

The biobinder was then mixed with the PG 64-22 asphalt binder at the rate of 5% by total weight using a mechanical shear device. The choice of using 5% swine waste biobinder is guided by earlier research by Fini et al. on the proposed use of swine waste biobinder (Fini et al. 2010). From their work, it is hypothesized that adding 5% of biobinder to petroleum-based asphalt binders could potentially enhance the performance of petroleum-based asphalt binders. In other research, Williams et al. (2009) worked with 2, 5, and 10% of biobinder from forest biomass sources. Using the mechanical shear equipment ensured a homogenous mixture of the control binder (PG 64-22) and the 5% biobinder.

Laboratory Experimental Program

The experimental program was designed to cover a comprehensive range of Superpave binder specification tests to determine the low-, intermediate-, and high-temperature rheological properties and performance of both the control PG 64-22 binder and the modified binder. The relevant samples of unmodified asphalt (PG 64-22) and samples of asphalt modified with 5% biobinder prepared and tested are unaged, rolling thin film (RTFO)–aged and pressure aging vessel (PAV)–aged. Fig. 1 shows the complete flow chart of the Superpave experimental test program for the research. It was shown that biobinder had a high level of nitrogen relative to typical asphalt binder but a very similar ratio of carbon to hydrogen content. The carbon-13 nuclear magnetic resonance (NMR) spectrum indicated that the biobinder is comprised mainly of carbons in straight chain aliphatic compounds. The 1H NMR spectrum showed presence of olefins and alcohols; this was also found by gas chromatography–mass spectrometry. The specific gravity of biobinder (1.01) was found to be close to that of asphalt binder (1.03). It was also shown that both materials have similar chemical composition and water and ash content. In terms of elemental comparisons, the PG 64-22 has approximately 81.6% carbon by percent weight of total elements, while the biobinder has approximately 72.6%. For hydrogen, the PG 64-22 has 10.8%, while the biobinder has 9.8%. Furthermore, the nitrogen and oxygen contents in the PG 64-22 were 0.8 and 0.9%, respectively, while the biobinder had 4.5 and 13.2% of nitrogen and oxygen, respectively.

The second aspect of this research involved the use of the Fourier transform IR (FTIR) spectroscopy characterization techniques to study the changes in chemical composition before and after the addition of biobinder. FTIR has proven useful for investigating the quantitative and qualitative analysis of functional groups present in bioasphalts (Wu et al. 2009a, b; Ouyang et al. 2006; Wei et al. 2010). With FTIR spectroscopy, the covalent bonds in molecules and the vibrations of its lattice crystals are measured. During the use of the FTIR, different types of bonds absorb light differently with respect to the infrared intensity and absorption behavior. This allows for the detection of the chemical functionalities within the asphalt molecules. According to research by Lamontagne et al. (2001), the change of chemical structure of bitumen could be obtained by the calculation of functional and structural indexes of some groups from FTIR spectra.

Rotational Viscosity Characterization

Brookfield rotational viscosity (RV) equipment was used following the ASTM 4402 (ASTM 2011) and AASHTO T316 (AASHTO 2010) standard specification procedure. The Brookfield viscometer determines the flow characteristics of the unmodified and modified PG 64-22 binder by measuring the torque required to maintain a constant rotational speed of a cylindrical spindle submerged in the sample at the test temperature of interest. The RV test was conducted at temperatures 120°C, 135°C, 150°C, 165°C, and 180°C to establish the trend of viscosity values over a wide range of temperatures.

Dynamic Shear Characterization

A high-resolution Bohlin CVO 120 dynamic shear rheometer (DSR) equipment was adopted in investigating the rheological viscoelastic properties of the samples according to the Superpave

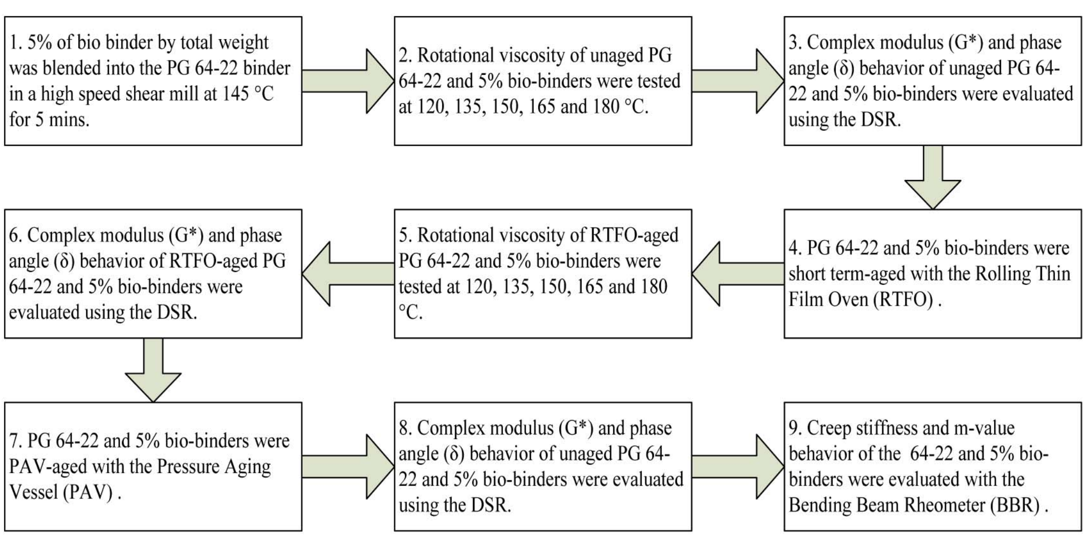

Fig. 1. Flow chart for the experimental program of the research tasks

binder specification ASTM 7552 (ASTM 2010) or AASHTO T315 (AASHTO 2010). The DSR was used to investigate both the viscous and elastic behavior by measuring the complex shear modulus property, denoted as $G*$, and the phase angle, denoted as δ of the samples. The DSR $G*$ is described as the measure of the total resistance to deformation after the exposure to the repeated pulses of shear stress. On the other hand, the DSR δ quantifies the amount of recoverable and nonrecoverable deformation. The DSR sweep test was run under strain-controlled modes at frequencies of 0.01, 0.1, 1, 5, 10, and 25 Hz and temperatures of 13°C, 21°C, 39°C, 52°C, and 70°C.

Short- and Long-Term Aging Characterization

Both short-term and long-term aging performance behavior was estimated during the experimental program. To simulate the short-term aging (hardening or oxidation) characteristics of the biomodified PG 64-22 binder, the RTFO equipment was used, according to the ASTM 2872 (ASTM 2010) and AASHTO T240 (AASHTO 2009). RTFO-aged samples were used for the (1) rotational viscosity test, (2) dynamic shear rheometer test, and (3) pressure aging test. Following the RTFO aging was the PAV aging procedure, performed following the ASTM D6521 (ASTM 2010) or AASHTO PP1 (AASHTO 2010) specification standards. The PAV simulated the in-service behavior of the biomodified binder compared with the control PG 64-22 binder after which the rotational viscosity, DSR, and bending beam rheometer (BBR) were used for further performance testing.

BBR Characterization

In order to better understand the biomodified binder properties when used at low pavement temperatures, the BBR was used to quantify the level of deflection or creep under a 980-mN seating load automatically applied for a total of 240 s. The BBR test was conducted according to *ASTM* D6648 (ASTM 2010) and *AASHTO* T313 (AASHTO 2008) standard test specifications. The performance parameters of interest are the creep stiffness, $S(t)$, and the m-value. The creep stiffness is the stiffness value at 60 s after the continuous application of the 980-mN constant load for 240 s while the m-value is the slope of the log stiffness versus log time curve at any time, t.

FTIR Characterization

In order to determine the variation in the chemical structure of binder before and after the addition of biobinder, the FTIR setup was used. This involved studying the functional and structural indexes of the PG 64-22 FTIR spectra and comparing it with that of the asphalt modified with 5% biobinder. Of special interest are the carbonyl index ($I_{c=o}$) and the suplhoxide index ($I_{s=o}$) based on the research developments of Lamontagne et al. (2001) the application of FTIR technique for investigating the aging behavior of asphalts have also been studied by Lamontagnea et al. (2001). They proved that how chemical functional groups change in absorption rates depicts the evolution of the asphalt chemical structure. From a typical FTIR spectrum on an asphalt binder, Lamontagne proposed a quantitative analysis of the carbonyl and sulphoxide indexes as follows:

$$I_{c=0} = \frac{\text{Area of the carbonyl band around } 1{,}700 \text{ cm}^{-1}}{\text{Area of the spectral bands between 2,000 and 600 cm}^{-1}} \quad (1)$$

$$I_{s=0} = \frac{\text{Area of the sulphoxide band around } 1{,}030 \text{ cm}^{-1}}{\text{Area of the spectral bands between 2,000 and 600 cm}^{-1}} \quad (2)$$

The FTIR spectroscopy was conducted using a Jasco FT-IR-4200 spectrometer, with 32 numbers of scan and the resolution of 4 cm^{-1}. To prepare the control and modified asphalt samples for the FTIR experiment, the PG 64-22 samples and the samples of asphalt modified with biobinder were heated to 120°C until liquid enough to be poured. With the aid of a brush, the liquefied asphalt binders were then painted onto the surface of a silicon slide to create a uniform asphalt coating of 0.5-mm approximate thickness. The FTIR tests were conducted on unaged, RTFO-aged, and PAV-aged samples.

Discussion and Analysis of Results

Rotational Viscosity Behavior

The rotational viscosity plots for unaged and RTFO-aged binders for both the control asphalt (PG 64-22) and asphalt modified with biobinder are shown in Fig. 2. Furthermore, Table 2 shows the average viscosity values and the average percent differences between the tested samples. Under all tested conditions, the samples passed the Superpave maximum viscosity specification value of 3 Pa · s (3,000 cP) at 135°C. The general trend for all cases is as expected; the unaged and RTFO-aged samples of both control and modified asphalt have low viscosities at higher temperatures and high viscosities at lower temperatures. However, unaged modified samples show 27.6% decrease in viscosity compared with unmodified asphalt. In the case of RTFO-aged samples, the modified samples showed 28.9% decrease in viscosity compared to control samples. Further rotational viscosity difference analysis is indicated in Table 2. Generally, the rotational viscosity results proved that the addition of swine waste asphalt binder can reduce the viscosity of traditional asphalt binders.

Dynamic Shear Behavior

The DSR tests were used to characterize the Superpave PG grade of the asphalt modified with biobinder and the frequency sweep behavior of both the control and modified samples.

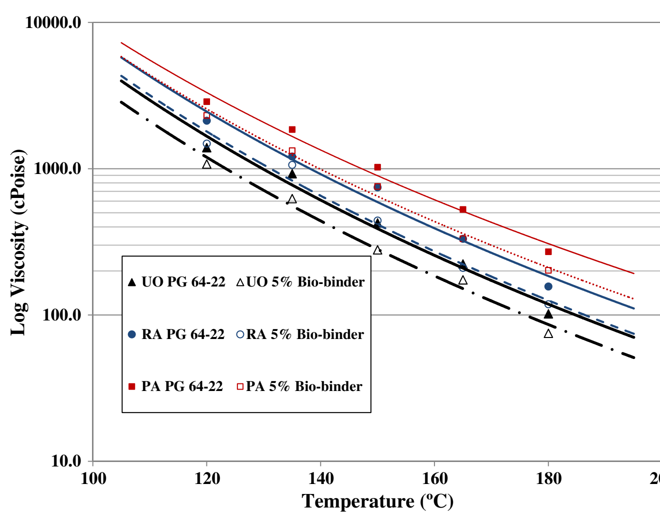

Fig. 2. Rotational viscosity plots for unaged and RTFO-aged binder samples

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Table 2. Rotational Viscosity Differences

Temperature (°C)	UO PG 64-22 Lot 1	RA PG 64-22 Lot 2	PA PG 64-22 Lot 3	UO 5% BMB Lot 4	RA 5% BMB Lot 5	PA 64-22 Lot 6
120	1,392.2	2,128.9	1,213.7	1,075.8	1,484.7	2,313.1
135	924.3	1,211.0	756.8	624.3	1,061.7	1,328.5
150	425.8	746.0	440.6	278.8	442.2	756.2
165	223.3	331.7	240.0	173.9	210.0	332.5
180	101.8	156.7	146.2	75.0	118.5	202.2
			% change			
Temperature (°C)	Lot 1 versus Lot 4	Lot 2 versus Lot 5	Lot 3 versus Lot 6	Lot 4 versus Lot 5	Lot 4 versus Lot 6	Lot 5 versus Lot 6
120	22.7	30.3	90.6	38.0	115.0	35.8
135	32.5	12.3	75.5	70.0	112.8	20.1
150	34.5	40.7	71.6	58.6	171.2	41.5
165	22.1	36.7	38.5	20.7	91.2	36.8
180	26.4	24.4	38.3	58.0	169.6	41.4
Average	27.6	28.9	62.9	49.1	131.9	35.1

Note: BMB = Biomodified binder; PA = PAV aged; PG = Performance grade; RA = RTFO aged; and UO = unaged original.

Table 3. Rutting Parameter Evaluation on PG Grade for 5% Biobinder

Test temperature (°C)	Phase angle (δ) average	$G*/\sin\delta$ (kPa) average	Pass/fail specification average
25	66.6	1.9	Pass
19	60.6	3.9	Pass
16	55.2	5.6	Pass
13	52.5	11.4	Pass
64	87.3	2.1	Pass
70	99.2	2.9	Pass

Performance Temperature Grading

In Table 3, the PG change results of the DSR are provided. It is evident that the addition of the 5% biobinder caused the PG 64-22 binder to pass the PG 70°C rutting specification for the high-temperature impact. This suggests that with the addition of 5% biobinder, there is the chance of raising the high-temperature rutting performance of asphalt binders by jumping the grade. In combination with the BBR test results, it is believed that swine waste binder can potentially benefit both the high- and low-temperature susceptibility of typical asphalt binders.

Phase Angle (δ) Behavior

Phase angle (δ) and complex modulus ($G*$) data were obtained from the DSR frequency sweep test. Figs. 3 and 4 show the plots of phase angles against frequency at 13°C and 70°C; from the trend, it is evident that (1) at lower frequencies the phase angles are higher (the more viscous the asphalt binder system), while at higher frequencies the phase angles are lower (more elastic the asphalt binder system); and (2) the addition of biobinder to the control PG 64-22 binder created lower phase angle values.

Complex Modulus ($G*$) Behavior

The DSR frequency sweep test data were developed into master curves (Fig. 5); it can be seen that generally for three cases of unaged, RTFO-aged, and PAV-aged conditions, the addition of the 5% biobinder decreased the complex modulus, $G*$, which was an indication of decreasing stiffness. This decreased stiffness is desirable for ensuring appreciable resistance to low-temperature or thermal cracking. Thus, from the $G*$ master curve, the swine waste bioasphalt can be described as a softener. The softening impact could be attributable to the interactive bonding between the normal asphalt molecular chains and those of the biobinder.

In addition to the master curve developed from the DSR test, the $G*$ was divided by the δ parameter to further understand the effect of biobinder on permanent deformation in an asphalt pavement. This is known as the Superpave rutting parameter. Fig. 6 shows a bar chart of the relative differences between the rutting parameters for the control and modified samples at the unaged, RTFO-aged,

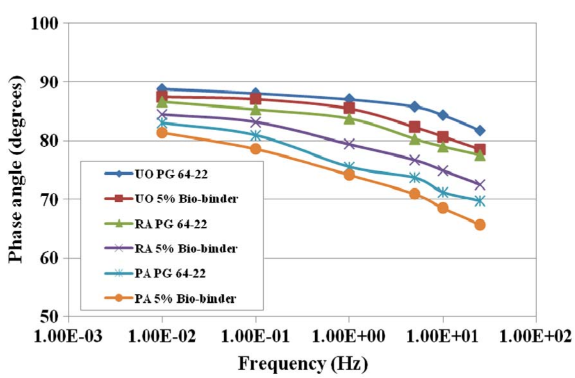

Fig. 3. Plot of phase angle versus frequency at 13°C for original and aged binder samples

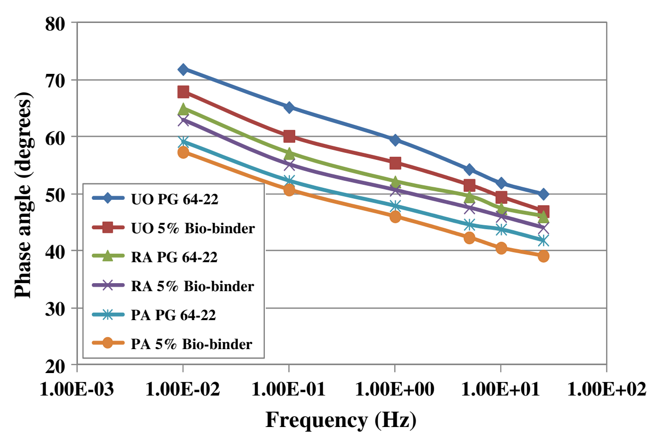

Fig. 4. Plot of phase angle versus frequency at 70°C for original and aged binder samples

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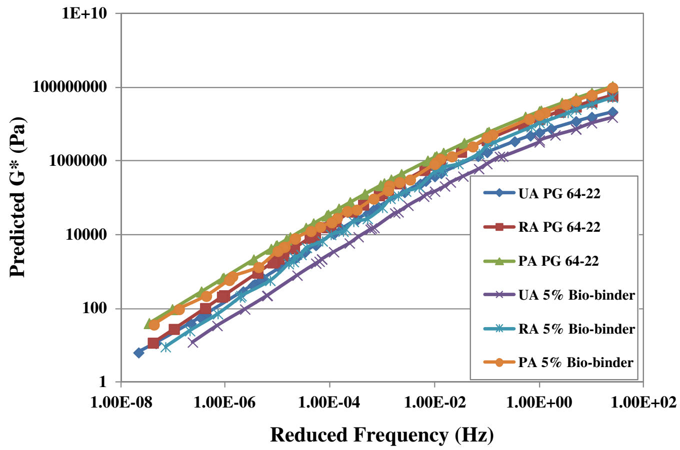

Fig. 5. Master curve plot of the frequency sweep behavior of the tested samples

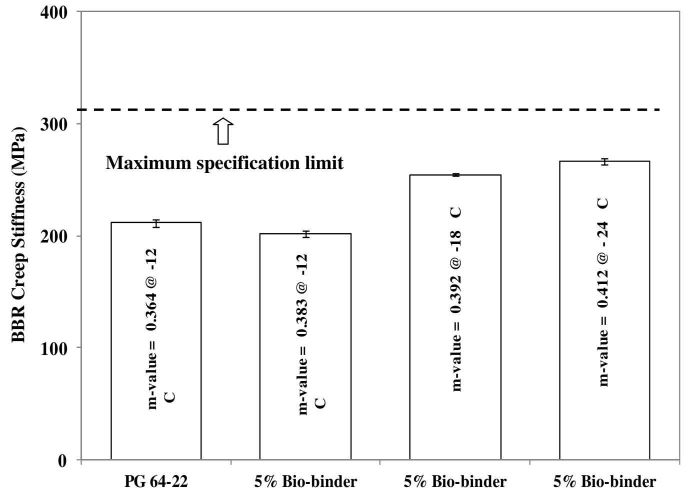

Fig. 7. Bar chart plots on the BBR creep stiffness behavior of samples

and PAV-aged conditions. It can be seen from Fig. 6 that for all cases, the modified samples had higher $G*/\sin\delta$ values. This suggests that the addition of the swine waste binder modifier increased the ability of the binder to resist high-temperature permanent deformation. This is added to the fact that all the samples tested passed the Superpave minimum standard specification of 1.00 kPa.

BBR Creep Stiffness Behavior

The BBR test results on both the control and modified samples that have been RTFO- and subsequently PAV-aged are given in Fig. 7. As expected, the PG 64-22 control binder passed the required Superpave maximum creep stiffness value of 300 MPa and a minimum m-value of 0.300 after 60 s of a constant load application of 980 mN at test temperature of −12°C. After adding 5% biobinder to the PG 64-22 control binder, the modified binder's creep stiffness decreased, while the m-value increased. This could be due to the fact that the polymer molecules of the less viscous swine waste binder create elastic interactions within the asphalt modified with biobinder system. Furthermore, the asphalt modified with biobinder passed the creep stiffness and m-value specifications at −18°C and −24°C. This indicates that the swine waste binder can cause a low-temperature grade improvement for traditional asphalt binders. Decreasing stiffness behavior of both asphalt binder systems and mixtures is beneficial for reducing the buildup of stresses during low-temperature pavement contraction, which will prevent thermal cracking conditions.

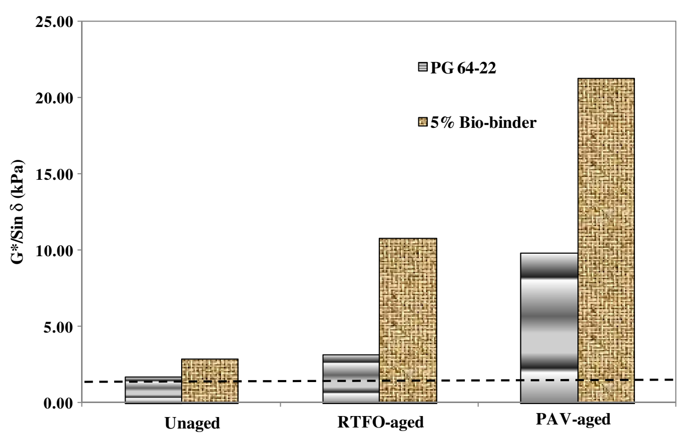

Fig. 6. Bar charts showing the rutting performance trend for control and modified samples

Bonding Index Behavior

The FTIR spectra of the control and modified samples are shown in Fig. 8. The raw spectra for each sample were baseline corrected in order to provide a common baseline for comparison. The corrected spectra were superimposed on one another to make it easier for understanding the variation in peaks between the PG 64-22 and the samples from asphalt modified with biobinder. The functional groups between the 600 and 2,000 cm^{-1} were identified based on past literature on the determination of functional groups in asphalt binders (Karlsson and Isacsson 2003). Between the control and modified asphalt, similar and symmetrical absorption peaks were identified. Table 4 shows the functional groups of the approximate absorption wave numbers in Fig. 8. The results showed that there was no variation in functional groups after adding the swine waste binder to the control petroleum-based PG 64-22. Carbonyl, aromatic, and heteroaromatic rings, sulphoxides, methyl (aliphatic), and methylene (aliphatic) functional groups were identified for the control and modified samples at the unaged, RTFO-, and PAV-aged conditions.

From Fig. 8, the relevant indexes were calculated from Eqs. (1) and (2). The peak area for 1,700 cm^{-1} was calculated between 1,690 and 1,710 cm^{-1}, while the peak area for 1,030 cm^{-1} was

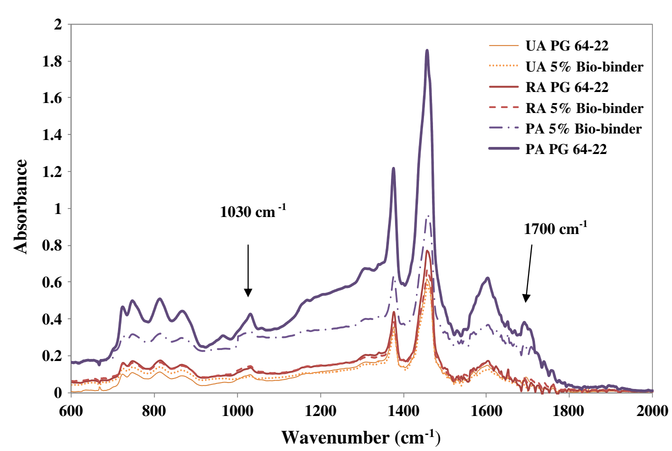

Fig. 8. FTIR spectra of the unaged PG 64-22 and 5% biobinder

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Table 4. Functional Groups Identified for Control and Swine Binder Modified Binders (data from Karlsson and Isacsson 2003)

Functional group	Typical absorption wave number (cm^{-1})
Carbonyl (C = O)	1,740 to 1,690
Sulphoxide (S = O)	1,055 to 1,030
Aromatic and heteroaromatic rings	1,600 (C = C ring stretch) 900 to 600 (C-H bend)
Methyl CH_3	1,450, 1,380 bend
Methylene CH_2	1,465, 1,720 bend

Table 5. Typical Indexes from FTIR Test for Control and 5% Bioasphalt Materials

Sample	Aging index	PG 64-22	5% Bioasphalt
Unaged	Carbonyl	0.0063[a]	0.0092
Unaged	Sulphoxide	0.0034[a]	0.0389
RTFO aged	Carbonyl	0.00468	0.00312
RTFO aged	Sulphoxide	0.0412	0.0282
PAV aged	Carbonyl	0.00588	0.00532
PAV aged	Sulphoxide	0.046	0.0405

[a]Outliers in data.

calculated between 1,985 and 1,048 cm^{-1}. The peak at 1,700 cm^{-1} was due to the stretch absorption of the carbonyl group, whereas the peak around 1,030 cm^{-1} was due to the stretch vibration of sulphoxide group following the past research work by Lamontagne et al. (2001). Table 5 shows the calculated carbonyl and sulphoxide indexes for the control and modified samples. From Table 5, it is evident that the swine waste biobinder recorded lower carbonyl index than the PG 64-22 asphalt binder, excluding the outlier results. Researchers have shown in past investigations that higher oxidation rate (or aging, which leads to increased stiffness behavior) leads to more carbonyl and sulphoxide groups at elevated temperatures (Cortizo et al. 2004). Therefore, the lower the carbonyl and sulphoxide indexes, the lower the potential for aging when petroleum-based asphalt is modified with biobinder from swine manure.

Two conclusions that can be made from the FTIR results are:

- Biobinder produced from swine manure was compatible with the bituminous-based binder (PG64-22). The similarity in terms of the peaks and symmetry of the FTIR results indicate that there was no significant variation in the functions groups even if any chemical reaction or otherwise occurred when the swine waste binder was mixed with the control binder. The biobinder from swine manure possesses similar if not the same molecular structure of the bituminous binder (PG 64-22). The symmetrical nature of the two spectra indicates that biobinder chemically behaves as the PG 64-22 hydrocarbon material. Many researchers have used spectra forms and nature to relate the development of new chemical structures when two polymers are intermixed. For example, after a PG 76-22 asphalt binder was modified with styrene-butadiene-styrene (SBS), new absorption peaks developed around wave number 968 cm^{-1}, information that was absent from the original PG 64-22 binder spectra (Wu et al. 2009a, b). The 968 cm^{-1} peak was obviously a representation of the stretch vibration of chain segments of the SBS in the SBS-modified PG76-22 binder. In addition, the FTIR results showed that the mechanical shear mixing at the elevated temperature facilitated mixing and resulted in the homogenous mixture. Further work will, however, need to be conducted in terms of chemical enthalpy reaction changes to establish the extent of the reaction and compatibility between swine waste and petroleum-based asphalts.
- Except for the outlier data sets that have been indicated in Table 5, it is evident that generally the carbonyl and sulphoxide bonding indexes were lower in all modified cases (unaged, RTFO-aged, and PAV-aged conditions) compared with the control PG 64-22. This trend supports the rotational viscosity and DSR $G*$ master curve trends, which proved that swine waste binder has the potential of reducing the viscosity, stiffness, and aging without compromising on the rutting performance. Typically, increase or decrease in the carbonyl and sulphoxide indexes correspond to increase or decrease in aging rate (Cortizo et al. 2004). Cortizo et al. have shown that the carbonyl and sulphoxide intensities are directly related to the severity of aging.

Potential Drawbacks for Swine Asphalt Use

Based on this research, the authors believe that asphalt from swine manure has potential for use alongside petroleum-based asphalt, although conservatively from the onset. Certain drawbacks or bottlenecks that need to be resolved or addressed for swine waste asphalt to have a smooth transition into the asphalt and hot-mix asphalt (HMA) industries include:

- Thermochemical conversion energy savings: It will be interesting to explore how the biogas and char resources produced alongside the swine waste asphalt during the thermochemical conversion process can be looped back into the reactor converter unit to generate sufficient electrical energy if large-scale swine waste asphalt is to be considered. This will greatly enhance the energy sustainability aspects of the whole process.
- The authors believe that the variability in swine feed across the country will affect the physiochemical properties of the final swine asphalt product. However, controlling pigs' diet is practical in large-scale production because most of the hog production facilities in the United States are confined facilities in which control of pigs' diet is commonly practiced (Ocfemia 2005). Although the study of the effect of pigs' characteristics and diet on the oil properties and efficiency is not within the scope of this paper, it is suggested that researchers advance the thermochemical process in order to produce swine asphalt that is highly independent of the variability in the swine feed types and chemical content.
- Although considerable amount of odor-bearing compounds in biooil are separated during the distillation, that biobinder does not have a noticeable odor at room temperature. The swine asphalt produced has a mild unpleasant smell when is heated. This can be overcome by further advancing the refining process and the thermochemical reaction, especially employing the use of catalysts that will neutralize the unpleasant smell.

Summary and Conclusions

The research investigation involved the preparation and characterization of a Superpave PG 64-22 asphalt binder modified with 5% biobinder produced from swine manure by weight of base binder. The hybrid blend of the 95% PG 64-22 binder and 5% swine binder was known as asphalt modified with biobinder. The biobinder from swine manure was prepared from a thermochemical liquefaction process at a temperature of 380°C and pressure of 10.3 MPa. With the aid of a high-speed mechanical shear mixer, biobinder was blended into the PG 64-22 binder to produce the hybrid asphalt binder. In order to investigate and understand the rheological performance of produced hybrid binder, a number of characterization tests were conducted. The rotational viscosity, dynamic shear rheometer, and bending beam rheometer tests were used for the

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rheological performance study, while the FTIR spectroscopy was used to study the chemical bond evolution of the asphalt modified with biobinder. All analyses were conducted in comparison with the control PG 64-22.

Based on the analysis of the Superpave characterization tests, the following summary of findings can be stated:

- The biobinder forms a homogenous polymeric mix with traditional asphalt binders;
- Addition of biobinder from swine manure decreased the viscosity of the base binder;
- Addition of the biobinder to the control binder creates lower phase angle (δ) values and thus more elastic biomodified binders systems;
- Complex modulus ($G*$) properties of the biomodified binder are decreased compared with the control PG 64-22 binder;
- At higher temperatures, the biomodified binder showed improved high-temperature rutting resistance performance;
- The biomodified binder can improve the low-temperature cracking properties of asphalt binders and mixtures; and
- The chemical functional groups of the PG 64-22 binder remained unchanged even with the addition of the swine waste asphalt.

The FTIR spectra proved the swine biobinder decreased the stiffness of the PG 64-22 binder through the reduction in molecular carbonyl and sulphoxide aging indexes investigations.

Future Work

A number of future research tasks are being considered based on the outcome of this particular paper. Prominent among them are:

- Determine optimum percentage of biobinder to create hybrid asphalt binder with enhanced rheological properties;
- Investigate the nanoscale compositional, phase images, and adhesive properties of the asphalt modified with biobinder to better understand the interactions between traditional asphalt binder and biobinder;
- Study the molecular-level reactions between biobinder and asphalt binder relating it to asphalt binder's aging and moisture susceptibility;
- Undertake asphalt mixture tests to build upon the findings of this binder level characterization;
- Conduct FTIR characterization on RTFO- and PAV-aged samples of asphalt modified with biobinder to further correlate the effect of the chemical bond formations on the different aged materials;
- Change thermochemical conversation variables and evaluate biobinder's viscoelastic properties for application in the paving industry; and
- Collect and process different swine manure (from different sources) into biobinder and evaluate biobinder properties in relation to the source of the swine diet and type.

Acknowledgments

This project was sponsored by National Science Foundation (Grants #1150695 and 0955001) and the Michigan Department of Transportation (MDOT). Feedstock evaluation and conversion as well as biobinder production and asphalt modification were conducted at North Carolina A&T State University and the rheology and morphology characterization were completed at Michigan Technological University. Extreme gratitude goes to Shu Wei Goh, James Vivian, Baron Colbert, and Yu Liu for their contributions toward the completion of the laboratory test program.

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