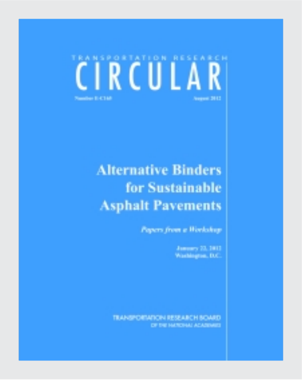


Alternative Binders for Sustainable Asphalt Pavement

DETAILS

0 pages | 8.5 x 11 | PAPERBACK
ISBN 978-0-309-43490-4 | DOI 10.17226/22725

AUTHORS

Characteristics of Asphalt Materials Committee; Characteristics of Nonasphalt Components of Asphalt Paving Mixtures Committee

TRANSPORTATION RESEARCH

CIRCULAR

Number E-C165

August 2012

Alternative Binders for Sustainable Asphalt Pavements

Papers from a Workshop

January 22, 2012
Washington, D.C.

TRANSPORTATION RESEARCH BOARD
OF THE NATIONAL ACADEMIES

TRANSPORTATION RESEARCH BOARD
2012 EXECUTIVE COMMITTEE OFFICERS

Chair: Sandra Rosenbloom, Professor of Planning, University of Arizona, Tucson
Vice Chair: Deborah H. Butler, Executive Vice President, Planning, and CIO, Norfolk Southern Corporation, Norfolk, Virginia
Division Chair for NRC Oversight: C. Michael Walton, Ernest H. Cockrell Centennial Chair in Engineering, University of Texas, Austin
Executive Director: Robert E. Skinner, Jr., Transportation Research Board

TRANSPORTATION RESEARCH BOARD
2012–2013 TECHNICAL ACTIVITIES COUNCIL

Chair: Katherine F. Turnbull, Executive Associate Director, Texas Transportation Institute, Texas A&M University, College Station
Technical Activities Director: Mark R. Norman, Transportation Research Board

Paul Carlson, Research Engineer, Texas Transportation Institute, Texas A&M University, College Station, *Operations and Maintenance Group Chair*
Thomas J. Kazmierowski, Manager, Materials Engineering and Research Office, Ontario Ministry of Transportation, Toronto, Canada, *Design and Construction Group Chair*
Ronald R. Knipling, Principal, safetyforthelonghaul.com, Arlington, Virginia, *System Users Group Chair*
Mark S. Kross, Consultant, Jefferson City, Missouri, *Planning and Environment Group Chair*
Peter B. Mandle, Director, LeighFisher, Inc., Burlingame, California, *Aviation Group Chair*
Harold R. (Skip) Paul, Director, Louisiana Transportation Research Center, Louisiana Department of Transportation and Development, Baton Rouge, *State DOT Representative*
Anthony D. Perl, Professor of Political Science and Urban Studies and Director, Urban Studies Program, Simon Fraser University, Vancouver, British Columbia, Canada, *Rail Group Chair*
Steven Silkunas, Director of Business Development, Southeastern Pennsylvania Transportation Authority, Philadelphia, Pennsylvania, *Public Transportation Group Chair*
Peter F. Swan, Associate Professor of Logistics and Operations Management, Pennsylvania State, Harrisburg, Middletown, Pennsylvania, *Freight Systems Group Chair*
James S. Thiel, General Counsel, Wisconsin Department of Transportation, *Legal Resources Group Chair*
Thomas H. Wakeman, Research Professor, Stevens Institute of Technology, Hoboken, New Jersey, *Marine Group Chair*
Johanna P. Zmud, Director, Transportation, Space, and Technology Program, RAND Corporation, Arlington, Virginia, *Policy and Organization Group Chair*

Transportation Research Circular E-C165

Alternative Binders for Sustainable Asphalt Pavements

Papers from a Workshop

January 22, 2012
Washington, D.C.

Sponsored by
Characteristics of Asphalt Materials Committee
Characteristics of Nonasphalt Components of Asphalt Paving Mixtures Committee
Transportation Research Board

August 2012

Transportation Research Board
500 Fifth Street, NW
Washington, D.C.
www.TRB.org

TRANSPORTATION RESEARCH CIRCULAR E-C165
ISSN 0097-8515

Design and Construction Group
Thomas J. Kazmierowski, *Chair*

Asphalt Materials Section
Robert B. McGennis, *Chair*

Characteristics of Asphalt Materials Committee
Delmar Salomon, *Chair*

Christopher David Abadie
Terry S. Arnold
Gaylon L. Baumgardner
Amit Bhasin
Andrew F. Braham
Silvia Caro
Stephane Charmot
Audrey R. Copeland
John A. D'Angelo
Stacey D. Diefenderfer
Elham H. Fini
Sylvia Harders
P. Michael Harnsberger
Darren G. Hazlett
Richard J. Jr. Holmgreen
Alan D. James
Carl M. Johnson
Gayle N. King
Robert Q. Kluttz
Leni Figueiredo Mathias Leite
Luis G. Loria-Salazar
Rebecca S. McDaniel
Karissa A. Mooney
J. Claine Petersen*
Pedro Romero
Geoffrey Michael Rowe
William Schiebel
Mike J. Southern
Anne Stonex
Kevin Merrill VanFrank
Raul Andres Velasquez
Adam M. Zofka

Characteristics of Nonasphalt Components of Asphalt Paving Mixtures Committee
John Haddock, *Chair*
Kamyar Cyrus Mahboub, *Secretary*

Thomas A. Bennert
Michael S. Buchanan
Arif T. Chowdhury
Matthew R. Corrigan
Jo Sias Daniel
Stacey D. Diefenderfer
Elie Y. Hajj
Baoshan Huang
Shin-Che Huang
Michael H. Huner
Prithvi S. Kandhal*
Karol J. Kowalski
Adrea Nicole Kvasnak
Juanyu Liu
Walaa S. Mogawer
Gale C. Page*
Brian D. Prowell
Bradley J. Putman
James A. Scherocman
Shihui Shen
Claude Villiers
Jarrett Michael Welch

*Emeritus Member

Frederick D. Hejl, *TRB Representative*
Michael DeCarmine, *Program Officer*
Joanice L. Cole, *Senior Program Associate*

Transportation Research Board
500 Fifth Street, NW
Washington, D.C.
www.TRB.org

Glenda J. Beal and Javy Awan, Production Editors; Jennifer Correro, Proofreader and Layout

Contents

Preface

The TRB Committees on Characteristics of Asphalt Materials and Characteristics of Nonasphalt Components of Asphalt Paving Mixtures jointly sponsored a workshop on alternative binders at the 91st Annual Meeting of the Transportation Research Board that was held January 22–26, 2012, in Washington, D.C. The workshop provided a forum for the exchange of recent research and development results among researchers, practitioners, and state department of transportation engineers involved in material characterization and field validation for short- and long-term performance of various sustainable asphalt pavements.

Eight presentations were selected for the workshop. This Circular contains seven technical papers and summaries of presentations made at the workshop. Because some of the studies are ongoing projects, conclusions will be available in the future.

Workshop Introduction

SHIN-CHE HUANG
Western Research Institute

DELMAR SALOMON
Pavement Preservation Systems, LLC

JOHN E. HADDOCK
Purdue University

Increasing energy costs and the strong worldwide demand for petroleum has encouraged the development of alternative binders to modify or replace asphalt binders. The benefits of using alternative binders are that they can help save natural resources and reduce energy consumption, while maintaining, and in some cases improving, pavement performance. Common alternative binders include fossil fuel, biobinder, soybean oil, palm oil, vegetable oil, engine oil residue, grape residues, swine waste, and pyrolized materials, among others. It has been observed that most, if not all, of these alternative binders contain chemical compositions somewhat similar to those of conventional asphalt binders (hydrocarbons, aromatics, saturates, and asphaltenes, etc.). However, tests indicate significant variability in the properties of alternative binders. In addition, the modification mechanism (chemical) for asphalt with alternative binders depends on the base asphalt and is therefore not well understood. It is critical to evaluate the technical feasibility of incorporating alternative binders into conventional asphalt binders for use in pavements. Because of the urgent need for infrastructure rehabilitation and maintenance, the introduction and application of such sustainable and environmentally friendly materials will have significant impact on the national economy as well as energy sustainability.

Use of alternative (or byproduct) materials in asphalt mixtures may be one of the most complicated of the highway uses. It is not a matter of throwing the alternative material into the mixture and coating it with asphalt. The best use must be carefully engineered and designed, including the design of the mixture itself, the effects of the alternative materials on the asphalt binder behavior, and the pavement into which it will be incorporated. It is necessary to know how to test the resulting mixture for specification compliance; in some cases, this knowledge is lacking.

It is for this reason that more research is needed to evaluate the alternative binders for use in asphalt pavements. It is necessary to determine what types of byproduct materials are suitable for use as alternative binders. Any alternative material under consideration must be adequate in chemical composition so that the asphalt material can be compatible using the highest amount of alternative binder possible. Furthermore, alternative binders should have good aging characteristics, adequate moisture resistance, and so on.

Considering the urgent need for infrastructure rehabilitation, the introduction and application of these sustainable and environmentally friendly materials could have significant impacts on the national economy as well as energy sustainability.

Considerations for Use of Alternative Binders in Asphalt Pavements
Material Characteristics

ROBERT KLUTTZ
Kraton Performance Polymers, Inc.

This brief presentation is not intended to be a how-to manual for evaluating alternative binders. Rather, it is intended to highlight some of the issues around substituting other materials for some or all of the asphalt in conventional paving mixes. These issues may be minor but they still deserve consideration in developing an overall research plan for evaluating new materials. Existing binder specifications are, at best, performance related and are based on the fundamental physical and chemical properties of asphalt. Assumptions on how binder properties translate to mixture properties also need to be verified. And ultimately what we care about is pavement performance. Field trials are the true test of a new material.

There are other concerns besides material properties. The asphalt construction infrastructure is built around the handling characteristics of asphalt. If a new material fits the bill for performance but requires substantial capital investment for suppliers and contractors, there will be a large hurdle to practical implementation. There may also be environmental or aesthetic concerns that are different than those of asphalt. And finally, the construction industry is a real-world economic environment. A new material may be truly exciting in performance, but unless it is close to asphalt in overall economics, it will not be able to compete.

ALTERNATIVE BINDERS TO ENHANCE OR REPLACE ASPHALT

Roughly half the papers in this Circular address material that are intended as additives to asphalt, and the other half discuss materials intended as a complete asphalt replacement. Some of the following issues are less concerning for low-concentration additives relative to wholesale change of the binder. Still, they should be taken into consideration.

BINDER PROPERTIES

When evaluating a new material, the first question most researchers ask is, “Does the binder meet current binder specifications?” A very valid response to that question is, “Do we care?” Asphalt is a mixture of moderate molecular weight hydrocarbons, dominantly aliphatic and aromatic, and containing moderate amounts of sulfur, small amounts of oxygen and nitrogen, and other trace elements including transition metals. The physical and chemical characteristics of asphalt are consequences of its chemical composition. Substantial changes in chemical composition may lead to unexpected physical property changes.

Current binder specs are, at best, performance related, so significant chemistry changes may give spurious test behavior. The first question that should be asked is, “From a scientific perspective, should the results of test XYZ for this new material translate to the necessary performance characteristics the same as they do for asphalt?” There are many obvious, tacit assumptions about asphalt to consider:

- It will have predictable aging characteristics.
- It will have predictable rheological properties.
- It will have predictable adhesion properties to aggregates.
- It will have predictable coating behavior in a mix plant.
- It will have predictable flow characteristics during construction.

There are also many other less obvious assumptions:

- It will have predictable leaching characteristics.
- It will have predictable water solubility.
- It will have predictable interactions with fuels, oils, etc.
- It will have predictable environmental characteristics.
- It will have predictable odor.
- It will have predictable mixing with virgin binder as reclaimed asphalt pavement.
- It will have predictable interaction with contiguous mixes.
- It will be available in bulk quantities on demand.

AGING

A basic assumption built into the rolling thin film oven (RTFO) and pressure aging vessel (PAV) procedures is that asphalt will, within a narrow range, exhibit consistent aging behavior and that that aging will have a predictable effect on the performance in mixtures and pavements. An alternative binder may have significantly different aging characteristics. Consequently, RTFO and PAV may not adequately represent plant and field aging.

It is suggested that experimental considerations start with determining an aging index to compare against conventional asphalt. RTFO should be run over a range of times and temperatures to see if normal time–temperature correlations still hold. The same applies for PAV. Run PAV at 60°C for extended times and compare the resulting behavior to the results at standard conditions.

MASTER CURVE SHAPE

Time–temperature superposition in rheological properties is a basic assumption of most asphalt binder tests. An alternative binder may give significantly different time–temperature correlations or it may completely break down. A clear example would be an alternative binder with a well-defined melting point. A binder with a melting point of 73°C may be perfectly suitable for use for heavy traffic in a PG 64 climate, but dynamic shear rheometer (DSR) testing at a grade-bumped 76°C will give irrelevant (melted!) results.

An experimental plan should include development of a full master curve for the material covering the full range from lowest pavement temperature to mixing temperature. Does the master curve fit the cement aggregate mixture or other conventional master curve models? Does the viscous component have similar slope to conventional asphalts? Are there discontinuities that may indicate important thermodynamic transitions? Odd behavior should be viewed as a red flag, particularly for tests that include temperature shifting in its theory.

FRACTURE AND STRENGTH PROPERTIES

While fracture and strength characteristics are critical to pavement performance, they are dominated by the aggregate and gradation and the contribution of alternative binder characteristics is not readily predictable. Other than low-temperature properties, it is probably necessary to default to mixture testing to define the impact of a new material on fracture and strength properties.

HIGH-TEMPERATURE PERFORMANCE

As noted above, alternative binders may have a different shape to the master curve. They may also have different stress tolerance. For several reasons, the nonrecoverable creep compliance, J_{nr}, from the multiple stress creep and recovery (MSCR) test is a better choice than $G^*/\sin\delta$ from oscillatory DSR to characterize high-temperature performance. MSCR is run at the actual expected high pavement temperature and so does not rely on time–temperature superposition. J_{nr} has been shown to correlate well with actual rutting performance for a wider range of materials than $G^*/\sin\delta$. Finally, stress tolerance is already a component of the MSCR test. Even so, it would be prudent to check a range of temperatures and stresses to look for unusual behavior that may impact rutting performance.

Mixture testing is also highly recommended.

LOW-TEMPERATURE PERFORMANCE

Low-temperature tensile and fracture properties of alternative binders may be different than conventional asphalt so bending beam rheometer (BBR) testing alone may not be sufficient. A fracture test such as the direct tension test or the asphalt binder cracking device will provide information on low-temperature fracture properties. If there is a substantial difference in predicted temperatures, there is still potential to use the fracture test results to recalibrate the BBR results to simplify testing in the long term.

One more caveat, these still only characterize single event thermal cracking. They may not adequately address low-temperature fatigue.

FATIGUE PERFORMANCE

Although there are some promising tests in development, there is currently no good way to characterize a binder for fatigue performance. The $G^*\cdot\sin\delta$ parameter from DSR was included in the Superpave® specifications to control the shape of the master curve and, as noted above, it may or may not be appropriate for a material different than asphalt.

There are a variety of mixture tests that relate to fatigue performance and, at least today, that is the only valid approach to address fatigue performance. As an added safety factor, expanding the temperature and stress or strain rates beyond the normal range would be a good idea.

MIXTURE AND PAVEMENT PROPERTIES

Mixture Characteristics

Properties related to binder–aggregate interaction such as moisture damage susceptibility should be investigated. Compaction techniques are not a perfect mimic for field compaction. There is no guarantee that an alternate material will respond the same as asphalt under different shear conditions so different compaction methods may give different results. Suggested tests include the asphalt mixture performance test for modulus and flow properties, Hamburg wheel tracking for rutting and moisture damage, and tensile strength reserve for moisture susceptibility. Note that an alternative binder may have different response to freeze–thaw cycles so that should be included. Another key question to investigate is the interaction the liquid antistrip agents and lime.

Pavement Characteristics

Bonding between lifts is a consideration to be addressed. How well will an alternative binder mix bond to an asphalt mix or to portland cement concrete? Do standard tack coats work as expected?

TRANSPORTATION AND HANDLING

Logistics

Logistics is an area that is often overlooked in evaluating new materials. Is an alternative binder stable during normal storage times and temperatures, days to weeks at 250°F to 350°F? Is the binder prone to phase separation or other physical or chemical changes and, if so, what precautions are needed? Are there any unusual safety or environmental concerns with transportation and storage?

Mixing, Paving, and Compaction

Does the alternative binder coat aggregate properly in a mixing process? Does it suffer unusual degradation during the mixing process? Can the mix be silo stored under normal conditions? Are there any issues with transporting mix such as stickiness, segregation, or blocking? Does it cause issues with paving? Hand work? Does it compact well using normal rolling patterns? Is it "traffic ready" immediately upon cooling?

Economic Reality Check

There is 30 million tons of asphalt used in North America annually. At roughly $500 per ton, that adds up to $15 billion a year, a substantial percentage of the entire United States pavement infrastructure spending. Money for highway construction, rehabilitation, preservation, and maintenance is very unlikely to increase and could potentially decrease. To be economically viable, an alternative binder must be economically competitive or offer substantial performance benefit. To be commercially viable it must be readily available on a scale of at least thousands of tons. It must be shipped, stored, and handled without onerous changes to conventional asphalt conditions. At the very least, before beginning a research program on a new material, there should be a cursory evaluation to determine if it may ultimately be produced economically and on a scale that allows commercial implementation.

FINAL COMMENTS

While this paper contains a laundry list of caveats, please do not consider them to be discouragement. Rather these should be checkpoints to note in developing a research program on new materials. Most of these points will likely be non-issues, especially for additives, but surprises are best found sooner rather than later.

The most important points:

- If an alternative binder is chemically “outside the box” of standard asphalts, conventional binder tests alone are not sufficient to predict performance.
- A thorough regimen of mixture testing should be included at as early a stage in the program as possible.
- An alternative binder must be economically and commercially viable if it will ever be more than a laboratory curiosity.

Disclaimer: The authors believe the information set forth above to be true and accurate, but recommendations or suggestions in the foregoing text are made without any warranty or guarantee and shall establish no legal duty or responsibility on the part of the authors or their employer. Furthermore, nothing set forth above shall be construed as a recommendation to use any product in conflict with any existing patent rights. Kraton Polymers expressly disclaims any and all liability for any damages or injuries arising out of any activities relating in any way to this publication.

Alternative Binder from Microalgae

Algoroute Project

EMMANUEL CHAILLEUX
MARIANE AUDO
IFSTTAR

BRUNO BUJOLI
CLÉMENCE QUEFFELEC
Université de Nantes (CEISAM)

JACK LEGRAND
Université de Nantes (GEPEA)

OLIVIER LÉPINE
Alpha Biotech, France

Renewable energy sources are developed worldwide because of high oil prices and to limit greenhouse gas emissions. In this context, some groups have focused their work on vegetable oils, and particularly, on microalgae. The last decade has seen an increased scientific interest in the extraction of lipids from microalgae for the production of biodiesel. Microalgae present many advantages compared to other energy crops including a high growth rate, a high biomass production, and noncompetition with human food production. For economical and ecological reasons, the byproducts resulting from the microalgae culture have to be valorized. The Algoroute project is based on the valorization of byproducts resulting from the microalgae production. Could they be used as a binder for aggregates? In that context, the nature and composition of those byproducts need to be identified and rheological properties of different nature of compounds need to be measured. Interesting preliminary results have been obtained. Several fractions from microalgae have been extracted and characterized by infrared (IR), nuclear magnetic resonance (NMR) (^{1}H and ^{13}C), and gas chromatography–mass spectrometry (GC-MS). The complex modulus was also determined on these different fractions. The comparison of rheological and chemical analyses allows highlighting some chemical species that show thermo-dependent behavior comparable to asphalt.

INTRODUCTION

At the moment, many alternative binders, derived from biomass, are already developed by some firms like Colas or Shell. They are principally based on vegetable oils (e.g., linseed, rape). To enhance their viscosity, a natural resin can be added (*1*) or a chemical modification is necessary. Nevertheless, it would be advantageous to find a new alternative binder, based on nonfood crops.

The last decade has seen an increased scientific interest in the extraction of lipids from microalgae for the production of biodiesel. Microalgae present many advantages compared to other energy crops including a high growth rate, a high photosynthetic yield, and high lipid content. Moreover, they do not compete with human feeding, as they can be grown on nonarable lands.

To reach the concept of "algo-refinery" all fractions of microalgae have to be valorized, and not only the triacylgycerols [which can easily be converted in biodiesel by transesterification (*2*)].

As asphalt is a co-product of the petroleum industry, it would be interesting to use byproducts of microalgae industry to produce an alternative road binder without harming the noblest uses of biomass.

Here, the authors propose to use some residues of a microalgae from which some proteins have been removed and to study the lipid fractions. To improve the properties of this potential binder, it is interesting to figure out at first its chemical composition. Then, relationships between composition from one hand, and rheological and mechanical properties from another hand, have to be highlighted. This approach is original and, to the authors' knowledge, no microalgae oil composition–rheological behavior relationship has been reported.

Algoroute project is included in the IFSTTAR Post Oil Pavement research program, dedicated to alternative binders for pavement. It is cofunded by Pays de la Loire region (France) and is a partnership between academic laboratories (such as CEISAM and GEPEA) and companies (such as Algosource Technologies and Alpha Biotech).

MATERIAL AND METHODS

Microalgae Preparation

Microalgae were obtained from Alpha Biotech in Assérac, France. The major part of water-soluble proteins was removed by centrifugation. Residue of microalgae, containing about 80% water, was frozen and then freeze dried for 1 week at –90°C.

Extraction and Fractioning Methods

A Soxhlet apparatus was used to extract lipids from microalgae. About 4 g of microalgae powder was loaded in a 70-mL cellulose thimber; 90 mL of n-hexane, chloroform, and chloroform–methanol (2:1, v/v) were successively used for 24 h. Solvents were removed under vacuum at 40°C. Oil yields were determined by gravimetry.

A sonication of the sample in CCl_4 allowed us to fractionate the oil in two parts: a CCl_4-soluble fraction and a CCl_4-insoluble one that were separated by simple filtration.

Fatty Acid Methylation

Fatty acid methyl esters (FAMEs) were prepared according to Morrison and Smith (*3*); 12 mL of boron trifluoride in methanol (14%) were added to 200 mg of the lipid extract. The mixture was heated in a sealed tube at 90°C overnight. FAMEs were extracted by hexane, washed with water, and dried over $MgSO_4$. The solvent was removed under vacuum at 40°C and FAMEs were dissolved in isopropanol for their analysis by GS.

Analytical Methods

Nuclear Magnetic Resonance

Samples were dissolved in a deuterated solvent (e.g., $CDCl_3$, MeOD, or D_2O). ^1H NMR spectra were recorded on a Bruker AVANCE (DPX 300 or 400) Ultrashield and ^{13}C NMR spectra were recorded at 75 MHz or 100.6 MHz. ^{31}P spectra were recorded at 121 MHz or at 161.97 MHz.

Gas Chromatography

GC was performed on a Agilent 6890 equipped with a flame ionization detector and a BPX70 capillary column (70% cyanopropyl dimethylpolysiloxane, 30 m x 0.32 mm ID, 0.25 µm film thickness). Helium was used as carrier gas at 1.3 mL/min. The oven temperature was 120°C, held for 4 min, then raised to 220°C at a 6°C/min rate and held at 220°C for 5 min. It was then raised to 250°C at a 15°C/min rate, and held at 250°C for 18 min. The injector and detector temperature were set at 250°C. The identification of fatty acids was performed by comparison with the retention time of standards.

Infrared

IR spectroscopy was carried out with an IR-TF Vector 22. Oil samples were dissolved in CCl_4 and placed into a KBr window for the acquisition. A KBr pellet was used for the analysis of solid samples (1% in weight).

Rheology

The complex modulus and phase angle of the samples were measured with a Metravib viscoanalyser DMA+450, in the shear mode, at a 1- to 125-Hz frequency range and 10°C-to-80°C temperature range.

RESULTS AND DISCUSSIONS

Soxhlet Extracts Composition

Three successive extractions were performed in order to fractionate lipids according to their polarity and chemical structure. For hexane, chloroform, and chloroform–methanol the extraction yields are 5%, 5%, and 12%, respectively, which lead to a 22% cumulative yield. Soxhlet extracts appears to be a highly viscous thermo fusible black paste (Figure 1).

Further sonication in CCl_4 showed the existence of an insoluble fraction (0% in hexane extract, 15% in chloroform extract, and 35% in chloroform–methanol extract).

The soluble fractions are only composed by free fatty acids (Figure 2, Table 1). Even though there is no physiological reason that microalgae could produce free fatty acids, we observed only the lipids by ^1H and ^{13}C NMR. This could be the result of an enzymatic lysis of complex lipids during the preliminary protein extraction process.

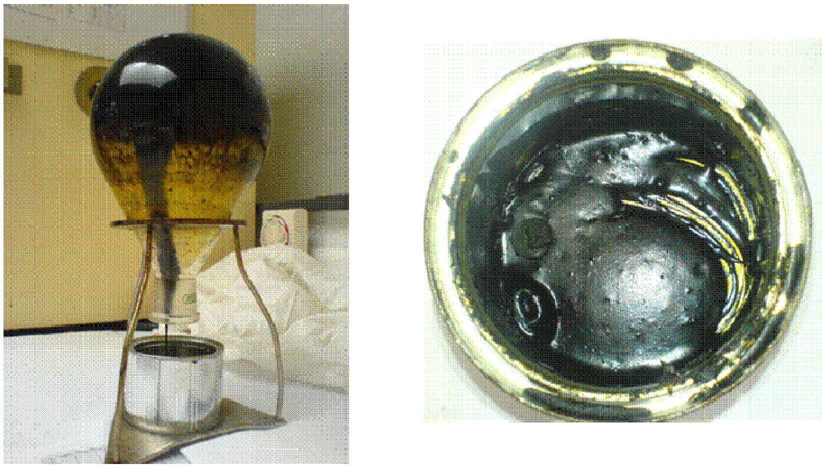


FIGURE 1 Soxhlet extract from microalgae.

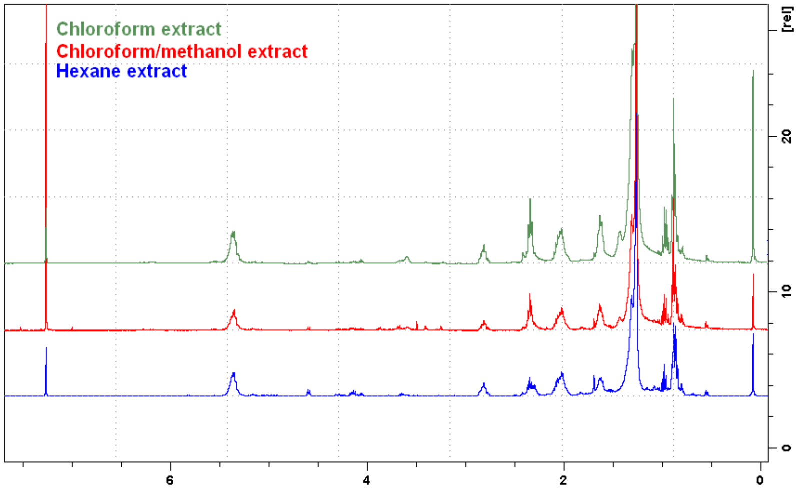


FIGURE 2 ^{1}H NMR spectrum comparison of the three extracts.

TABLE 1 ^{1}H NMR Assignment

δ (ppm)	Chemical Structure
0.9	$C\underline{H}_3-(CH_2)_n-$ of ω6 and ω9
1	$C\underline{H}_3-(CH_2)_n$ of ω3
1.2	$-(CH_2)_n-$
1.6	$-C\underline{H}_2-CH_2-COO-$
2.0	$-\underline{H}_2C-HC=CH-C\underline{H}_2-$
2.3	$-H_2C-COO-$
2.8	$=HC-C\underline{H}_2-HC=$
5.3	–HC=CH–

To allow their analysis by GS, free fatty acids were analyzed as their methyl esters. At all, 18 fatty acids were identified but the main ones were palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid as seen in Figure 3 [classical ones found in microalgae (*4*)]. The only difference between the three extracts is the ratio between all those free fatty acids.

IR spectrum of the CCl_4 insoluble extract (Figure 4) shows some specific absorption bands. The broad band around 3,400 cm^{-1} is attributed to the O – H elongation of some hydroxyl groups. The two signals at 2,915 and 2,850 cm^{-1} are because of the C–H elongations of CH_2 and CH_3. The broad band center around 1,640 cm^{-1} can be attributed to the C = O elongation, similar to polyester. From comparison with literature data (*4*), we suspect the CCl_4 insoluble extract to be algaenans, a biopolymer highly resistant and nonhydrolysable, already encountered in microalgae (*5*, *6*).

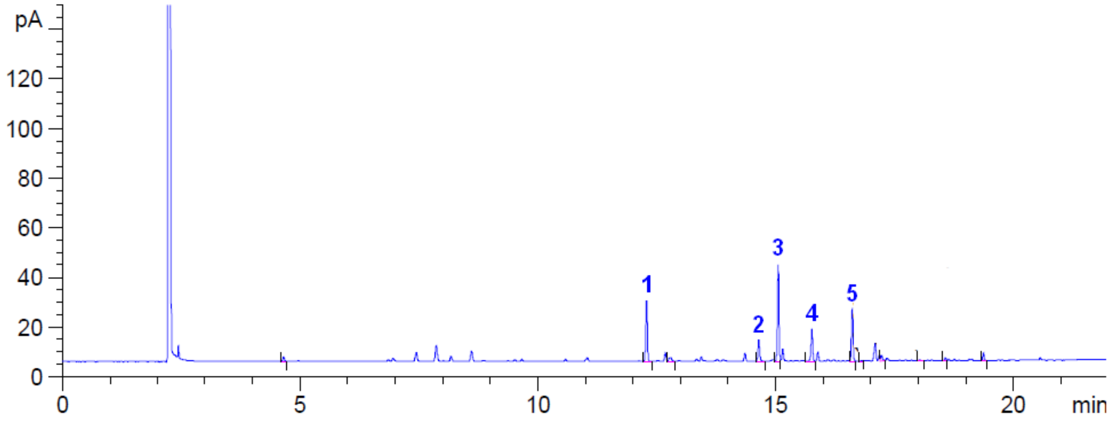


FIGURE 3 Typical GC profile of FAMEs obtained by Soxhlet extraction (1 = C16:0; 2 = C18:0; 3 = C18:1; 4 = C18:2; and 5 = C18:3).

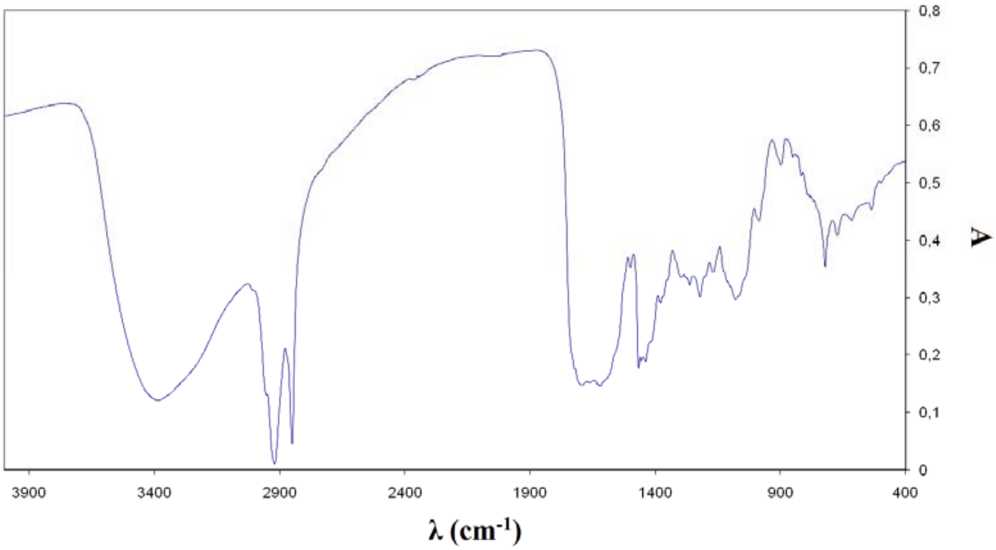


FIGURE 4 IR spectrum (KBr pellet) of CCl_4 insoluble extract.

Soxhlet Extracts Properties

In order to have a better understanding of the influence of each constituent (i.e., free fatty acids and algaenans) on the physical properties of the mixtures, the authors performed a rheological study (measurement of phase angle and norm of the complex modulus), varying the percentage of algaenans.

Three samples, with 0%, 20%, or 35% algaenans, were studied. An easy way to visualize the differences between all the samples is to depict the black curves (plotting phase angle φ against the complex modulus |E*|).

As seen on the Figure 5, the sample composed by only free fatty acids shows a discontinuity between all the isotherms. This is revealing a molecular reorganization at each temperature (i.e., melting of free fatty acids). An increasing from 0% to 20% of the algaenans content engenders a better arrangement of the isotherms, even if they are still discontinuous. A totally different behavior is observed at 35% of algaenans. In this case, as for asphalt, there is continuity between each isotherm, showing the thermo-rheological stability of the material.

The results suggest that it is possible to adjust the rheological properties of the material by adjusting the ratio algaenans versus free fatty acids. It could be an easy way to obtain alternative road binders with similar properties as asphalts. Indeed, complex modulus norm (measured at 1 Hz), was compared to two paving-grade asphalts. On the temperature range tested, microalgae show a thermosusceptibility similar to the one of asphalts (Figure 6). Consequently, it seems possible to obtain alternative road binders with the same rheological properties as asphalts.

Finally, a mix was manufactured with this microalgae oil (Figure 7). Even if more tests need to be done, it is particularly interesting from a qualitative point of view as the oil allowed to give a great consistency to the mix.

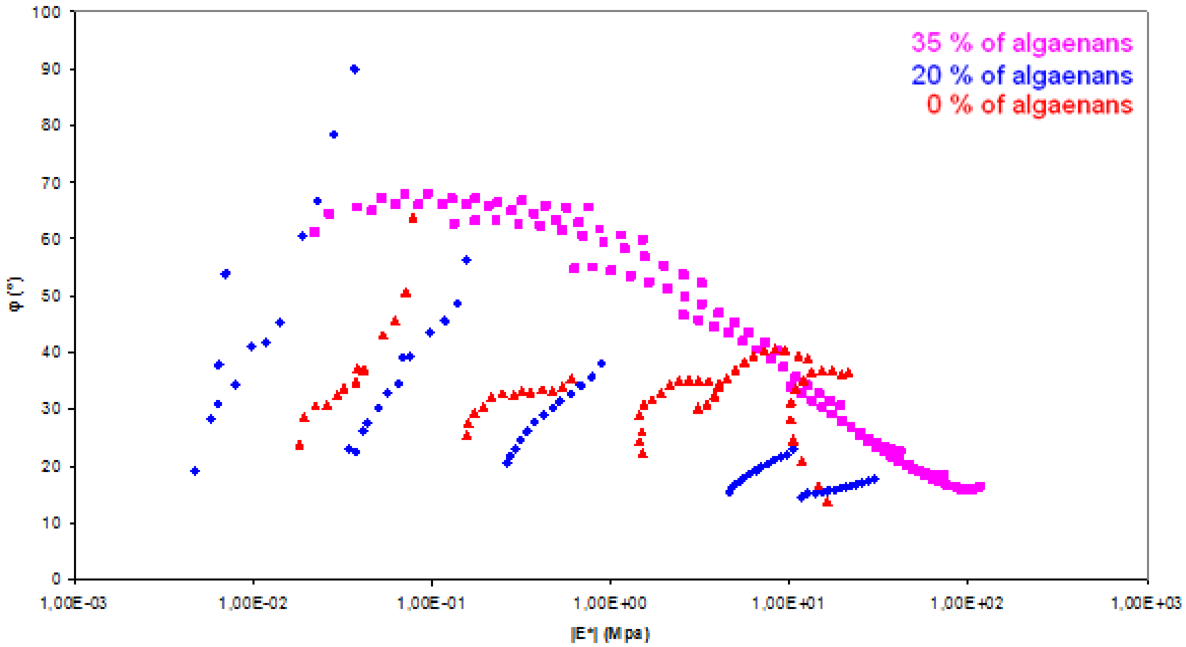


FIGURE 5 Evolution of black curves according to the algaenans content.

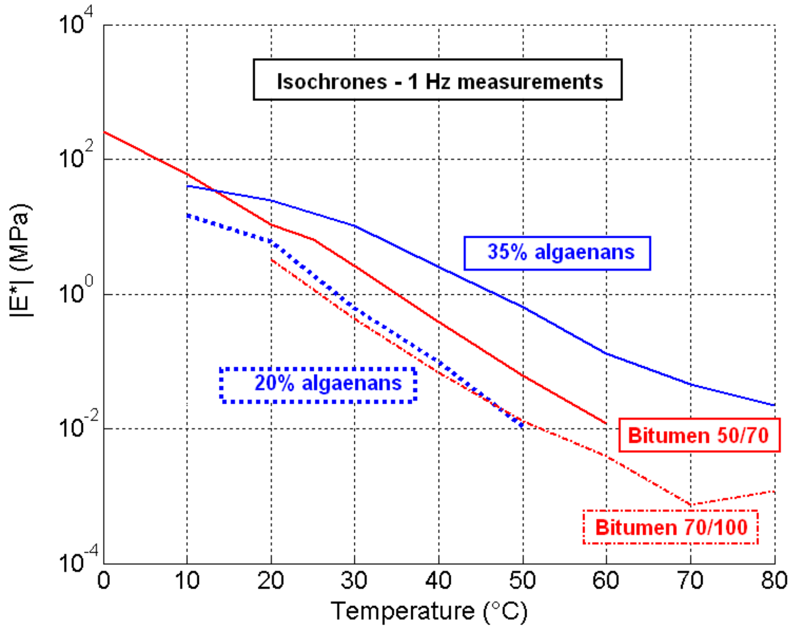


FIGURE 6 Rheological comparison between microalgae extracts and asphalt.

FIGURE 7 Mix manufactured with microalgae oil, using oedometric compaction system.

CONCLUSIONS

Through this study, the authors suggest that the design of microalgae-based road binders should be feasible. The isolated lipid fraction of the studied microalgae is made of a fatty acid polymer (commonly named algaenans) suspended in a free fatty acids oil. This thermofusible viscoelastic material shows rheological properties similar to those of asphalt. Moreover, a tuning of those properties can be achieved by adjusting the percentage of algaenans in the oil.

While only a fraction of the microalgae residue was addressed in the this paper, investigation of innovative and environmentally clean processes (i.e., low energy-demanding and solvent-free protocols) that would allow full valorization of the total residue is needed.

Other residues, from other strains of microalgae, will also be studied, in order to generalize those results.

REFERENCES

1. Ballie, M. Liant de nature végétale pour la réalisation de matériaux pour le bâtiment et/ou les travaux. Publics patent FR 2853647. October 15, 2004.
2. Halim, R., M. K. Danquah, and P. A. Webley. Extraction of Oil from Microalgae for Biodiesel Production: A Review. *Biotechnology Adviser*, Vol. 30, No. 3, 2012, pp. 709–732.
3. Morrison, W. R., and L. M. Smith. Preparation of Fatty Acid Methyl Esters and Dimethylacetals from Lipids with Boron Fluoride Methanol. *Journal of Lipid Research*, Vol. 5, No. 4, 1964, pp. 600–608.
4. Lee, J.-Y., C. Yoo, S.-Y. Jun, C.-Y. Ahn, and H.-M. Oh. Comparison of Several Methods for Effective Lipid Extraction from Microalgae. *Bioresource Technology*, Vol. 101, No. 1, Supplement 1, 2010, pp. S75–S77.
5. Allard, B., M.-N. Rager, and J. Templier. Occurrence of High Molecular Weight Lipids (C80+) in the Trilaminar Outer Cell Walls of Some Freshwater Microalgae: A Reappraisal of Algaenan Structure. *Organic Geochemistry*, Vol. 33, No. 7, 2002, pp. 789–801.
6. Allard, B., and J. Templier. High Molecular Weight Lipids from the Trilaminar Outer Wall-Containing Microalgae *Chlorella emersonii*, *Scenedesmus communis,* and *Tetraedron minimum*. *Phytochemistry*, Vol. 57, No. 3, 2001, pp. 459–467.

Soy Fatty Acids as Sustainable Modifier for Asphalt Binders

JOSEPH C. SEIDEL
JOHN E. HADDOCK
Purdue University

Diversification of material resources is important in the construction and maintenance of sustainable asphalt pavements. Once it has been verified that a particular material is sustainable, characterization of this new material and its interaction with asphalt is foundational. Vegetable-based materials (e.g., soy) are appealing as flexible pavement materials because of their short-term renewable nature and hydrocarbon chemical structure. Little is published regarding the rheological properties of asphalt–vegetable oil blends. This research investigates some high-temperature rheological properties [i.e., viscosity in terms of mixing and compaction temperatures and complex modulus ($|G^*|$)] of four well-studied SHRP binders and just the complex modulus of a recycled asphalt binder, all modified with 1% and 3% soy fatty acids, a specific portion of soybean oil. These rheological tests show that as soy fatty acids (SFAs) are added in small percentages the binder becomes less stiff and more workable. These results suggest that SFAs have potential application as a fluxing agent for binders that are stiff and hard to mix (e.g., recycled asphalt binders).

INTRODUCTION

The road paving industry is interested in utilizing alternative and sustainable binder materials to aid in the production, placement, and performance of flexible pavements. For resource materials to be considered sustainable they must be technically, economically, and environmentally viable. From a technical standpoint, this material should be compatible with other component materials and make sense to use with existing production and paving equipment. From an economic standpoint, a sustainable material is available in quantities appropriate for the application. Also, to justify its use, this material adds value to a product in an affordable manner. Environmental viability ensures that the environment is not affected in a negative way.

Soy oil has components chemically similar to asphalt. Asphalt molecular structures can be classified as oils, resins, and asphaltenes (*1*), or as a mixture of polar and nonpolar molecules (*2*). The binding properties of asphalt are because of the functional groups of the polar or asphaltene portion of the binder (*2*). The flow characteristics are attributed to the oil-like molecules. Carboxylic acids are present in the polar portion of the asphalt and its molecular structure has both a nonpolar and polar end. Soy oil contains long chain fatty acids that fit under the classification of carboxylic acids. Little information exists in regard to how vegetable-based fatty acids interact with asphalt. It is expected that the similar hydrocarbon molecular structure of both materials will make them compatible and therefore usable in existing production and paving equipment.

Economically, SFA derived from soybeans make sense from a supply-and-demand point of view. According to the U.S. Department of Agriculture, in 2010 the United States was responsible for 35% of the world's production of soy (*3*). In Midwestern states, soybeans represent a significant renewable resource for food, biofuel, and various industrial applications.

In the processing of soy, approximately 80% goes toward flours, proteins, and concentrates, while the other 20% is the oily portion to be further refined for specific applications (*4*). Of the oil produced, 86% is directed toward foods while the rest is used in industrial products (*3*). Retrieving the fatty acids from the refined oil would be expensive and would also compete with food, biofuel, and other industries. However, a coproduct of the soy oil refining process is a product called soapstock, so named because historically it served as a raw material for soaps. With the addition of an acid, the SFA can be separated from the remaining organic compounds in concentrations approaching 95%. It is then known as acidulated soy soapstock. Isolating the fatty acids to such a high level allows the evaluation of the contribution of just the fatty acids and minimizes the introduction of other variables. These fatty acids have been used to supplement animal feeds and to control dust on roadways. It was estimated that two-thirds of the acidulated soy soapstock produced in 1986 was directed toward animal feeds and pet foods where it competes with feed-grade animal fat (*5*). As far as suitability for the North American paving asphalt market, the demand for paving asphalt was approximately 47 billion pounds in 2010 and expected to rise 6.5% over the next couple of years (*6*). Around 1 billion pounds of soy soapstock are produced per year in the United States (*7*). Although not all of the soapstock will be directed toward asphalt modification, technically and economically small modification levels are warranted.

From an environmental standpoint, acidulated soy soapstock does not adversely affect the environment. It has been used as a dust suppressant and ground stabilizer on unpaved roads in various states. Soy soapstock is known to be biodegradable and, as long as it is applied at suggested levels, the material will not migrate into the ground water (*8*). The Minnesota Department of Transportation tested water quality in the vicinity of soapstock-stabilized roads and found no ill effects. These results were verified by the Minnesota Pollution Control Agency (*8*). Climate conditions for soybean production also play a part in sustainability, however, because new technology soy is able to grow well in adverse climate conditions such as drought (*9*).

Technically, economically, and environmentally it may be plausible for SFA from soapstock to serve as a paving asphalt additive at low modification levels. However, it is uncertain from the limited amount of literature what the outcome will be when small percentages of SFA are added to asphalt binder. This research investigates high-temperature rheological properties [i.e., viscosity in terms of mixing and compaction temperatures and complex modulus ($|G^*|$)] of five asphalt binders modified with 1% and 3% SFA.

MATERIALS

Asphalt Binders

Samples of four asphalt binders used in SHRP, were obtained from FHWA Material Reference Library (MRL) in Sparks, Nevada. By name and FHWA MRL code, the binders are a Canadian Lloydminster (AAA-1), a California Coastal (AAD-1), a West Texas (AAM-1), and a Mexican Mayan blend (AAT). The binders were chosen to represent typical North and Central American asphalts having varying chemical compositions and two specified performance grades, PG 58-22 and PG 64-16. In addition, for limited testing, the North Central Superpave Center provided a small sample of binder recovered from reclaimed asphalt pavement (RAP) labeled as SMFD. It came from 9.5-mm crushed and screened full-depth millings.

Soy Fatty Acids

Acidulated soy soapstock serves as a source for SFAs. A research sample of acidulated soy soapstock was obtained from a commercial supplier

METHODS

The four SHRP binders and the recycled asphalt binder were each mixed with 1% and 3% SFA and compared to the control in various high-temperature rheological tests (Figure 1). Each asphalt binder was annealed in an oven set at 140°C until sufficiently fluid to mix thoroughly with a glass rod. Roughly 350 mL of asphalt binder was added to a 600 mL Griffin beaker. The binder was then uniformly heated in a temperature-regulated heating mantle and continuously stirred using a low-shear drill mixer, maintaining a vortex sufficient for thorough mixing. As the asphalt binder was brought to the target temperature of 135±5°C, the SFA was added and mixing continued for 40 min. After 40 min little change was observed in angular velocity of the mixing propeller for all binders, indicating a steady state condition. The fatty acids dissolved readily into the asphalt binder producing a homogeneous mixture.

Three high-temperature rheological properties, rotational viscosity, small strain linearity, and shear complex modulus were determined for each of the asphalt–SFA blends. The complex modulus was also determined for a blend of recycled asphalt binder and SFA. The viscosity, as described in AASHTO T316-04, Standard Test Method for Viscosity Determination of Asphalt Binder Using Rotational Viscometer, is a measure of the resistance to flow as determined by a specific metal spindle within a sample chamber filled with asphalt binder. The rotational viscosity was measured at temperatures of 135°C, 150°C, and 165°C in order to establish mixing and compaction temperatures. A plot of these temperatures and associated viscosities indicate when the binder will attain viscosities of 0.17 ± 0.02 Pa-s and 0.28 ± 0.03 Pa-s. These are the viscosities determined by the Asphalt Institute as being appropriate for mixing and compacting respectively (*10*). The viscosities were determined using a number 27 spindle at a shear rate

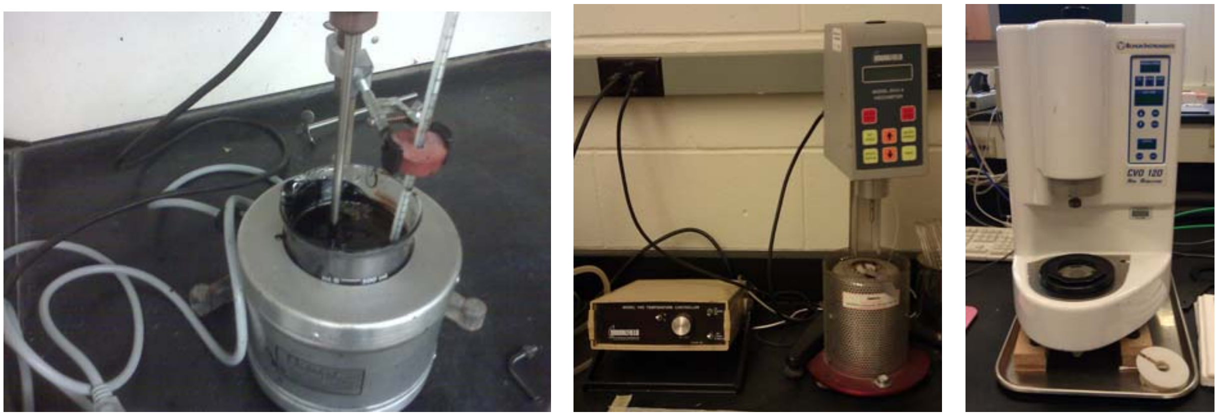

(a) (b) (c)

FIGURE 1 (*a*) Mixing equipment, (*b*) rotational viscometer, and (*c*) dynamic shear rheometer.

of 93 s^{-1}, with the exception of AAM-1 which required a lower shear rate with the same spindle. AAM-1 binders were tested at a shear rate of 46.5 s^{-1}.

AASHTO T 315-06, Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer, was used to determine the |G*| for high-temperature grade testing and to verify the linearity of the material at small testing strains. In the rheometer, the asphalt binder sample is sandwiched between an oscillating metal plate and a fixed-base plate. Only if the binder behaves in a linear viscoelastic manner is this parallel plate geometry applicable. Therefore, a linearity check is performed first by monitoring the |G*| at various strains from 2% to 12%. If the complex shear modulus changes by more than 10% then the material is nonlinear and must be tested differently. If the material is linear viscoelastic then it can be tested further for establishing a high-temperature grade. This is determined by testing the original binder at a target strain value of 12%. The temperature at which |G*| equals 1.00 kPa is the actual high-temperature performance grade. For specification purposes the temperature is measured in degrees Celsius and rounded down to specific temperatures in 6-degree intervals (e.g., 64, 70, and 76).

RESULTS

Mixing and Compaction Temperatures

The viscosity versus temperature relationship is shown in Figures 2 through 5 for each of the SHRP asphalt binder–SFA blends. The upper range outlines the approximate temperature suitable for compaction, while the lower range encompasses the approximate temperature needed for mixing and thorough coating of the aggregate by the binder. The original binder and the binder at the two modification levels show a linear relationship between viscosity plotted on a log scale and the temperature. With each percentage of SFA added, the viscosity–temperature relationship line is lowered in an almost a parallel manner with the exception of one binder.

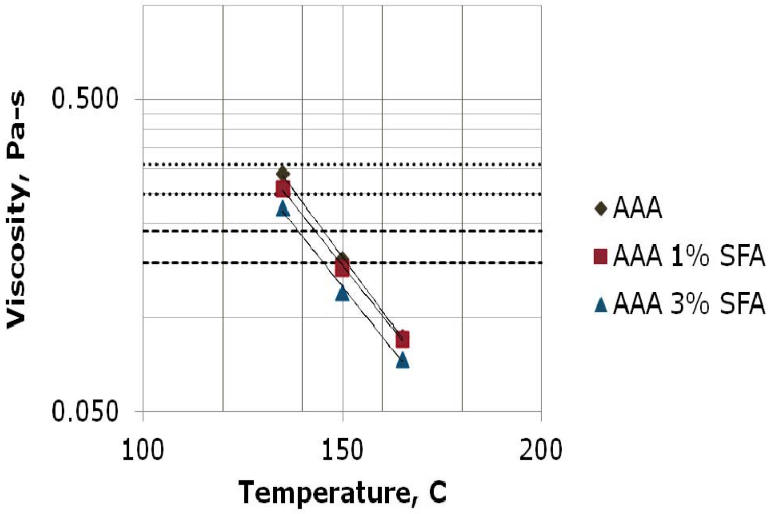


FIGURE 2 Mixing and compaction temperatures for AAA-1 binder modified with 1% and 3% percent SFAs.

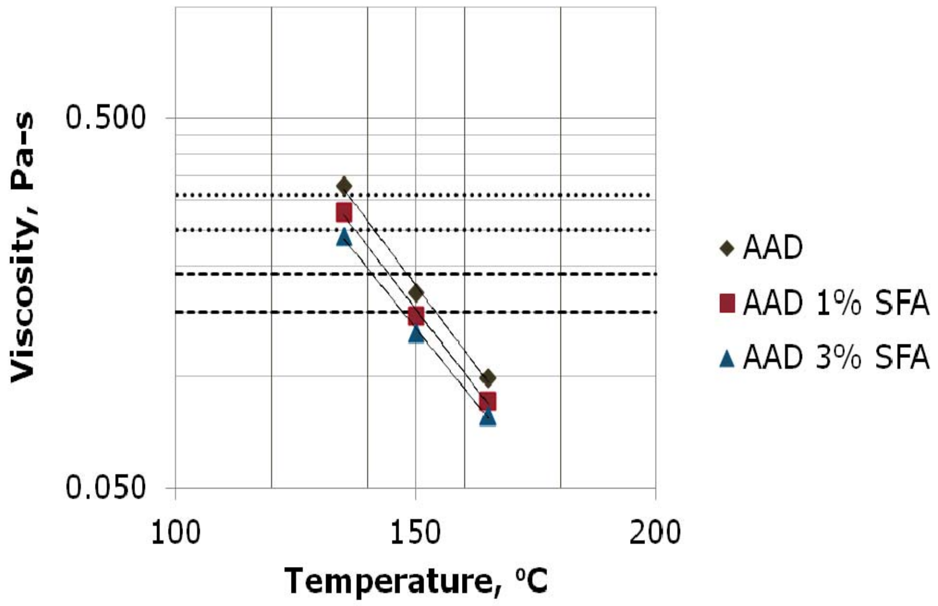


FIGURE 3 Mixing and compaction temperatures for AAD-1 binder modified with 1% and 3% SFAs.

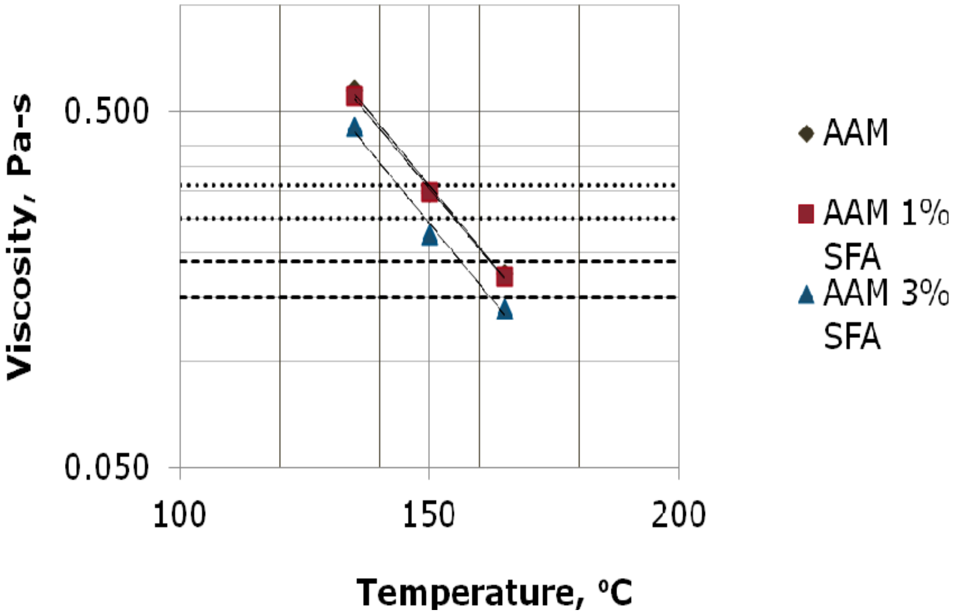


FIGURE 4 Mixing and compaction temperatures for AAM-1 binder modified with 1% and 3% SFAs.

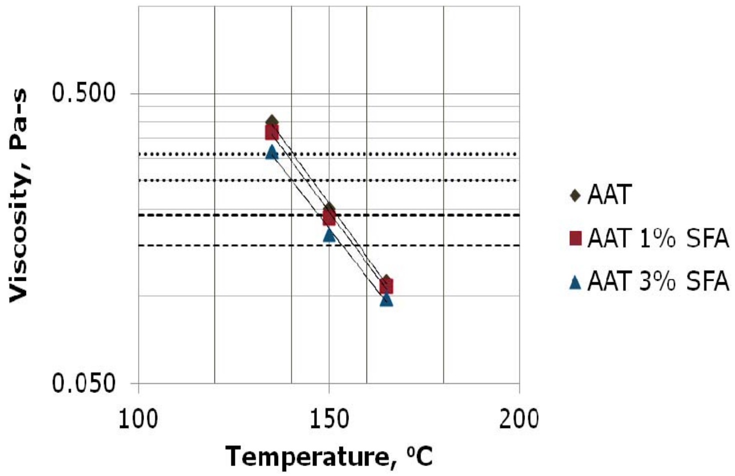


FIGURE 5 Mixing and compaction temperatures for AAT binder modified with 1% and 3% SFAs.

Figure 4 shows when mixed with SFAs, the AAM-1 binder acts somewhat differently than the other three binders. SFAs added at 1% by binder mass appear to have no effect on the mixing and compaction temperatures of the AAM-1 binder. However, when 3% SFAs are added, the same parallel reduction as seen with the other binders is noticeable. It is believed that there needs to be a sufficient amount of small SFA molecules to navigate around the large waxy molecules present in the AAM-1 binder in order to have an effect on viscosity

Linearity

When blending additives with asphalt binders, linearity testing should be done verify that the additive does not cause the resulting modified binder to behave in a nonlinear manner. Performance-graded test methods assume that the material being tested is linear viscoelastic within the loading range of the tests. The linearity limit is 10% below the initial 2% strain. As long as a binder stays above this limit it is considered to behave in a linear manner. As can be seen in Table 1, adding SFA did not affect the linearity in a negative way. In the instance of the AAA-1 binder, the modulus ratio—the ratio of the complex modulus at 2% strain divided by the complex modulus at 12% strain—was improved or brought closer to 1.000.

Complex Modulus

The relationship of |G*| versus temperature is shown for the SMFD binder in Figure 6. The shear complex modulus is a measure of stiffness of the binder at high in-service temperatures. As SFAs are added at a 3% level there is a noticeable shift to the left. This behavior is seen for all five binders tested. This behavior would be seen as a negative effect for normal binders in terms of deformation resistance at high temperatures. However, extracted RAP binders typically have more than enough stiffness to resist permanent deformation at high temperatures and must have softer binder grades or recycling agents added to make them sufficiently workable and resistant to cracking.

TABLE 1 Strain Sweep Results for the Determination of Linearity

Binder	High PG Temperature (°C)	|G*|, Pa		Linearity Limit (Pa)	Modulus Ratio
		2% Strain	12% Strain		
AAA	58	1,410	1292	1,269	0.916
AAA 1% SAS	52	2,217	2,085	1,995	0.940
AAA 3% SAS	52	1,330	1,410	1,197	1.060
AAD	58	1,638	1,709	1,474	1.043
AAD 1% SAS	58	1,280	1,226	1,152	0.958
AAD 3% SAS	52	1,538	1,589	1,384	1.033
AAM	64	1,393	1,507	1,254	1.082
AAM 1% SAS	64	1,227	1,271	1,104	1.036
AAM 3% SAS	58	1,732	1,864	1,559	1.077
AAT	64	1,433	1,479	1,290	1.032
AAT 1% SAS	64	1,113	1,066	1,002	0.958
AAT 3% SAS	58	1,672	1,615	1,504	0.966

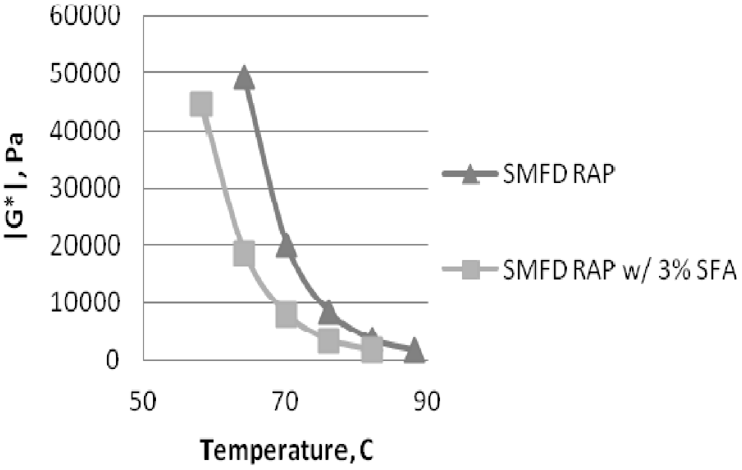


FIGURE 6 Typical high-temperature grade results showing the reduction in |G*| because of the addition of 3% SFA.

CONCLUSIONS

The main conclusions from this research are that SFAs are a plausible, sustainable modifier for asphalt binders and that they decrease the viscosity and stiffness of asphalt binders. This fluxing ability is particularly applicable to stiff binders (e.g., recycled asphalt) with the intent to make them more workable. The mixing and compaction temperatures were lowered; even more so as more fatty acids are added. The AAM-1 binder did not see a decrease in viscosity until 3% of SFA were added. The larger molecules present in the binder are believed to be the reason for this observation. The complex modulus, determined from high-temperature grade testing using the dynamic shear rheometer lowered the complex modulus at a given temperature. The lowering effect is less as the temperature increases. If looked at as a characteristic curve of the material, adding SFA causes a lateral shift to the left. This behavior was observed for all binders tested.

RECOMMENDATIONS

More research is warranted using SFA with stiff binders. It is recommended that various recycled asphalt binders mixed with small percentages of SFA be characterized. Classifying the SFAs using AASHTO R14-88, Classifying Hot Mix Recycling Agents, would allow producers a more specific application of the SFAs.

REFERENCES

1. Nicholls, R. L. *Composite Construction Materials Handbook*. Prentice-Hall, 1976.
2. Robertson, R. E., J. F. Branthaver, and J. C. Petersen. Development of a Performance Related Chemical Model of Petroleum Asphalt for SHRP. *ACS Fuels*, Vol. 37-3, Fall 1992, pp. 1272–1278.
3. www.soystats.com. Accessed February 2012.
4. Petrie, E. M. Soybean Adhesive. SpecialChem. www.specialchem4adhesives.com. Accessed Jan. 13, 2010.
5. Woerfel, J. B. Soapstock. *Proc., World Conference on Emerging Technologies in the Fats and Oils Industry* (A. R. Baldwin, ed.). American Oil Chemists' Society, 1986, pp. 165–168.
6. Global Demand for Asphalt to Approach 120 Million Metric Tons in 2015. *Public Works Magazine,* Feb. 28, 2012. www.pwmag.com. Accessed February 2012.
7. Haas, M. Improving the Economics of Biodiesel Production Through the Use of Low Value Lipids as Feedstocks: Vegetable Oil Soapstock. *Fuel Processing Technology*, Vol. 86, 2005, pp. 1087–1096.
8. *Questions and Answers: Road Dust Control with Soapstock—A Soybean Oil By-Product.* www.usroads.com. Accessed November 2011.
9. USDA Scientist Expresses Appreciation for Soybean Checkoff's Consistent Funding. 2009. http://checkbiotech.org/node/24366. Accessed November 2011.
10. Asphalt Binder Testing: Technician's Manual for Specification Testing of Asphalt Binders. MS-25, 2nd edition, 2008.

Development of Rubber-Modified Fractionated Bio-Oil for Use as Noncrude Petroleum Binder in Flexible Pavements

JOANA PERALTA
R. CHRISTOPHER WILLIAMS
MARJORIE ROVER
Iowa State University

HUGO M. R. D. SILVA
University of Minho

The increasing demand for petroleum-derived products coupled with decreasing world crude reserves has led to substantial increases in asphalt pricing. Society's additional interest in energy independence and use of renewable sources of energy is also a motivation for developing and using more sustainable materials such as binders derived from noncrude petroleum sources for use in highway applications. Iowa State University has been developing noncrude petroleum binders derived from the production of bio-oil via fast pyrolysis of non-food source bio-renewable residues. Currently, research has demonstrated that bioasphalt can be used as a modifier, extender, or even as an antioxidant when added to petroleum asphalt. Previous research illustrated concerns with low-temperature cracking and the ability to produce typical binder grades used in the United States. This work aims to develop a biobinder that can replace 100% of the petroleum derived asphalt used in constructing flexible pavements utilizing bio-oil and crumb rubber. Both ambient and cryogenic crumb rubber were used in the research. The outcomes of the processes and formulations illustrates that noncrude petroleum binders can be developed effectively to replace typical paving grades of asphalt such as a PG 64-22 binder.

INTRODUCTION

The United States has numerous efforts under way working to establish a bio-based economy which generates energy from renewable organic matter rather than fossil fuels (*1*). The substantial increase in asphalt pricing in the past 8 years coupled with the installation of coking facilities at many refineries, which can reduce the supply of asphalt, is also creating an impetus for alternative nonpetroleum binders.

Most bituminous binders that are used for pavement materials are derived primarily from fossil fuels. With petroleum oil reserves becoming depleted and the drive to establish a bio-based economy, there is a push to produce binders from alternative sources, particularly from bio-renewable resources.

A biobinder is an asphalt binder alternative made from nonpetroleum-based renewable resources, which should not rival any food material, and have environmental and economical benefits. Presently, biobinders are produced by upgrading bio-oils produced from the rapid heating of biomass in a vacuum condition. Bio-oils are produced from plant matter and residues, such as agricultural crops, municipal wastes, and agricultural and forestry byproducts (*1*, *2*).

Currently, the state of the art for the utilization of bio-oils is concentrated on its use as biorenewable fuels to replace fossil fuels. However, there has been a limited amount of research investigating the applicability of bio-oils as a bitumen modifier or extender. Williams et al. conducted research on the usage of bio-oils fractions as an extender in original and polymer modified asphalt binders (*3*). They reported that the bio-oils can considerably increase the performance grade of polymer-modified asphalt binders by nearly 6°C (*3*). In addition, it was concluded that the effect of bio-oils was dependent upon many factors including the base asphalt, source of the biomass from which the bio-oils were derived, and the percentage of bio-oils blended with asphalt binders (*3*). Moreover, Williams et al. reported that up to 9% of a bio-oil could be blended with asphalt binders with significant improvement in the performance grade of the bio-oil modified asphalt binder. Concurrently, Fini and others have found that the use of swine manure-based biobinder as an asphalt modifier can enhance the asphalt low-temperature performance (*4, 5*). Based on the conclusions of these investigations, the utilization of bio-oils as a bitumen modifier is very promising. Nevertheless, there has been no research conducted until recently that studies the applicability of using bio-oils as a bitumen substitute (100% replacement) to be used in the paving industry.

One of the thermochemical processes used to produce bio-oils is fast pyrolysis. The yields from fast pyrolysis vary with the biomass feed stock and the reactor conditions (*6*). Generally, this process generates bio-oil, biochar, gases, and moisture. The biochar can be used for carbon sequestration as a soil modifier by improving the soil's ability to retain liquid fertilizers and thus reducing liquid fertilizer application rates. The bio-oil is a liquid fuel containing lignin that can be combusted by some engines or turbines for electricity generation (*7*).

Fast pyrolysis is a thermal decomposition process that requires a high heat transfer rate to the biomass particles and a short vapor residence time in the reaction zone (*8*). In other words, fast pyrolysis is the rapid decomposition of organic matter (biomass) in the absence of oxygen to produce solids such as char, pyrolysis liquid or oil (bio-oils), and gas (*9*, *10)*.

Generally, fast pyrolysis is used to obtain high-grade bio-oil. Organic biomass consists of biopolymers, such as cellulose, hemicelluloses, and lignin. Because of the different sources of biomass, the amount of production of the liquid bio-oils, solid char, and noncondensable gases varies. For example, fast pyrolysis processes produce about 60 to 75 wt% of liquid bio-oil, 15 to 25 wt% of solid char, and 10 to 20 wt% of noncondensable gases (*2*).

Figure 1 shows the 25 kWt fast pyrolysis system developed at Iowa State University by the Center for Sustainable Environmental Technology where bio-oils are produced from different biomass materials.

The pilot unit consists of a 16.2-cm diameter fluidized bed reactor, a burner to externally heat the reactor, a two-stage auger to feed the solid, two cyclones to remove particulate matter, and a vapor-condensing system consisting of four condensers and an electrostatic precipitator. The system can process 6 to 10 kg/h of solid feed. The separation of bio-oils into multiple fractions was conducted using a fractionation condenser system which facilitated the selection of bio-oil fractions that would be optimal for being used as a pavement binder. However, bio-oils cannot be used as biobinders–pavement materials without any heat pre-treatment, since an upgrading procedure is required (*11*).

Raouf (*11*) also found that the biobinders developed from oakwood, switchgrass, and corn stover bio-oils cannot be treated at temperatures higher than 120°C because of the volatilization of some bio-oil compounds. Raouf (*11*) further found considerable differences between the properties of the bio-oils and asphalt at the same temperatures, and thus the Superpave test criterion should be modified to comply with the biobinders properties, namely the Superpave specifications for the rolling thin film oven test (RTFOT) and the pressure aging

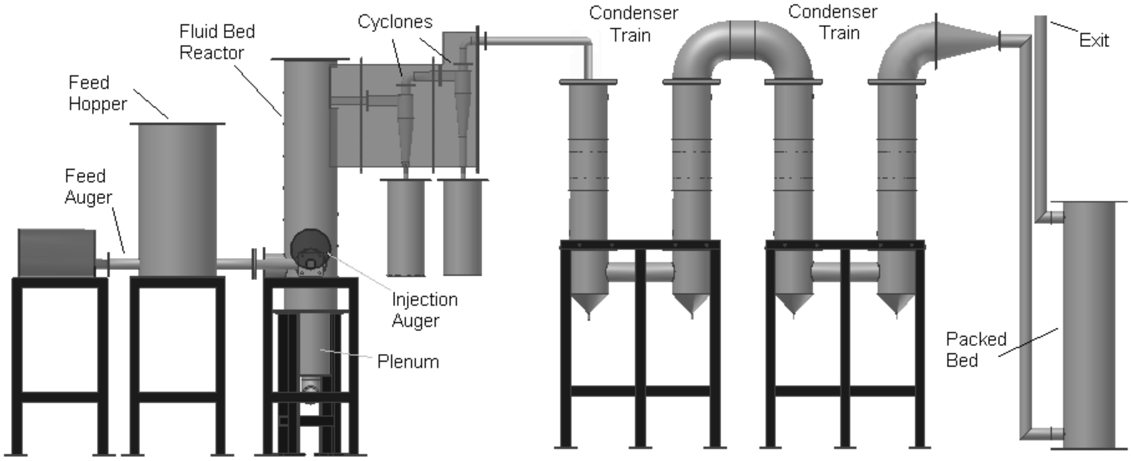


FIGURE 1 Bio-oil fast-pyrolysis pilot plant. (Source: Iowa State University.)

vessel (PAV) procedures. Longer in-situ aging studies would need to be done to understand the aging mechanisms of biobinders such that simulative laboratory criteria can be established.

Based on the tested bio-oils, the following suggestions were made (*11*). First, the RTFOT temperature should be modified to 110°C to 120°C instead of 163°C to be consistent with the intended mixture production temperature. Also, a period of 20 min was established to be the duration that resembles the mixing duration. Second, the aging duration in the PAV should be shortened to 2.5 h instead of 20 h and the temperature of the degassing container should be lowered to 120°C instead of 170°C. Raouf found that it was difficult to reach low-temperature grades of binders when attaining the appropriate high-temperature grades (*11*).

In many cases, the characteristics of asphalt binders need to be changed to improve their elastic properties at low temperatures for sufficient cracking resistance, and to increase its shearing resistance during sustained loads and high temperatures for rutting resistance. The physical properties of bitumen are typically modified with the addition of styrene-butadiene-styrene (SBS) polymers to produce an improved asphalt grade that enhances the performance of asphalt paving mixtures. A viable alternative to using SBS polymers would be the use of recycled rubber from tires.

According to ASTM D 6814-02, rubber is a natural or synthetic elastomer that can be chemically cross linked or vulcanized to enhance its useful properties. Cross-linked rubbers or elastomers are three-dimensional molecular networks with the long molecules held together by chemical bonds. They absorb solvent and swell but do not dissolve. The glass transition temperature, T_g, of natural rubber is about –70ºC. Furthermore, they cannot be reprocessed simply by heating (*12*).

Gawel et al. (*13*) also found that, of the nonpolar components, the n-alkanes and n-alkylbenzenes possess the highest propensity to penetrate into rubber particles. Preferential absorption of the compounds with linear aliphatic chains into the rubber suggests that these components have better skeletal compatibility with the linear polymeric skeleton of the rubber.

Despite natural rubber being a constituent of tires, because of its vulcanization, they cannot be easily recycled. Every year approximately 9 to 10 kg of rubber tires per inhabitant are discarded in industrialized countries. Although tires are not regarded as a dangerous residue, their hollow shape usually creates sanitary problems and difficulties in their final disposal. A technical challenge is the vulcanized rubber of tires cannot be recycled or used for the same purpose as the unvulcanized polymer. Furthermore, society is not utilizing the valuable materials that exist in tires, namely its main constituent, the vulcanized natural and synthetic rubbers.

Therefore, the main objective of this work is the development of a biobinder capable of fully replacing conventional asphalt in flexible pavements. The utilization of recycled tires blended with bio-oil is examined to determine if the materials are chemically compatible as well as the recycled tires can enhance the low-temperature properties of biobinders.

EXPERIMENTAL PLAN

The experimental plan consists of a description of the materials, including the production of the biobinders, and the chemical and rheological testing. The specific components of the experimental plan are discussed in the following subsections.

Materials

The main material used in this work was the bio-oil derived from the fast pyrolysis of red oak wood residues in the Iowa State University pyrolysis unit (Figure 1) and two sources of crumb rubber from used tires from different suppliers that were obtained using two different processing methods: (*a*) mechanical-shredding ambient rubber and (*b*) and cryogenic-milled rubber.

The asphalt binder chosen as control for this study, for comparison to the developed biobinders, is AAM-1 from FHWA's Materials Reference Library. AAM-1 is a PG 64-16 and is from a west Texas crude source.

Biobinder Production

In order to obtain a biobinder with the suitable characteristics to be used as a comparable replacement of the conventional petroleum derived asphalt, the bio-oil produced from the fast pyrolysis unit needs to be upgraded. According to previous studies the bio-oil by itself possesses very good characteristics, similar to asphalt, at high and medium temperatures (*11*). However, the performance at low temperatures was not acceptable for the use in the majority of the United States as they were too stiff at low temperatures and susceptible to low-temperature cracking. The approach to try to solve this issue was to add rubber to the bio-oil.

Rubber swells in contact with some solvents and is time–temperature dependent. Additionally, the characteristics of the final binder also depend on the concentration and properties of the rubber. Therefore, the first approach to this concept was to determine whether the rubber swells or not in contact with bio-oil. Since the swelling rate directly depends on the interaction temperature, the temperature used for the biobinder production was maximum possible that minimizes the degradation of the bio-oil, i.e., 125°C. The selected concentration of rubber for the first test was 15%. The rubber was allowed to interact with the biobinder in a mechanical (Figure 2) at 1,000 rpm and small samples of the material were collected every 30 min (interaction times: 30 min, 1 h, 1 h 30 min, 2 h, 2 h 30 min, and 3 h) for visual and physical inspection. As a result, an interaction time of 1 h 30 min was initially considered adequate.

In order to determine the parameters that would produce a biobinder with the adequate characteristics, the two sources of rubber were used in two different percentages, 10% and 15%, for blending with the bio-oil.

Applying the aforementioned parameters, four biobinders were produced:

- A: 90% bio-oil plus 10% cryo rubber;
- B: 85% bio-oil plus 15% cryo rubber;
- D: 90% bio-oil plus 10% amb rubber; and
- E: 85% bio-oil plus 15% amb rubber.

Additionally, to assess the changes that occur in the bio-oil that were independent from the interaction with the rubber particles, the bio-oil was heated with agitation for 1.5 h at 125°C to obtain the aged bio-oil.

After the biobinder production, a sample was taken for subsequent analysis and testing. The remaining biobinder was separated using a centrifuge consisting of a cylindrical cage with a fine meshed wire and a cloth filter (Figure 2). The binder accelerated separation (BAS) method was developed to separate the two phases of the biobinder, namely, the residual bio-oil (Res) and the swelled rubber.

The main constituents of the separation equipment are the aforementioned filter and the centrifuge. The method consists in introducing the biobinder in the filter, place the filter in the heated residual bio-oil receptacle and centrifuge at a velocity about 2,000 rpm for 3 min. The centrifuged material (Res) could then be rheologically tested as well as a chemical analysis done and the retained material weighed to determine the rubber swelling.

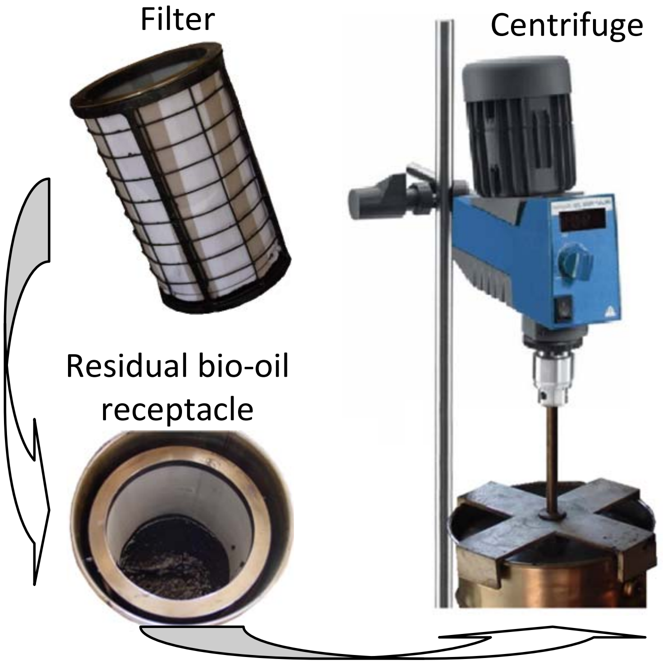


FIGURE 2 BAS method.

Chemical Analysis and Performance Grading of the Biobinders

The Res bio-oil was subjected to two aging methods in order to be possible to evaluate its grade. Therefore, first the Res bio-oil was aged by the aforementioned modified RTFOT that was performed at 120°C for 20 min. After taking a sample for analysis, the remaining material was aged using the PAV at 100°C for 2.5 h. The degassing was performed at 120°C for 30 min.

The chemical analysis of the materials was made using the Fourier transform infrared spectroscopy (FTIR) method and the resulting spectra were compared. Thus the characterized materials were: (*a*) the base bio-oil; (*b*) the aged bio-oil; (*c*) the ambient and cryogenic rubbers; (*d*) the four biobinders; and (*e*) the four Res bio-oils that resulted from the BAS method.

The evaluation of the critical temperatures (T_c) of the materials was performed using a dynamic shear rheometer (DSR) for high and intermediate temperatures and using a bending beam rheometer (BBR) for low temperatures.

The materials characterized in the DSR were the base bio-oil, the aged bio-oil, the four Res bio-oils (two each for each type of rubber at the two different percentages), the four RTFOT Res bio-oils, and the four PAV Res bio-oils. The BBR testing was performed only on the four biobinders.

RESULTS AND DISCUSSIONS

The results and subsequent discussion are presented in three sections: physical characteristics of the blended rubber (swelling), chemical analysis using FTIR, and performance grading of the biobinders.

Physical Characteristics of Rubber

The first important result obtained from the application of the BAS method was the amount of rubber swelling. Despite of the accepted knowledge that rubber only swells at high temperature and in the presence of solvents derived from petroleum, both crumb rubber samples swelled significantly (Table 1).

At the selected interaction temperature (125°C) for a reduced time of interaction (1.5 h), the rubber swelled an average of nearly 300% of its initial weight. The rubber swelling in the bio-oil is similar to that observed in the conventional asphalt (*14*, *15*), been higher for the lower concentration of crumb rubber. Despite the small differences between the two types of rubber, the cryogenic rubber swelled more than the ambient one.

TABLE 1 Amount of Rubber Swelling

Samples	Crumb Rubber	% Rubber	Swelling (% of the initial crumb rubber weight)
A	Cryogenic	10	351
B		15	270
D	Ambient	10	325
E		15	228

As previously described, the biobinder production process consists of a blending and heating process, during which two phenomena occur simultaneously: (*a*) the diffusion of parts of the bio-oil causes the rubber to swell and (*b*) the volatilization of some molecules of the bio-oil increases its stiffness.

Chemical Analysis of the Biobinders

To understand the relative effects of the chemistry, FTIR of the base bio-oil was compared with that of the bio-oil aged at 125°C with agitation, mimicking the biobinder production, but without the addition of rubber (Figure 3).

The bio-oil chemical composition can be determined from a qualitative point of view by assessing Figure 3. By observing the comparative spectra, the bio-oil did not have significant changes because of aging during biobinder production. To confirm these observations, a similarity match was done, namely match values from the base bio-oil with the aged bio-oil were computed and compared.

The similarity match is a spectral classification technique that indicates how closely an unknown material matches a known material. The similarity match method compares the spectral information in the specified region or regions of an unknown sample spectrum with that of a known set of standard spectra to determine how closely the sample matches the standards. The result of this comparison is called a match value. The match value represents the unexplained variation in the spectrum of the unknown sample; the maximum similarity is indicated by a match value equal to zero.

The match value of the base bio-oil compared with the aged bio-oil was about 0.30, which shows that there were almost no changes in the chemical composition of the bio-oil during the bio-oil to biobinder production.

Additionally, since the cryogenic and ambient rubber were provided by two different companies (one in the Chicago metropolitan area and the second in the Atlanta metropolitan area), the spectra of the two crumb rubbers were also compared (Figure 4).

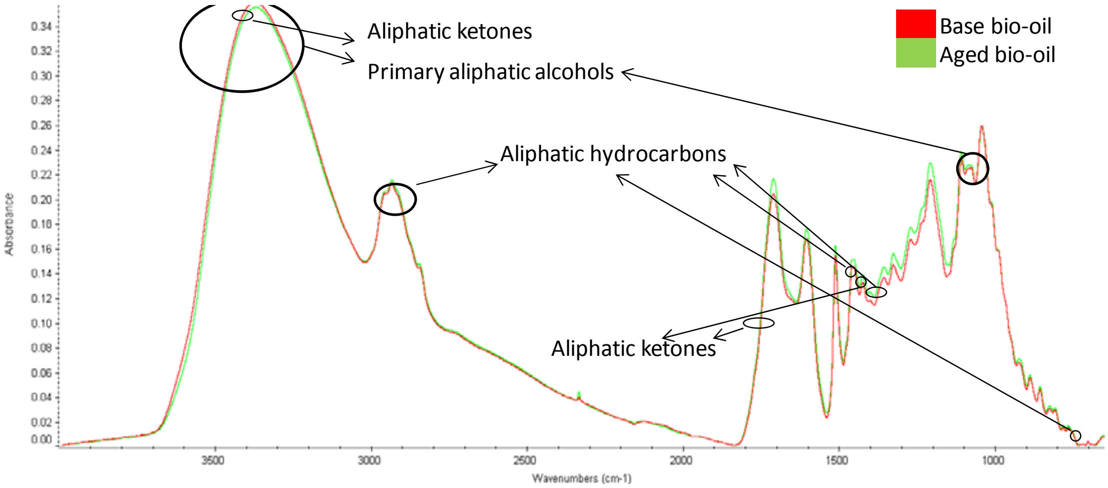


FIGURE 3 Comparative FTIR spectra of the base and aged bio-oils.

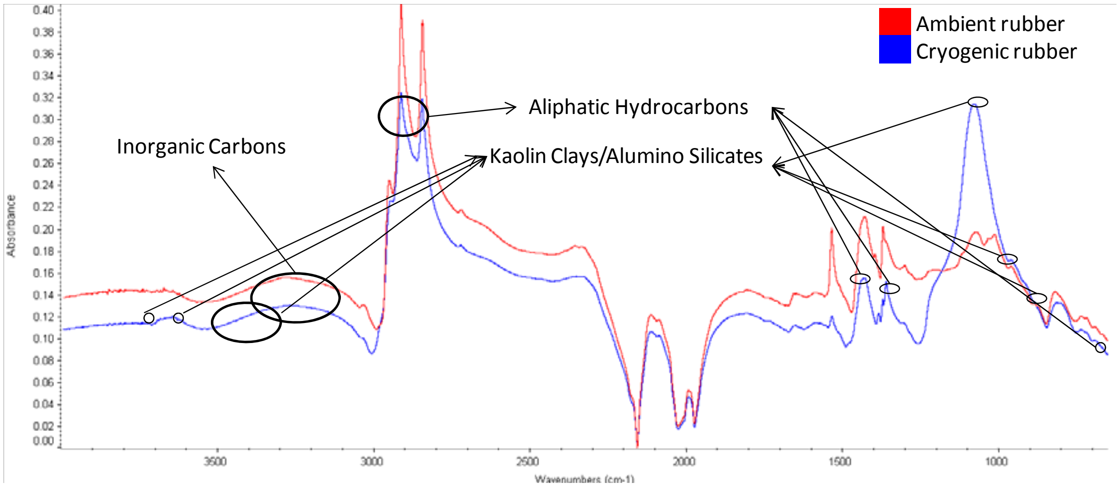


FIGURE 4 Comparative FTIR spectra of the cryogenic and ambient crumb rubbers.

As expected, the FTIR spectra of the two crumb rubbers (Figure 4) present the peaks in the same wave numbers, showing very similar constitutions. The higher difference is observed at a wave number around 1,000 cm^{-1} that can be identified as aliphatic hydrocarbons. The match number computed for the comparison between cryogenic and ambient crumb rubbers is around 1.0 reflecting the small differences between the two materials.

Several materials, including the swelled rubber, were obtained after the biobinder production and the application of the BAS method, namely the biobinder and the Res biobinder that result from the separation of the biobinder. The analysis of these materials can provide very important information about the way that the bio-oil and the different crumb rubber samples interact. Thus, the FTIR spectra of the referred materials were also compared (Figures 5 and 6).

In Figure 5 the spectra of the base bio-oil and the cryogenic crumb rubber were compared with the biobinder B (15% of cryogenic rubber), and Res bio-oil B.

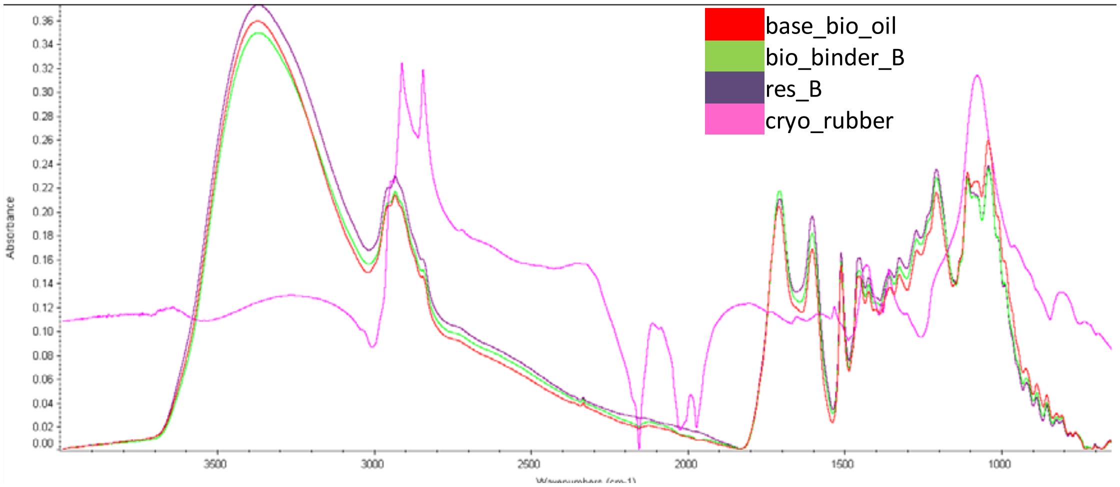


FIGURE 5 Comparative FTIR spectra of the base bio-oil, cryogenic crumb rubber, biobinder B (15% of cryogenic rubber), and Res bio-oil B.

From the analysis of the spectra presented in Figure 5, it is noticeable the transferences of parts of rubber to the bio-oil and from the bio-oil to the rubber.

Between wave numbers 800 and 1,150 cm^{-1} it is clear that some molecules disappear from the bio-oil (this is not because of volatilization as previously observed in Figure 3) meaning that these molecules are most probably diffusing into the rubber particles making them to swell. This region of the spectra can be correlated to the aliphatic hydrocarbons from the rubber, but can also be related to primary aliphatic alcohols from the bio-oil. Since these molecules decreased from the base bio-oil to the biobinder and the residual bio-oil, they are probably the molecules that facilitate the swelling process in the rubber.

These observations are consistent with the results previously reported by Gawel et al. (*13*), that refers a preferential absorption of the compounds with linear aliphatic chains into the rubber and suggests that these components have better skeletal compatibility with the linear polymeric skeleton of the rubber.

Besides the movement of material from the bio-oil to the rubber, there are also many different molecules that migrate from the rubber to the bio-oil, namely the ones between wave numbers 2,800 and 3,000 cm^{-1}, that correspond to aliphatic hydrocarbons that can result from the depolymerization of the unvulcanized rubber. In the regions between 1,200 and 1,500 cm^{-1} and 3,100 and 3,500 cm^{-1}, it is obvious the transfer of some kaolin clays–alumino silicates and inorganic carbon, carbon black, from the rubber to the bio-oil, and this is an expected result since these materials represent about 30% of the tire rubber.

The same approach was adopted to assess the changes in the base bio-oil and the cryogenic crumb rubber reflected in biobinder E (15% of ambient rubber) and Res bio-oil E (Figure 6).

Comparing Figures 5 and 6 it is clear that the interaction between both types of rubber with the bio-oil is similar in all the study regions. Nevertheless, the extension of the transference between the rubber and the bio-oil is more effective when the cryogenic rubber is used.

The comparison between the FTIR spectra is a preliminary approach to the chemical transformations that occur during the biobinder production, and a more profound study is needed. However, the FTIR results are a very useful tool to show that chemical interactions are

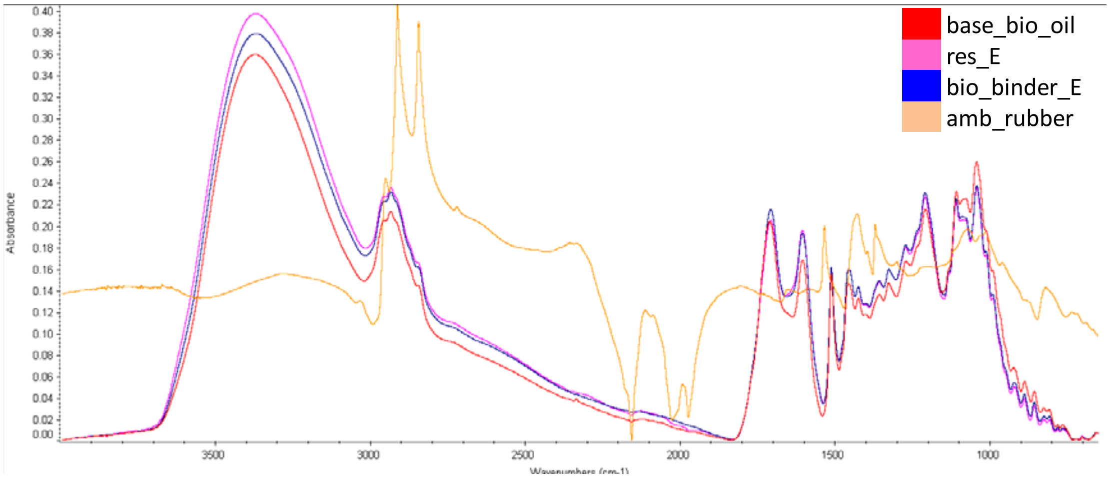


FIGURE 6 Comparative FTIR spectra of base bio-oil, ambient crumb rubber, biobinder E (15% of ambient rubber), and Res bio-oil E.

occurring and contribute to explain the results from the performance grading of the materials presented in the subsequent subsection.

The difference between the materials occurred during the biobinder production, that can be observed in their spectra, were also quantified using the similarity match method. The resulting match values, evaluated as being the variation in the spectrum of the materials compared to the bio-oil, are presented in Figure 7.

The match values presented in Figure 7 show a noticeable difference between the aged bio-oil and the Res bio-oil, demonstrating the chemical changes related to its interaction with the two types of rubber. Other noticeable changes are caused by the RTFO aging test and the PAV test. The greatest dissimilarity is measured in relation to the biobinder, since the rubber is still present in this material.

The match values also show that, as observed in the spectra, the similarity is lower when cryogenic rubber is used and thus indicates a higher interaction between this material and the bio-oil then that observed with the ambient rubber. In addition, the similarity is also related with the rubber concentration in the biobinder, since the materials produced with a lower content of rubber are more similar. These results confirm those of the rubber swelling.

Performance Grade of Biobinders

Since the objective of this work is to develop a biobinder capable of replacing traditional asphalt derived from crude oil, it is necessary to assess the biobinder performance grade and compare it with known paving asphalt. As mentioned previously, the asphalt binder chosen as a control for this study was AAM-1 from the FHWA's Materials Reference Library. AAM-1 is a PG 64-16 and is obtained from a west Texas crude source.

The DSR critical temperatures of the AAM-1 and the biobinders at the various stages of aging used for grading paving asphalt are presented in Table 2.

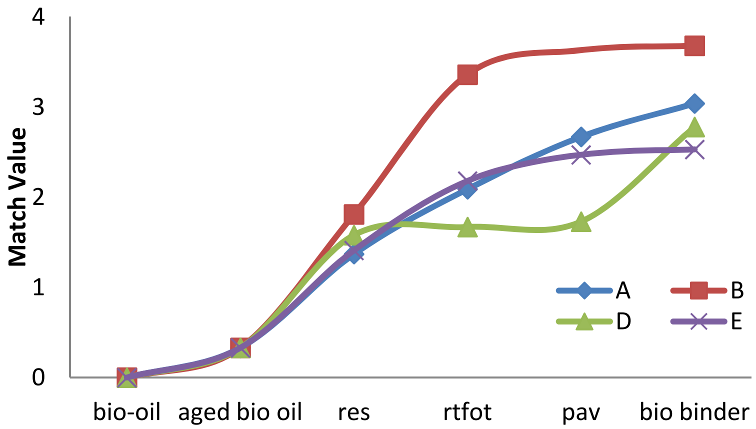


FIGURE 7 Comparative evolution of the match value between the bio-oil and the different materials assessed in this study.

TABLE 2 Critical Temperatures—T_c (°C) for Asphalt AAM-1 and the Biobinders

	Control	Biobinder			
Bio-Oils	**AAM-1**	**A**	**B**	**D**	**E**
Base	67.77	47.87	47.87	47.87	47.87
Aged		49.20	49.20	49.20	49.20
Res		60.51	67.50	62.58	68.12
RTFOT Res	66.68	67.76	70.66	68.06	71.57
PAV Res	20.26	22.43	30.35	26.71	32.60

The performance grade of the biobinder was determined indirectly by the analysis of the Res bio-oil, since that in the biobinder the material that effectively behaves as binder is the Res bio-oil (the swelled rubber particles provide elasticity and toughness at low temperatures but do not have binding characteristics). Furthermore, the difficulties and errors associated with the rheological analysis of heterogeneous materials are known, such as the biobinder or asphalt rubber binders with high volumetric fractions of rubber particles. In fact, the T_c determination is made using parallel plate geometry consisting of a 1- and 2-mm gap, and the particles in those binders would interfere with the movement of the plates because of their size and swelling, thus producing variability in the results. Therefore, the materials presented in Table 2 are the base and aged bio-oils before the biobinder production and the Res bio-oil separated from the biobinder by the BAS method, which was sequentially aged by the RTFOT and PAV methods.

From the results presented in Table 2 is possible infer that the bio-oil presents very similar results to the control asphalt after interacting with rubber, namely at high and medium test temperatures. Considering the high-temperature results for the Res bio-oils, it can be inferred that the high-temperature binder grades are of at least PG 58 and PG 64 for the biobinders containing 10% and 15% cryogenic rubber, respectively, whereas the biobinders containing 10% and 15% ambient rubber produced high-temperature binder grades of at least PG 58 and 64, respectively. These results suggest that the developed material is adequate to be used as a binder in the construction of flexible pavements.

Previous studies pointed out that the principal difficulty to use bio-oils as binders is their behavior at low temperatures (*11*). Figures 8 and 9 present the results from the BBR testing of the four studied biobinders.

The different biobinders were tested in the BBR between –6°C and –24°C or at a performance criteria ranging from –16°C to –34°C. The stiffness values obtained were plotted against the test temperatures for the different binders, as shown in Figure 8. The best performance results at low temperatures were surprisingly obtained for the biobinders produced with the lower percent of rubber (10%), and the binder produced with the cryogenic rubber was better than that obtained with the ambient rubber. The performance of all binders was very good, always below a test temperature of –10°C, which corresponds to a field temperature of –20°C. The biobinder consisting of 10% cryogenic rubber has a low-temperature grade around –34°C.

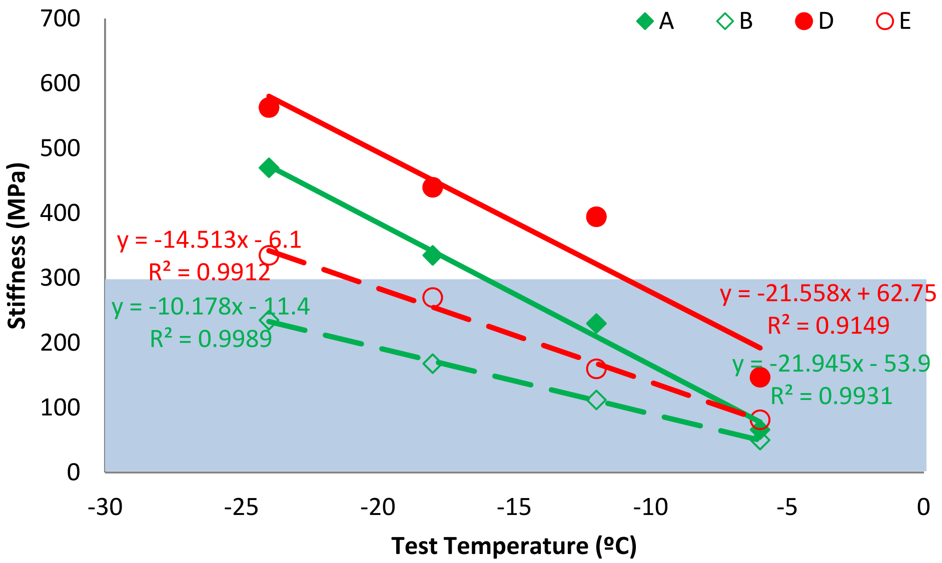


FIGURE 8 Evolution of the stiffness in the BBR test of the four biobinders with the test temperature.

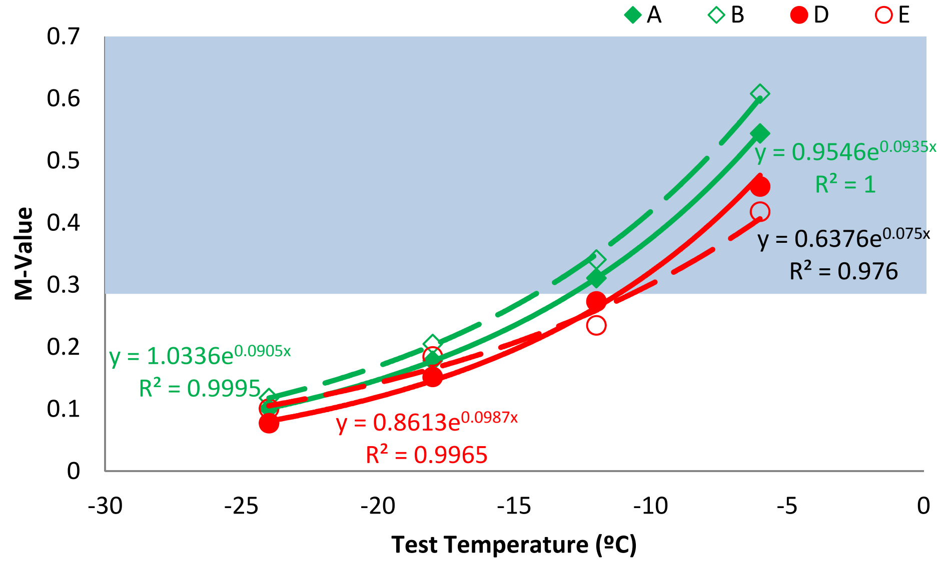


FIGURE 9 The BBR *m*-values of the four biobinders with the test temperature.

Assessing the *m*-values (Figure 9), the very good behavior of the biobinders at low temperatures maintains below the test temperature of –10°C. However, by using this parameter the specifications for the biobinder B are achieved at a maximum test temperature around –15°C (specification temperature of below –22°C). The materials with the best performance in relation to this parameter were the two biobinders produced with the cryogenic rubber. Overall, the *m*-value clearly dominates the low-temperature grade of the biobinders

Summarizing the behavior of the biobinders at low temperatures, it can be stated that all the materials fulfill the specifications for temperatures equal or superior to a field temperature of –20°C.

The continuous grades for the biobinder produced with the ambient rubber are 62.6 to 20.7 and 68.1 to 20.1 for 10% and 15%, respectively. The continuous grades obtained for the biobinder produced with 10% and 15% of cryogenic rubber were 60.5 to 22.4 and 67.5 to 23.7, respectively. Therefore, the overall binder grades of PG 58-22 and PG 64-22 were obtained for the biobinders containing 10% and 15% cryogenic rubber, respectively, whereas the biobinders containing 10% and 15% ambient rubber produced binder grades of PG 58-16 and 64-16, respectively.

CONCLUSIONS

The main conclusions drawn from this study are

- A biobinder consisting of fractionated bio-oil reacted with crumb rubber can produce a binder that is comparable to asphalt binders derived from crude petroleum.
- The bio-oil can successfully react with crumb rubber at 125°C, which is a substantially lower temperature than that used in normal asphalt binders, typically around 185°C.
- The rubber swells approximately three times its weight.
- The cryogenic rubber is more effective than the ambient ground rubber at producing lower temperature grades—the stiffness of the biobinders containing the cryogenic rubber is lower than that of the environmental rubber at low temperatures.
- The FTIR results indicate that the styrene-butadiene rubber from the tire rubber is likely migrating and chemically combining with the fractionated bio-oil.

This paper summarizes the successful development of a biobinder that is derived from a renewable source of material and represents a green technology. Additional work needs to be done using field trials and this will best assist in understanding the oxidative aging mechanisms of these new materials as well as their field performance. Laboratory performance testing of mixtures containing the biobinders is under way and subsequent reporting of these results is anticipated.

REFERENCES

1. Demirbas, M. F., and M. Balat. Recent Advances on the Production and Utilization Trends of Biofuels: A Global Perspective. *Energy Conservation and Management*, Vol. 47, 2006, pp. 2371–2381.
2. Mohan, D., C. U. Pittman, and P. H. Steele. Pyrolysis of Wood/Biomass for Bio-Oil: A Critical Review. *Energy and Fuels*, Vol. 20, No. 3, 2006, pp. 848–889.
3. Williams, R. C., J. Satrio, M. Rover, R. C. Brown, and S. Teng. Utilization of Fractionated Bio-Oil in Asphalt. Presented at 88th Annual Meeting of the Transportation Research Board, Washington, D.C., 2009.
4. Fini, E. H., S.-H. Yang, and S. Xiu. Characterization and Application of Manure-Based Biobinder in Asphalt Industry. Presented at the 89th Annual Meeting of the Transportation Research Board, Washington, D.C., 2010.

5. You, Z., J. M. Beale, H. E. Fini, S. W. Goh, and B. Colbert. Evaluation of Low Temperature Binder Properties of Warm Mix Asphalt, Extracted and Recovery RAP and RAS, and Bioasphalt. *Journal of Materials in Civil Engineering*, 2011.
6. Diebold, J. P., A. Lilley, K. Browne, R. R. Walt, D. Duncan, M. Walker, J. Steele, M. Fields, and T. Smith. Method and Apparatus for Automated, Modular, Biomass Power Generation. Community Power Corporation, EP1896368, Patent, 2008. Available at http://www.freepatentsonline.com/EP1896368A2.html. Accessed June 26, 2009.
7. Bridgwater, A. V., and M. L. Cottam. Opportunities for Biomass Pyrolysis Liquids Production and Upgrading. *Energy Fuels*, Vol. 6, No. 2, 1992, pp.113–120.
8. Oasmaa, A., S. Czernik, D. K. Johnson, and S. Black. Stability of Wood Fast Pyrolysis Oil. *Biomass Bioenergy*, Vol. 7, 1999, pp.187–192.
9. Demirbas, A. Conversion of Cornstover to Chemicals and Fuels. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, Vol. 30, No. 9, 2008, pp. 788–796.
10. Mullen, C. A., and A. A. Boateng. Chemical Composition of Bio-Oils Produced by Fast Pyrolysis of Two Energy Crops. *Energy Fuels*, Vol. 22, No. 3, 2008, pp. 2104–2109.
11. Raouf, M. A. Development of Non-Petroleum Binders Derived from Fast Pyrolysis Bio-Oils for Use in Flexible Pavement. PhD thesis. Iowa State University, 2010.
12. Hamed, G. R. *Materials and Compounds. Engineering with Rubber: How to Design Rubber Components.* Alan N. Gent, Hanser Publishers, Germany, 1992.
13. Gawel, I., R. Stepkowski, and F. Czechowski. Molecular Interactions Between Rubber and Asphalt. *Industrial & Engineering. Chemistry Research*, Vol. 45, No. 9, 2006, pp. 3044–3049.
14. Airey, G. D., M. M. Rahman, and A. C. Collop. Absorption of Bitumen into Crumb Rubber Using the Basket Drainage Method. *International Journal of Pavement Engineering*, Vol. 4, No. 2, 2003, pp. 105–119.
15. Peralta, J., H. M. R. D. Silva, A. V. Machado, J. C. Pais, P. A. A. Pereira, and J. B. Sousa. Changes in Rubber Due to its Interaction with Bitumen When Producing Asphalt Rubber. *International Journal of Road Materials and Pavement Design*, Vol. 11, No. 4, 2010, pp. 1010–1031.

Organo Montmorillonite Nanoclay

Alternative Modifier to Sustain Durability of Asphalt Pavement

G. Liu
M. F. C. van de Ven
A. A. A. Molenaar
Delft University of Technology

S. P. Wu
Wuhan University of Technology

Three types of montmorillonite (Mt) clay (one natural and two organo) with 4 wt% were used to modify bitumens with different penetration grades. X-ray diffraction (XRD) was employed to observe structures of Mt in bitumen. Rolling thin film oven testing (RTFOT) and pressure-aging vehicle (PAV) methods were used to simulate the short-term and long-term aging on base and Mt-modified bitumens, respectively. XRD results showed an intercalated structure of organo Mt in the bituminous matrix. Results indicated that organo Mt improves the short-term aging resistance of base bitumen. The barrier properties of Mt layers hindering the penetration of oxygen are the main reason for this improvement. Meanwhile, the reduction of volatilization of the oily components of bitumen because of these barrier properties can be another reason. However, less effective aging improvement was observed after PAV results because of tough conditions and consequently a certain degree of accumulation on basal spacing of Mt. However, this accumulation will not happen under the conditions in the field. Because of barrier function and stable physicochemical properties, organo Mt can be an alternative to modifiers used in the bitumen to sustain the durability of asphalt pavements.

INTRODUCTION

In modern industrial society, bitumen is manufactured by the distillation process of crude oil in refineries and has been widely used in the construction of asphalt pavements all over the world. To stabilize the stone aggregate skeleton in asphalt pavement, mortar consisting of bitumen, filler, and sand at a certain ratio acts as a real glue in the asphalt mixture. Bitumen is a viscoelastic material and makes the asphalt pavement flexible and comfortable.

In practice, the properties of bitumen change during its service life because of vehicle loads and environmental factors (*1*, *2*). At high temperatures, low frequency of loading, bitumen could become soft with a low stiffness and susceptible to permanent deformation. As a complex mixture of aliphatic, aromatic, and naphthenic hydrocarbons, bitumen easily gets aged because of the diffusion of oxygen and ultraviolet radiation. Repeated loads will result in decreasing strength because of fatigue. Rainwater can influence the adhesion between bitumen and the aggregate and the brittleness of bitumen at low temperatures often causes thermal cracking. All these factors can lead to failure of the asphalt pavement.

On the other hand, society's development demands better-performing pavements as the number and axle loading of vehicles increase year by year. Good structural design and high construction quality are necessary to provide safety and comfort to the road user. The use of modified bitumen is an important solution to reduce the frequency of maintenance and sustain the pavement's durability. According to practical needs and requirements on site, different modifiers are available to improve properties of the bitumen. For example, improvements in deformation resistance can be achieved using thermoplastic polymers and rubbers, as well as some chemicals, such as sulphur. Thermoplastic elastomers could improve the thermal cracking and fatigue resistance. Hydrated lime and some antioxidants could increase the aging resistance and some adhesion improvers are available in the market to reduce moisture damage (*3*).

In recent decades, Mt nanoclay, a member of the smectite family, has been successfully used to modify polymers. As shown in Figure 1, Mt is a layered silicate mineral with a 2:1-type layer structure, two tetrahedrals sandwiching one octahedral (*4*, *5*). The single Mt layer has a thickness of around 1 nm and a cross-sectional area of 100 nm^2. There are some hydrated cations, such as Na^+, residing between the layers. To make the Mt more compatible with the polymer, some surfactants, such as quaternary ammonium salt, are usually used to modify them in which organic cations will replace the interlayer hydrated cations. In this way, the normally hydrophilic silicate surface becomes organophilic (*6*).

The Mt helps polymer systems form polymer-clay nanocomposites (PCN) in which Mt layers are randomly and homogeneously dispersed at a molecular level in the polymer matrix (*7*, *8*). With only a small amount of Mt, about 1 to 5 wt%, some properties of PCN are superior to those of virgin polymers. This concerns improved mechanical properties, thermal, and chemical resistance, decreased gas and moisture permeability, etc. The first PCN of nylon six-clay hybrid invented in 1985 has to be mentioned (*4*).

Based on the idea of PCN, Mt was adopted in this study to modify the base bitumen with different penetration grades. Structures and ageing properties of Mt-modified bitumen were investigated.

MATERIALS

Three types of Mt clay—Mt0, Mt1, and Mt2—were used in this study, which were provided by Fenhong Clay Chemical Factory, China. Mt0 is the only inorganic clay, with Na^+ cations residing in the interlayer space of Mt. It has a cation exchange capacity of 110 meq/100 g. The other two clays, Mt1 and Mt2, were obtained through organically treating Mt0 with octadecyl trimethyl ammonium salt and benzyl dimethyl hexadecyl ammonium salt, respectively. After the

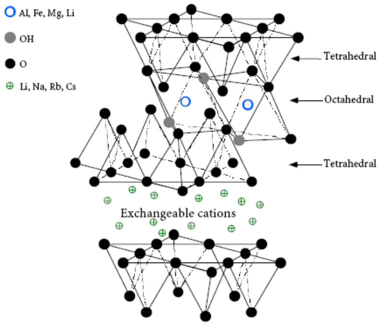
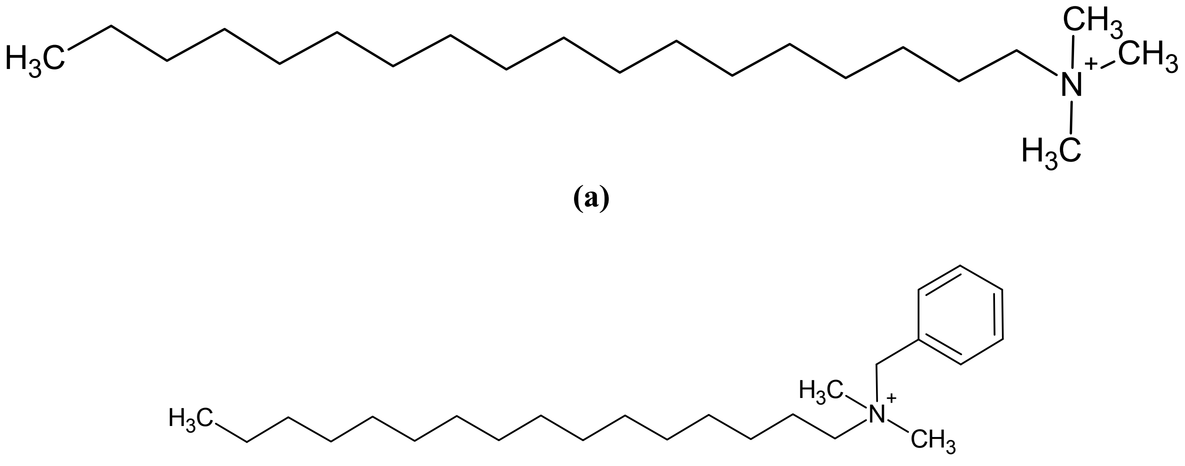


FIGURE 1 Molecular structure of Mt (*9*).



(a)

(b)

FIGURE 2 Schematic molecular structure of quaternary ammonium salt cations: (*a*) octadecyl trimethyl ammonium cation in Mt1 and (*b*) benzyl dimethyl hexadecyl ammonium cation in Mt2.

replacement reaction, the surfactant cations (Figure 2*a* and *b*) replaced Na^+ cations and the inorganic Mt became hydrophobic.

Three types of base bitumen were involved in this study, with normal paving grades, 40/60 (A), 70/100 (B), and 160/220 (C). All of them were provided by Kuwait Petroleum Research & Technology B.V. Empirical rheological properties of the bitumen are given in Table 1.

Three Mts mentioned above were chosen to modify the base bitumens at a certain mass content of 4%. All samples were coded and the codes are listed in Table 2. The details of the modification process have been published before by Liu and Wu et al. (*10*).

TABLE 1 Empirical Rheological Properties Before and After Short- and Long-Term Aging

Bitumens	Penetration[a] @ 25°C (0.1 mm)			Softening Point[b] (°C)		
	Fresh[c]	RTFOT[d]	PAV[e]	Fresh	RTFOT	PAV
A (40/60)	42	27	17	50.0	55.4	61.6
B (70/100)	77	47	28	46.0	51.2	57.2
C (160/220)	171	100	46	38.4	44.2	52.0

NOTE: PAV is performed after RTFOT.
[a] and [b] were done according to European standards, EN 1426 and EN 1427, respectively.
[c] Properties of the virgin bitumen.
[d] Properties of the bitumen after aging in the RTFOT (EN 12607-1).
[e] Properties of the bitumen after PAV test at 100°C (EN 14769).

TABLE 2 Codes of Modified Bitumens

Codes	Base Bitumen	Nanoclay Type
A + 4% Mt1	A	Mt1
A + 4% Mt2		Mt2
B + 4% Mt0	B	Mt0
B + 4% Mt1		Mt1
B + 4% Mt2		Mt2
C + 4% Mt1	C	Mt1
C + 4% Mt2		Mt2

TEST METHODS

X-Ray Diffraction

In this study, a D/Max-RB diffractometer was adopted to characterize the basal spacing of Mt. The X-ray tube in the apparatus produces X-rays with a certain wavelength (λ) and scans the surface of the specimen which contains crystal materials at different incident angles. The constructive interference of X-ray is recorded by the detector when the lower beam traverses an extra length of $2d\sin\theta$ which is equal to an integer multiple of the wavelength (λ) of the radiation. This phenomenon can be expressed by Bragg's law, as follows:

$$2d\sin\theta = n\lambda \tag{1}$$

where

d = interplanar distance, specifically referring to d_{001} in this study;
n = an integer; and
θ = angle between the incident ray and the scattering planes.

In this test, Cu–Kα radiation (40 kV and 50 mA) was used with $\lambda = 0.15406$ nm and 2θ ranging from 0.5° to 10° at a speed of 3°/min. To make the specimen, hot liquid bitumen was poured on an aluminum holder (Figure 3, right) lying on silicone paper. After cooling down to the room temperature, a specimen with a clear and smooth surface (Figure 3, left) was obtained. This surface was exposed to the X-ray radiation during the test.

Aging Method and Evaluation

The RTFOT (EN 12607-1) and the PAV (EN 14769) were used to simulate the short-term and long-term aging of bitumen, respectively.

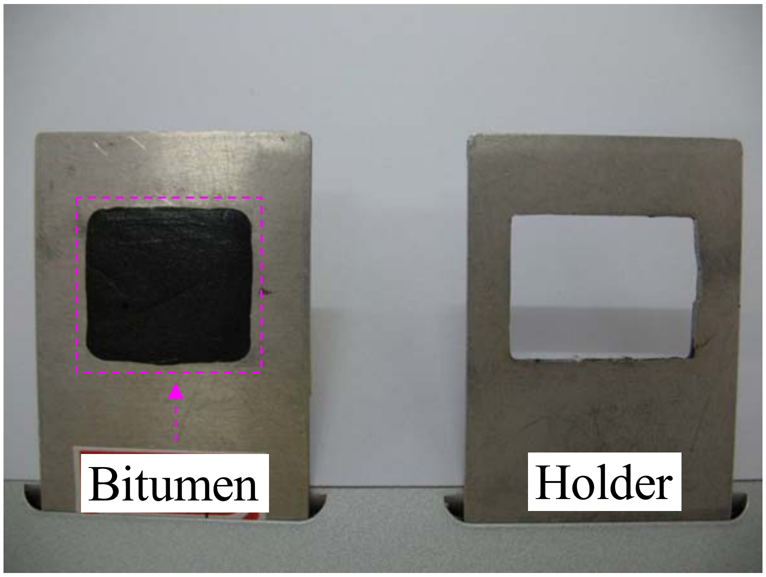


FIGURE 3 Bitumen specimen used for XRD test.

The empirical rheological properties, penetration (EN 1426) are used to evaluate the hardening of bitumen because of aging (*11*), as follows:

$$\text{Retained penetration} = \frac{\text{Penetration after aging}}{\text{Penetration before aging}} \tag{2}$$

Although the measurement of empirical rheological properties did reflect the aging properties of base and modified bitumens, it was not possible to apply a certain factor in comprehensively characterizing the aging behavior. A fundamental method was recommended in which the aging was characterized by the aging index (*AI*) defined as:

$$AI = \frac{\left|G^*_{aged}\right|}{\left|G^*_{fresh}\right|} \tag{3}$$

where $\left|G^*_{fresh}\right|$ and $\left|G^*_{aged}\right|$ are the complex modulus of the bitumen before and after artificial aging, respectively.

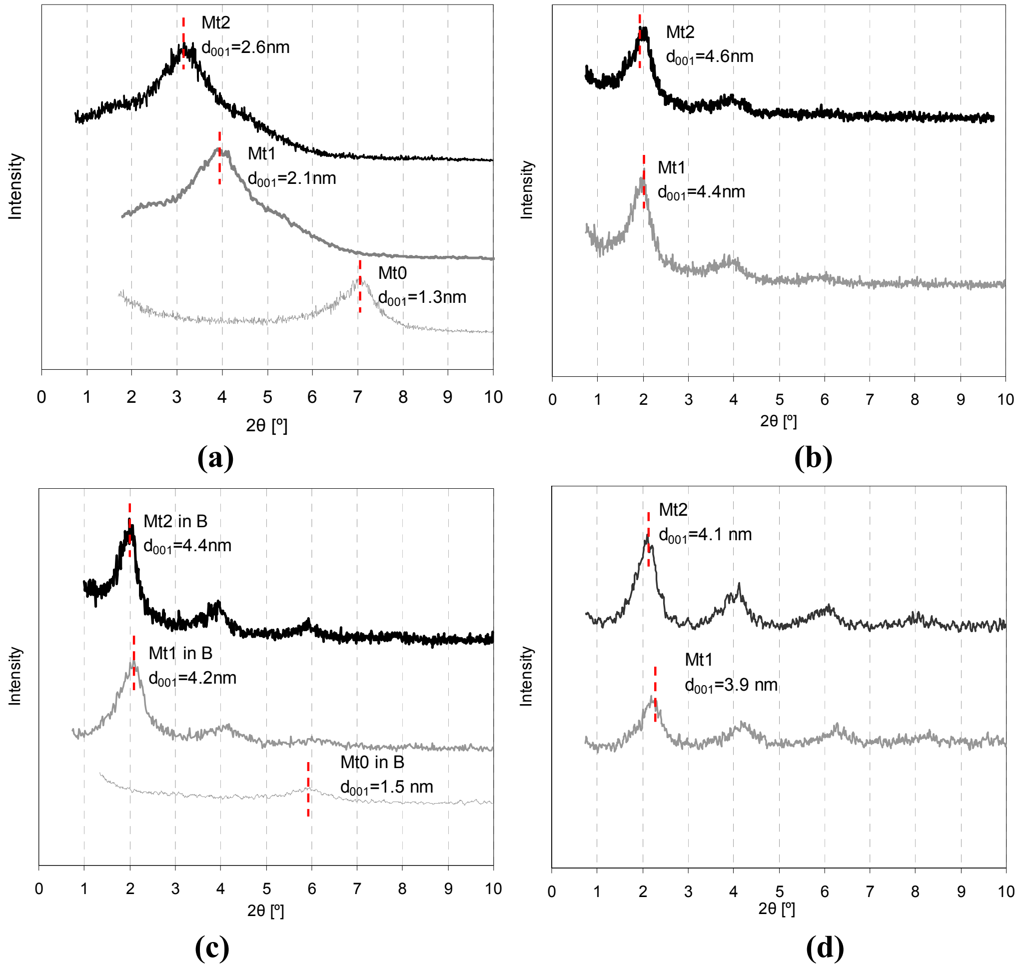
RESULTS AND ANALYSES

Structures

As shown in Figures 4*a*–*d*, the basal spacing (d_{001}) of Mt before and after mixing with bitumen were characterized using XRD. After mixing with bitumen, the first diffraction peak in most curves is shifted towards a lower angle which means an increase in d_{001}.

According to Bragg’s law, d_{001} and its increase rate before and after mixing were calculated and the results are given. In Bases A and B, Mt1 and Mt2 had increased in d_{001} with almost a factor of 2. However, they exhibited a relatively small change (46.0% and 37.3%, respectively) in softer Base C. intercalated structures have formed in the three base bitumens. Another important characteristic is that intercalated structures commonly have more, even up to 13 order peaks or reflections in the XRD curve compared with the pure Mt (*12*). The only inorganic Mt0 shows little change in d_{001} which means that it owns an immiscible or a phase separated structure in Base B.

It was mentioned above that the structures of Mt in the matrix depend on the nature of the components used and the method of preparation. Different bitumens and Mts have been used in this study and two structures were formed, the intercalated for organo Mt and the phase separated for inorganic Mt, using the same preparation method. It was indicated that the high-shear mixing method could not result in an exfoliated structure of Mt in the bituminous matrix. The reason could be that the exfoliated structure of Mt with a specific surface area (BET) normally bigger than 100 m^2/g is not stable in the liquid bitumen because of its huge surface energy. The Mt



(a) **(b)**

(c) **(d)**

FIGURE 4 XRD curves of Mts (*a*) before mixing with bitumens; (*b*) in Base A; (*c*) in Base B; and (*d*) in Base C.

layers would automatically gather together to reduce this energy, and consequently stabilize the whole system. This can easily occur when the viscosity of the matrix is low. The smaller d_{001} change of Mt1 and Mt2 in the softer Base C also reflects the influence of the viscosity or the state of the matrix on the Mt structures.

Synthesis methods for nanocomposites mainly include solution intercalation, melt intercalation, roll milling, in situ polymerization, and high-shear mixing (*7*). High-shear mixing is most accessible to prepare bituminous materials not only in the lab, but also in the factory. To achieve an exfoliated state of organo Mt, two other physical methods, melt intercalation and roll milling, are recommended for future research. The matrixes in these methods are close to solid, and the silicate layers can easily get exfoliated and stay stable.

Aging and Evaluation

Figure 5 shows the retained penetration versus the viscosity values for the base and modified bitumens. The viscosity at 150ºC which was obtained based on EN 13702-1 is used in this figure. Although it should be more reasonable to adopt the viscosity at the testing temperature of 163ºC, it was regarded that the viscosities at these two temperatures were very close and the difference between them would not influence the trend of test results.

For base bitumens, soft C shows a low retained penetration, hard A has a high retained penetration, and B is just in the middle. The relationship between retained penetration and viscosity at 150ºC shows a linear trend. This proves that the viscosity of bitumen can influence the ageing effect of RTFOT.

With respect to the modified bitumens, their retained penetration increases with increasing viscosity. However, these data points in this figure were not on the trend line of base bitumens; they are located above this line. This means that the improvement of aging resistance was not only because of the increase of viscosity, but also because of the enhancement of Mt particles in the aging behavior of bitumen. Especially, Mt1 contributed a little to the change of the viscosity of Base B, but a relatively high increase in its retained penetration.

To fundamentally understand the aging properties of modified bitumens, the aging index (*AI*) are shown in Figure 6. As indicated, all *AI* curves of Bases A, B, and corresponding modified bitumens show a similar trend. A high *AI* value means a high degree of bitumen aging. The curve of Base A was located at the top of the clusters in Figure 6*a* and was followed by the curves of A + 4% Mt2 and A + 4% Mt1, respectively. This implies that Base A has a relatively poor aging resistance and the addition of Mt can change this behavior. In comparison, Mt1 gave more improvement of the aging behavior of Base A more than Mt2.

As indicated in Figure 6*b*, the curve of B + 4% Mt0 is very close to that of the base. This indicates comparable aging properties between them. Generally, the curves of B + 4% Mt1 and B+4%Mt2 were located at the bottom of the graph, which implies improved aging behavior. However, it is difficult to compare the behavior of B + 4% Mt1 with B + 4% Mt2 because their curves crossed between 20ºC and 30ºC. This may be because of different temperature susceptibility of the modified bitumens.

As shown in Figures 7*a* and *b*, the curves for all modified bitumens after PAV aging became closer to those of Base A and B. This implies a less effective improvement in the long-term aging resistance. The reason for this could be that the oxygen under high pressure of 2.1 MPa and at the temperature of 100ºC weakens the barrier effect of Mt and it becomes easier for the oxygen to penetrate the bitumen film.

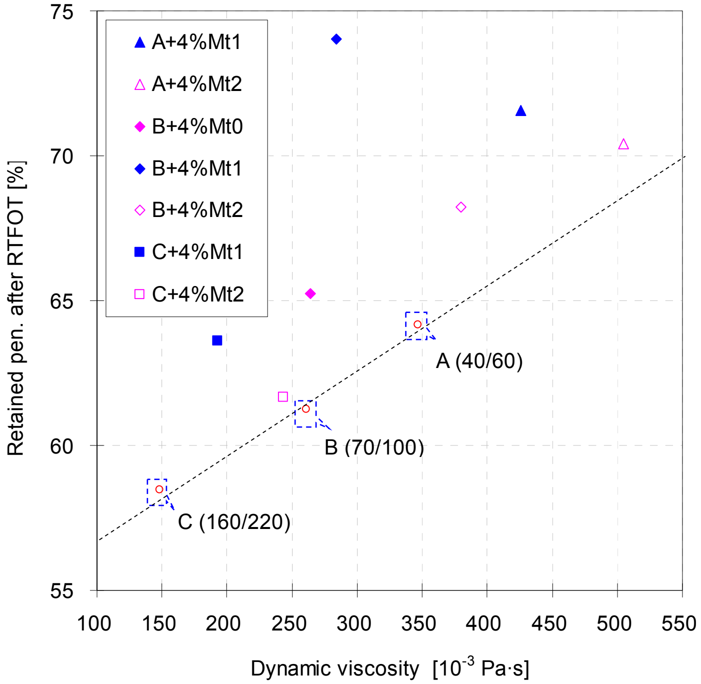
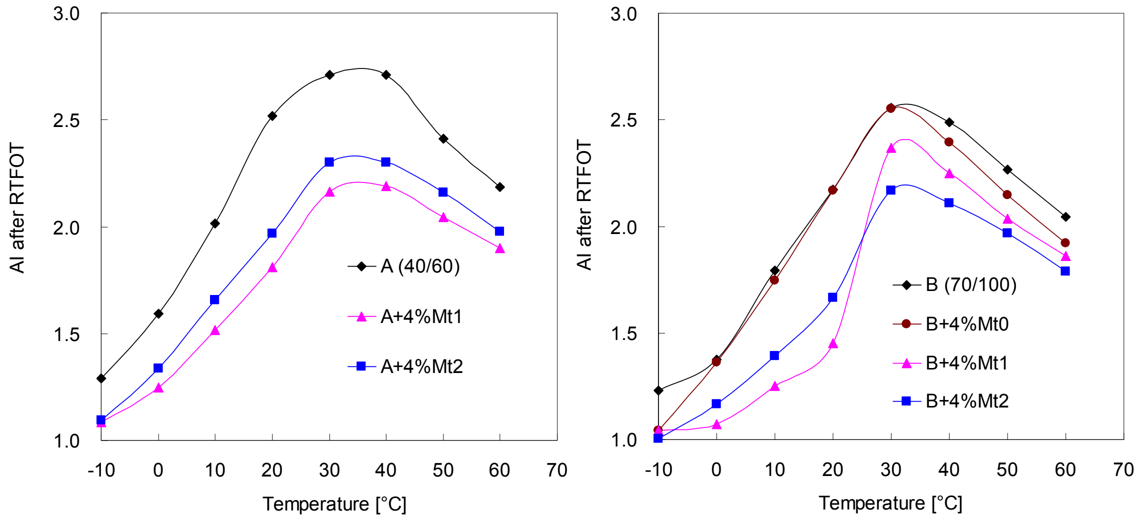
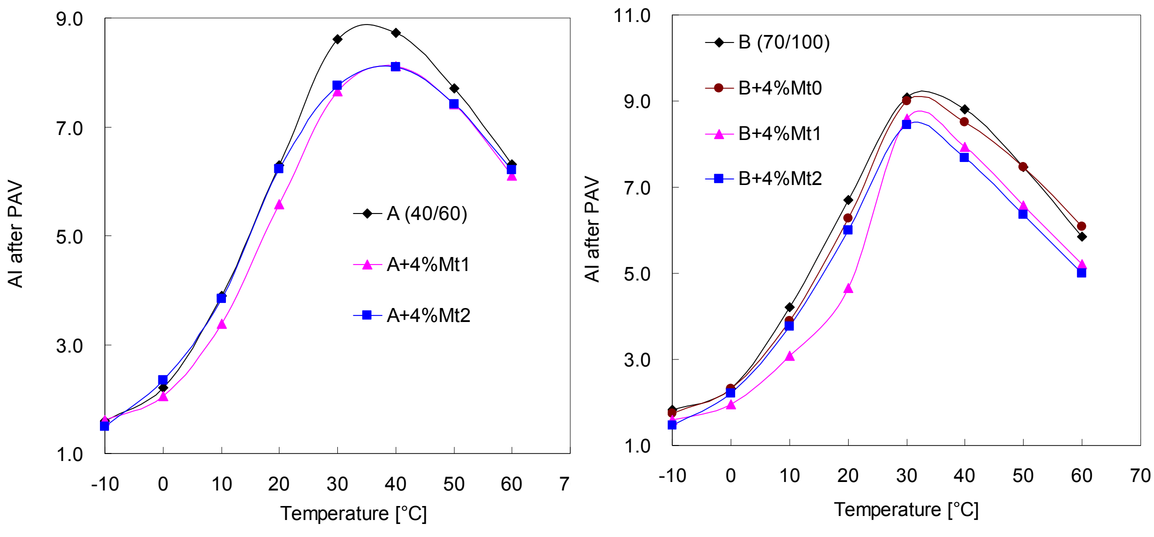


FIGURE 5 Retained penetration versus dynamic viscosity at 150ºC for base and modified bitumens.



(a) **(b)**

FIGURE 6 RTFOT aging curves for (*a*) Base A and its modified bitumens and (*b*) Base B and its modified bitumens.



(a) **(b)**

FIGURE 7 PAV aging curves for (*a*) Base A and its modified bitumens and (*b*) Base B and its modified bitumens.

The improvement of the short-term aging behavior of the modified bitumen could be because of the high surface area of Mt and, consequently, its barrier property. This property not only hinders the penetration of the oxygen molecules, but also increases their average path length (*13*). This interpretation is illustrated in Figure 8. For bituminous materials, another reason can be that the volatilization of the oily components decreases because of this barrier property. Although less-effective aging improvement was observed from the PAV results, it is believed that the long-term aging behavior can be enhanced in the field because the temperature and the air pressure are low compared to the test conditions. The function of Mt could work well during the service life because of its stable physicochemical properties.

As observed from the aging curves, the *AI* value of base and modified bitumens is more sensitivity at a temperature range between 20ºC and 40ºC. To build a relationship with the retained penetration at the same temperature, a median *AI* value at 25ºC was obtained based on

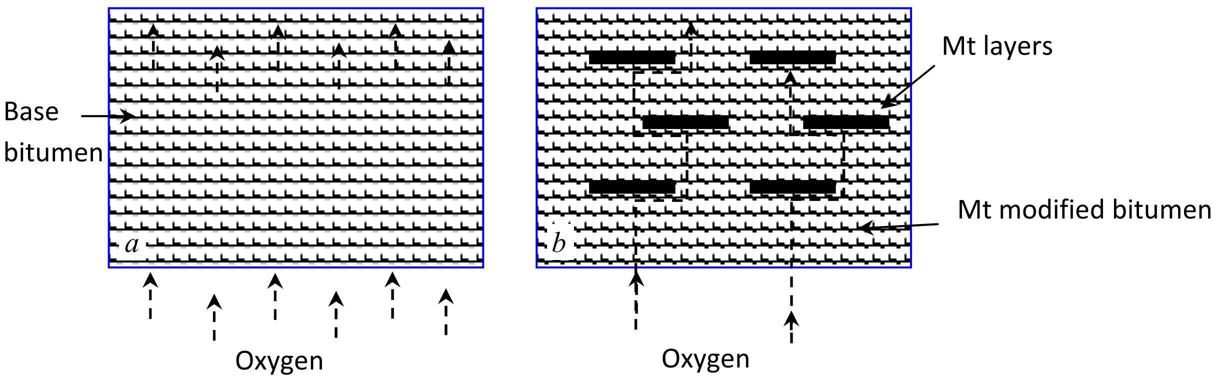


FIGURE 8 Schematic of the penetration of oxygen in (*a*) the base and (*b*) Mt-modified bitumen.

the values at 20ºC and 30ºC. As shown in Figure 9, there is a linear relationship between the two evaluation methods for RTFOT and PAV, respectively. It is logical that the trend lines have a negative slope because a low *AI* value and a high retained penetration both mean good aging resistance. As observed, the trend line for the PAV was steeper than that for the RTFOT. It was shown that the PAV aging reduced the bitumen's sensitivity to the penetration. Therefore, it is more suitable to characterize aging after PAV with the *AI* (the ratio of $\left|G^*_{aged}\right| / \left|G^*_{fresh}\right|$) instead of retained penetration.

Structure Change Because of Aging

XRD was performed to observe the change of Mt's morphology because of aging. As shown in Table 3, the XRD peak for B + 4% Mt1 after RTFOT was the same as that for the fresh. However, it moved a little towards a higher 2θ value after PAV aging. As indicated, basal spacing d_{001} shrank from 4.24 to 4.11 nm, which means a decrease in d_{001} by 6.6% from RTFOT to PAV. With respect to B + 4% Mt2, its peak began to shift earlier after RTFOT, and its peak band after PAV even becomes smaller. As indicated in this table, d_{001} of B + 4% Mt2 after RTFOT and PAV aging reduced by 4.4% and by 9.4%, respectively.

Because the Mt is highly dispersed into the bitumen after high shear mixing, its surface area becomes very large. Therefore, the Mt layers would automatically accumulate to reduce the surface energy in the bitumen at a liquid state. Especially during the PAV test with a high air pressure (2.1 MPa), this activity takes place easier. Therefore, there is always a certain degree of shrinkage of d_{001} after PAV aging. The accumulation of Mt would reduce its scale effect and negatively influence its contribution to aging resistance of bitumen. This is one of the reasons that we see a less effective improvement in the PAV aging resistance of modified bitumen.

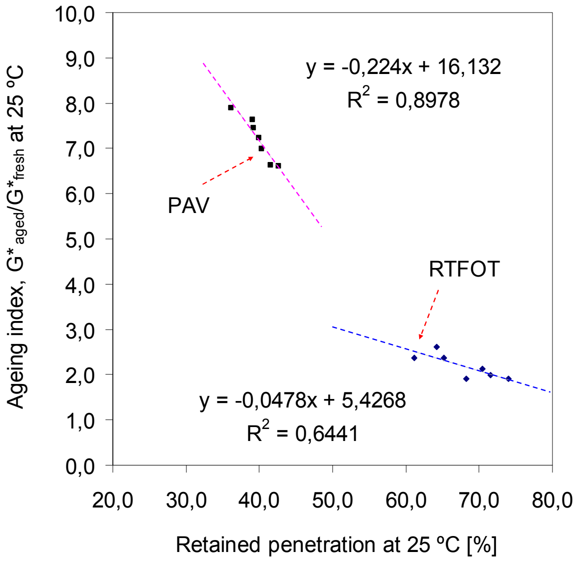


FIGURE 9 Relationship between aging index (the ratio of $\left|G^*_{aged}\right| / \left|G^*_{fresh}\right|$) and retained penetration at 25ºC after RTFOT and PAV aging, respectively.

TABLE 3 Basal Spacing (d_{001}) of Mt in the Bitumen and Its Change Because of Aging

Materials	2θ (°)	Basal Spacing (d_{001}) (nm)	Increment Rate in d_{001} (%)[a]
Mt1	4.20	2.10	—
Fresh_B + 4% Mt1	2.08	4.24	101.9
RTFOT_B + 4% Mt1	2.08	4.24	101.9
PAV_B + 4% Mt1	2.15	4.11	95.3
Mt2	3.14	2.81	—
Fresh_B + 4% Mt2	2.02	4.37	55.4
RTFOT_B + 4% Mt2	2.08	4.24	51.0
PAV_B + 4% Mt2	2.15	4.11	46.0

[a] Increment rate here is based on d_{001} of the pure Mt clay.

CONCLUSIONS

- XRD results indicated that an intercalated structure for organo Mt was formed in the three base bitumens. A phase separated structure was found when natural Mt was used in one base bitumen
- Organo Mt improves the short-term aging resistance of base bitumen. The barrier properties of Mt layers hindering the penetration of oxygen are the main reason for this improvement. Meanwhile, the reduction of volatilization of the oily components of bitumen because of these barrier properties can be another reason.
- Less-effective aging improvement was observed after PAV results because of tough conditions and consequently a certain degree of accumulation on basal spacing of Mts. However, this accumulation will not happen under the conditions in the field. Therefore, the long-term aging behavior of bitumen can be enhanced during the service life
- Because of barrier function and stable physicochemical properties, organo Mt can be an alternative to modifiers used in the bitumen to sustain the durability of asphalt pavements.

REFERENCES

1. Petersen, J. C. Chemical Composition of Asphalt as Related to Asphalt Durability: State of the Art. In *Transportation Research Record 999*, TRB, National Research Council, Washington, D.C., 1984, pp. 13–30.
2. Halstead, W. J. Relation of Asphalt Chemistry to Physical Properties and Specification. *Journal of the Association of Asphalt Paving Technologists*, Vol. 54, 1985, pp. 91–117.
3. Read, J., and D. Whiteoak. *The Shell Bitumen Handbook*. Thomas Telford Ltd., London, 2003.
4. Okada, A., and A. Usuki. Twenty Years of Polymer Clay Nanocomposites. *Macromolecular Materials and Engineering*, Vol. 291, No. 12, 2006, pp. 1449–1476.
5. Bergaya, F., B. K. G. Theng, and G. Lagaly. *Handbook of Clay Science*. Elsevier Science Ltd., 2006.
6. Giannelis, E. P. Polymer Layered Silicate Nanocomposites. *Advanced Materials*, Vol. 8, No. 1, 1996, pp. 29–35.
7. Koo, J. H. *Polymer Nanocomposites: Processing, Characterization, and Applications*. McGraw-Hill Professional, 2006.

8. Pinnavaia, T. J., and G. W. Beall. *Polymer-Clay Nanocomposites.* John Wiley & Sons Ltd., Chichester, 2000.
9. Giannelis, E., R. Krishnamoorti, and E. Manias. Polymer-Silicate Nanocomposites: Model Systems for Confined Polymers and Polymer Brushes. *Polymers in Confined Environments,* 1999, pp. 107–147.
10. Liu, G., et al. Influence of Sodium and Organo-Montmorillonites on the Properties of Bitumen. *Applied Clay Science*, Vol. 49, 2010, pp. 69–73.
11. Morgen, P., and A. Mulder. *The Shell Bitumen Industrial Handbook.* Shell Bitumen Publications, London, 1995.
12. Vaia, R. A., et al. New Polymer Electrolyte Nanocomposites: Melt Intercalation of Poly (Ethylene Oxide) in Mica Type Silicates. *Advanced Materials*, Vol. 7, No. 2, 1995, pp. 154–156.
13. Osman, M. A., V. Mittal, and U. W. Suter. Poly (Propylene) Layered Silicate Nanocomposites: Gas Permeation Properties and Clay Exfoliation*. Macromolecular Chemistry and Physics*, Vol. 208, No. 1, 2007, pp. 68–75.

Laboratory Evaluation of Waste Cooking Oil–Based Bioasphalt as Sustainable Binder for Hot-Mix Asphalt

HAIFANG WEN
SUSHANTA BHUSAL
Washington State University

BEN WEN
United Environmental and Energy LLC

In the United States, 96% of roads are surfaced with asphaltic materials. Hot-mix asphalt (HMA) consists of aggregate particles (coarse and fine) that are bonded together by asphalt binder at elevated temperatures. Traditional asphalt binder is residue obtained during the crude petroleum refining process. Increased environmental regulations for new drilling, dwindling existing resources, modifications to the refining process that maximize the fuel quantity while minimizing asphalt residue have increased the cost of asphalt in recent years. To address these challenging problems, industries are seeking an alternative binder to replace or reduce the petroleum-based asphalt used in HMA. The new asphalt binder should be eco-friendly and made from green technology. The sustainability approach taken by the highway industry has led the authors to develop ecologically sound asphalt, called bioasphalt. Research industries are now producing bioasphalt either from biomass or biowaste products (*1–3*). Making bioasphalt from these byproducts can also reduce the need of landfill areas and help mitigate the release of greenhouse gases (*1*, *2*).

Fini et al. (*3*) researched the application and characterization of manure-based bioasphalt in the asphalt industry. A thermochemical liquefaction process was carried out to convert swine manure into bio-oil and the remaining heavy residue was used as an asphalt modifier (i.e., biobinder). They reported that adding swine manure–based bioasphalt improved the low-temperature properties, but compromised the resistance to rutting at high temperatures (*3*).

Williams et al. (*4*) conducted a study on the utilization of fractionated bio-oil in asphalt. Three different sources of biomass (oak wood, switchgrass, and corn stover) were pyrolysed and fractionated to generate biobinder. The electrostatic precipitates of these biomasses were blended with asphalt binder at three different percentages (3%, 5%, and 9%) by the weight of the total binder and characterized in accordance with AASHTO M320. The study found considerable benefits of blending the bio-oil obtained from oak wood and switchgrass with traditional polymer-modified asphalt binders. A chemical composition study shows similarity between bioasphalt and conventional asphalt. To study the engineering behavior of the biobinder, the biobinder was mixed with base binder (petroleum-based asphalt) at three different percentages by the mass of the base binder. The rheological properties of the biomodified binder were determined using the dynamic shear rheometer (DSR) and bending beam rheometer (BBR) tests. The DSR tests showed that the addition of the biobinder increased the rutting parameter ($G^*/\sin \delta$), indicating an increased rutting resistance. The BBR test showed that the addition of the biobinder reduced the *m*-value of the binder. In other words biobinder decreased resistance to the lower thermal temperature. These findings indicated that biobinder can improve the rutting properties while compromising lower thermal performance (*4*).

You et al. (*5*) evaluated low-temperature binder properties using bioasphalt. The bioasphalt was produced from swine waste using the thermochemical liquefaction process. The bioasphalt was blended with a conventional PG 64-22 binder at three different percentages (2%, 5%, and 10%) by the weight of the conventional binder. Both BBR and an asphalt binder cracking device test were carried out to evaluate the low-temperature binder properties. Results showed that an increase in bioasphalt percentage reduced the lower cracking temperature of the biomodified binder. This finding indicated that a blend of bioasphalt and conventional binder can improve the resistance to lower-temperature cracking (*5*).

According to the U.S. Environmental Protection Agency (*6*), approximately 3 billion gallons of waste cooking oil are collected annually from restaurants and fast food establishments in the United States (*6*). Waste cooking oil can be polymerized to produce asphalt. The objective of this study is to evaluate the laboratory performance (fatigue, rutting, thermal cracking, and moisture susceptibility) of waste cooking oil–based bioasphalt in HMA. Both binder and HMA performance tests were carried out by blending the bioasphalt with conventional asphalt and the results are analyzed. The bioasphalt used in this study was provided by United Environmental and Energy, LLC, New York. The bioasphalt was produced from waste cooking oil after undergoing the thermochemical process. The specific gravity of the bioasphalt is 1.54. The three petroleum-based asphalt binders used in the research are PG 58-28, PG 76-22, and PG 82-16. The aggregate type is basalt.

EXPERIMENTS AND RESULTS

Experiments

The bioasphalt was mixed with base asphalt at three different percentages by weight of base asphalt binder. For the PG 58-28 base binder, 30% bioasphalt and 60% bioasphalt were blended by the weight of the base binder. Based on the previous test results, for the PG 82-16 and PG 76-22 binders, the bioasphalt was blended at 10% and 30% by the weight of the base binder. Blending the bioasphalt with the conventional asphalt was carried out using a power mixer to obtain a homogeneous blend of bioasphalt with base binders. PG testing of the blended binder was performed in accordance with AASHTO M320 (*7*). A Malvern Gemini 150 DSR and Applied Testing System BBR machine were used for running the binder tests. Recent studies on asphalt binder has developed further tests to better predict the fatigue and rutting behavior of asphalt pavement (*8*, *9*). Johnson et al. (*8*) found that critical strain energy density obtained from monotonic fracture test correlated well with field fatigue behavior of asphalt pavement. This monotonic constant shear test (displacement controlled) was performed using an 8-mm diameter parallel plate with a gap thickness of 2 mm. A constant shear load was applied to the test specimens until the clear peak failure load was observed. The critical strain energy density (CSED) was then determined by measuring the stress and strain area below the failure stress. Figure 1 presents the typical stress–strain curve of monotonic fracture test. D'Angelo et al. (*9*) found that nonrecoverable creep compliance (J_{nr}) correlated better with the field rutting better than the rutting factor (G*/sin δ) in the Superpave binder specifications, especially for the modified asphalt (*9*). In this test asphalt binder is allowed to shear under creep load for 1 s and then rest for 9 s using 25-mm parallel plate with gap thickness of 1 mm. The test was carried out following the AASHTO TP 70 (*10*).

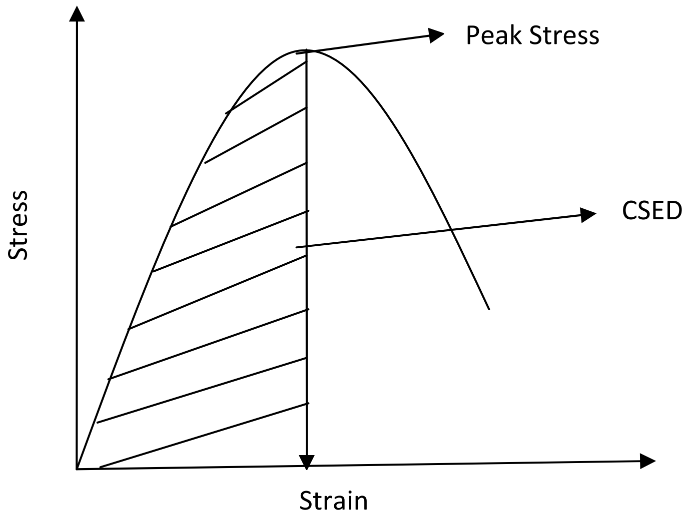


FIGURE 1 Typical stress–strain curve for monotonic fracture test.

For the bioasphalt mixture performance test, HMA mix design using bioasphalt was carried out following the Superpave mix design method (*11*). Single-mix design was used for all the mixes. For the PG 58-28 binder, bioasphalt was added at 0%, 30%, and 60% by weight of base binder. The 0% bioasphalt mix represents the traditional control mix. Based on previous test results on the PG 58-28 base binder blended with bioasphalt, for the PG 82-16 and PG 76-22 binders, bioasphalt was added at 0%, 10%, and 30% by weight of base binder, respectively. The mixing temperature of bioasphalt mixes was 5°C higher than conventional mixes because of the longer mixing time required in order to obtain uniform coating of mix. After mixing, the mixes were oven cured for 2 h prior to compaction. The compaction temperature of the bioasphalt mixes and the control mixes is the same.

Dynamic modulus of HMA is input under level 1 criteria to predict field fatigue and rutting behavior (*12*). Dynamic modulus testing was carried out to determine the stiffness of the mixes with bioasphalt. The test was performed in accordance with the AASHTO TP 79 (*13*). Three replicates were used for each test. To measure the rutting potential of bioasphalt mixes, flow number test was performed. Witczak et al. (*14*) found that flow number of the mixes correlated well with field rutting behavior (*14*). The flow number is the maximum number of cycles required to reach the lowest minimum rate of strain of the specimen. The higher the flow number, the better the mix rutting resistance is. These tests were performed in accordance with the AASHTO TP 70-10 (*13*).The dynamic modulus test is a nondestructive test and thus the same specimens used for the dynamic modulus testing were used also for the flow number tests. To quantify the fatigue and thermal cracking behavior of bioasphalt mixes indirect tensile test (IDT) was performed in accordance with AASHTO T322 (*15*). Fracture energy (*16*) and fracture work (*17*) obtained from IDT test at intermediate temperature were reported to correlate with field fatigue performances. Higher fracture energy or fracture work indicates better the mix performance against fatigue. The fracture energy represents the area under stress and strain curve below peak stress whereas the fracture work represents the area under load and vertical deformation curve until load reduces to zero. The IDT tests were conducted at 20°C and –10°C for fatigue and thermal cracking, respectively. The rate of displacement loading for the fatigue monotonic fracture IDT test was 50.8 mm per minute (*16*). Fracture energy at the low temperature was also found to predict the thermal cracking behavior of asphalt concrete (*18*). The rate of displacement loading for thermal monotonic fracture IDT test was 12.7 mm per minute (*15*). To measure the moisture damage potential of bioasphalt mixes, moisture susceptibility test was carried out in accordance with AASHTO T283 (*19*). The moisture damage potential was evaluated based on tensile strength ratio (TSR) of mixes. TSR is calculated as average wet strength divided by dry strength of mix.

Results

The Superpave PG test results showed that the addition of bioasphalt in the base binder bumped down the high and low PG of the blended binders. The addition of 30% and 60% bioasphalt in the base binder PG 58-28 reduced the base binder to PG 52-34 and PG 46-40, respectively. The addition of 10% and 30% bioasphalt in the base binder PG 82-16 reduced the base binder to PG 76-24 and PG 70-28, respectively. The addition of 10% and 30% bioasphalt in the base binder PG 76-22 reduced the base binder to PG 76-22 and PG 70-34, respectively. This indicated that by blending bioasphalt with traditional binder, resistance of mixes to rutting was decreased, whereas the resistance to thermal cracking was increased. The PG results agree to that of Fini et al. (*3*) and You et al. (*5*). Further binder evaluation test using monotonic constant shear test results showed that addition of bioasphalt in the base binder reduced the fatigue failure strength and CSED. Table 1 presents the monotonic constant shear test results. The lower CSED of blended bioasphalt binder was because of lower shear strength compared to conventional binder whereas the failure strain of bioasphalt binder was higher than conventional binder. Table 2 presents the MSCR test results for bioasphalt blended with three conventional binders. Results show that the addition of bioasphalt in the mix increased the nonrecoverable creep compliance (J_{nr}) except for 60% bioasphalt blended with PG 58-28. Overall, the MSCR test results indicated that adding bioasphalt increased susceptibility to rutting. This findings agrees with G*/sin δ obtained from Superpave PG test.

Figures 2, 3, and 4 present the dynamic modulus master curves of the three bioasphalt mixes. To generate the dynamic modulus master curves, the dynamic moduli at each temperature were shifted horizontally to the reference temperature based on the time–temperature

TABLE 1 Fatigue Test Result of Bioasphalt Blended with Conventional Binders

PG	Shear Rate (per second)	Bioasphalt (%)	Failure Strength (Pa)	Fracture Energy (Pa)
58-28	3	0	553,310	544,612
58-28	3	30	406,920	372,504
58-28	3	60	59,124	162,137
82-16	0.1	0	511,940	1,738,025
82-16	0.1	10	239,650	780,239
82-16	0.1	30	48,837	139,705
76-22	0.05	0	1,329,600	1,276,480
76-22	0.05	10	1,036,400	1,144,723
76-22	0.05	30	579,840	658,054

TABLE 2 MSCR Test Results of Bioasphalt Blended with Conventional Binder

PG	Bioasphalt (%)	Stress Level (Pa)	J_{nr}(1/Pa)
58-28	0	100	0.94
58-28	0	3,200	1.14
58-28	30	100	1.24
58-28	30	3,200	1.60
58-28	60	100	0.50
58-28	60	3,200	1.07
82-16	0	100	1.02
82-16	0	3,200	2.17
82-16	10	100	1.30
82-16	10	3,200	3.61
82-16	30	100	1.94
82-16	30	3,200	7.04
76-22	0	100	0.94
76-22	0	3,200	1.36
76-22	10	100	1.45
76-22	10	3,200	2.43
76-22	30	100	2.37
76-22	30	3,200	4.70

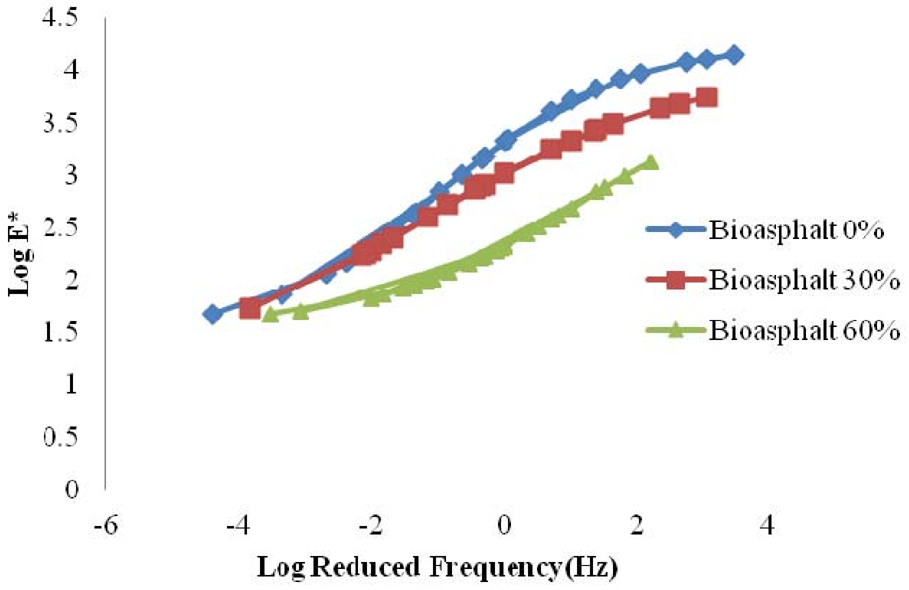


FIGURE 2 Dynamic modulus master curves of bioasphalt with PG 58-28.

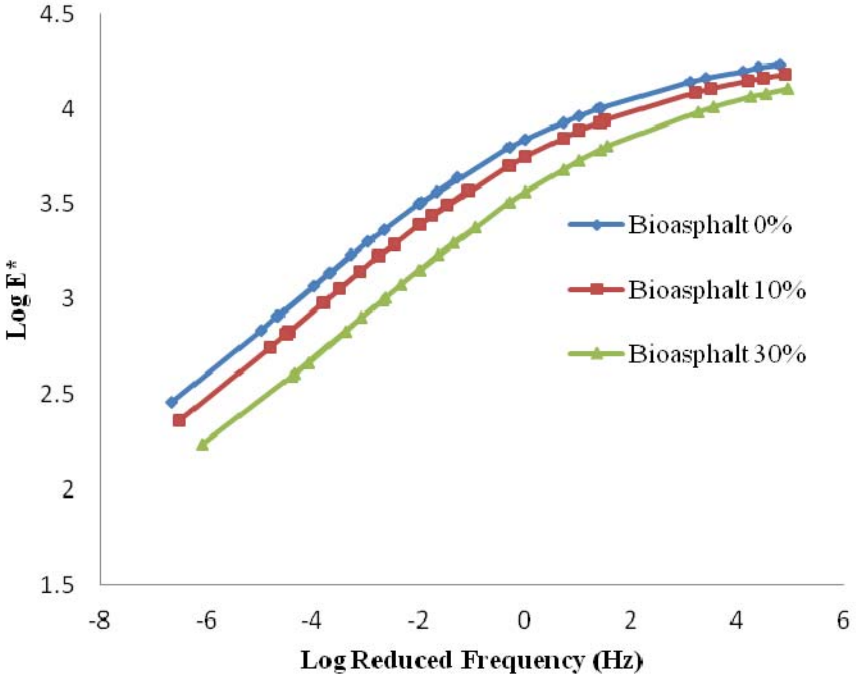


FIGURE 3 Dynamic modulus master curves of bioasphalt with PG 82-16.

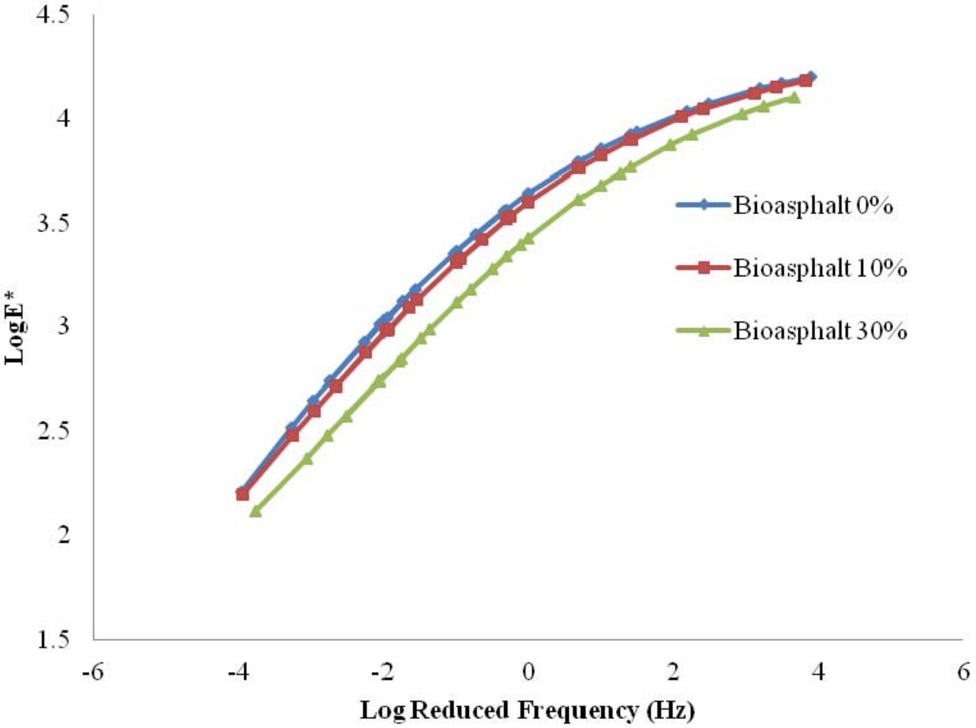


FIGURE 4 Dynamic modulus master curves of bioasphalt with PG 76-22.

superposition principle. The master curves were then fitted using the sigmoidal model. The dynamic modulus master curves indicated that increasing the percentage of bioasphalt in the mix decreased the stiffness of the mixes. Figures 5, 6, and 7 display the flow numbers of the bioasphalt mixes. The figures indicated that the addition of bioasphalt in the mix reduced the rutting resistance of the mixes, as evidenced by the reduced flow numbers. These results are consistent with binder rutting test results based on nonrecoverable creep compliance (J_{nr}) and Superpave G*/sin δ.

Table 3 presents the IDT fatigue test results for all three bioasphalt mixes. The test results showed that the addition of bioasphalt reduced the failure strength, fracture energy (FE), and fracture work density of the mixes. This indicated that addition of bioasphalt reduced the resistance to fatigue cracking at intermediate temperatures. These results also agree with binder fatigue results obtained based on the monotonic constant shear load. Table 4 presents the IDT thermal test results for the bioasphalt mixes. Results showed that increasing the bioasphalt percentage increased the FE of the mix at low temperature, indicating an increased resistance to low-temperature thermal cracking. The increase in FE at low temperature is because of increased ductility of bioasphalt mixes at lower temperature. Figures 8 and 9 show the TSR of the bioasphalt mixes. The test results showed that all the bioasphalt mixes passed the AASHTO minimum TSR requirement, which is 80%. After visual inspection of broken samples, no sign of asphalt stripping was noticed. The effects of bioasphalt on moisture susceptibility depend on the individual mix and bioasphalt percentage. No general conclusions on the effects of bioasphalt can be drawn.

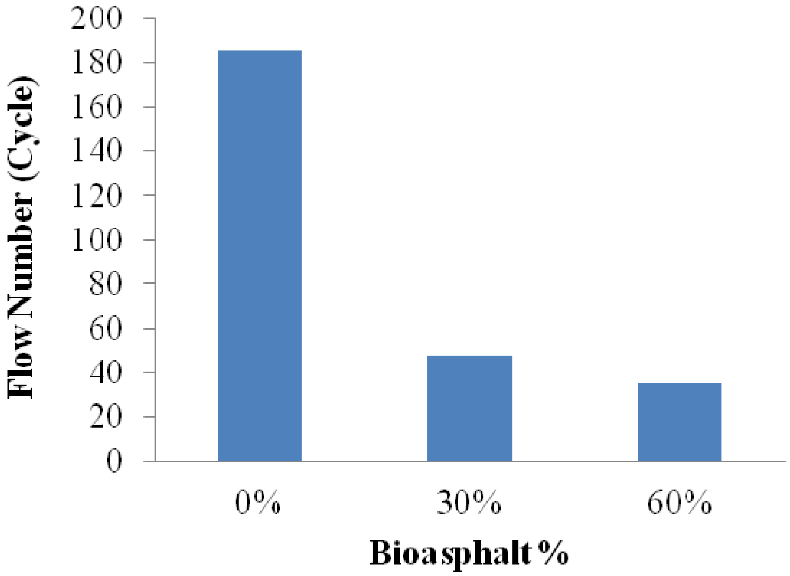


FIGURE 5 Flow number of bioasphalt with PG 58-28.

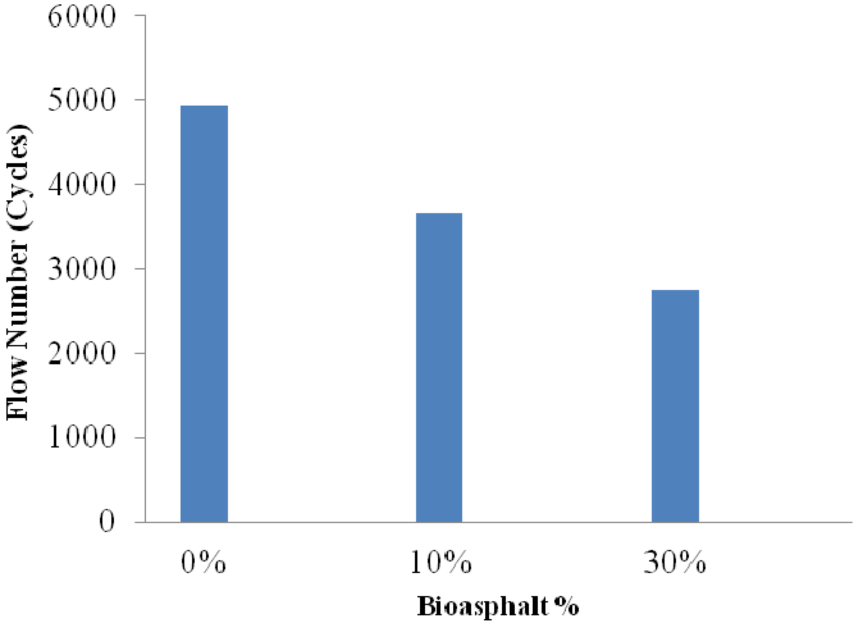


FIGURE 6 Flow number of bioasphalt with PG 82-16.

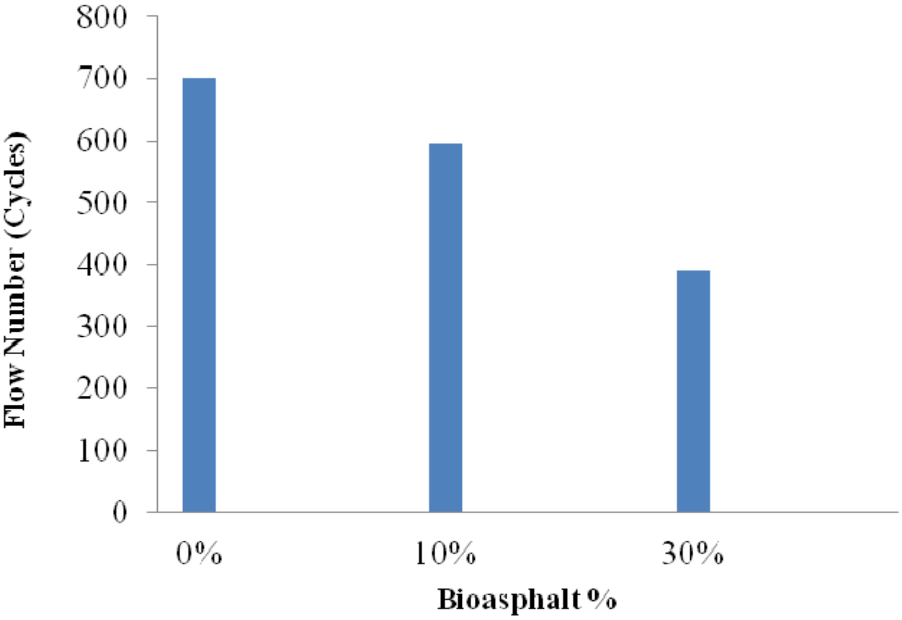


FIGURE 7 Flow number of bioasphalt with PG 76-22.

TABLE 3 Fatigue Test Results of Bioasphalt Mixes

PG	Bioasphalt (%)	Failure Strength (Pa)	Fracture Energy (Pa)	Fracture Work (N-mm)
	0	1,086,409	9,524	Not tested
58-28	30	643,816	5,670	Not tested
58-28	60	350,951	3,119	Not tested
82-16	0	2,775,770	20,686	45,618
82-16	10	2,227,055	16,688	37,117
82-16	30	1,783,134	10,522	25,424
76-22	0	2,778,322	13,693	35,390
76-22	10	2,507,714	12,539	31,043
76-22	30	2,033,478	9,068	26,523

TABLE 4 Thermal Test Results of Bioasphalt Mixes

PG	Bioasphalt (%)	Failure Strength (Pa)	Fracture Energy (Pa)	Fracture Work (N-mm)
58-28	0	6,501,831	5,992	34,656
58-28	30	4,961,625	12,437	55,255
58-28	60	4,503,408	16,280	33,508
82-16	0	6,827,405	7,477	36,835
82-16	10	6,235,349	7,797	33,570
82-16	30	4,664,153	10,633	30,500
76-22	0	6,069,766	7,614	33,777
76-22	10	5,801,009	7,721	33,426
76-22	30	5,156,961	8,927	29,751

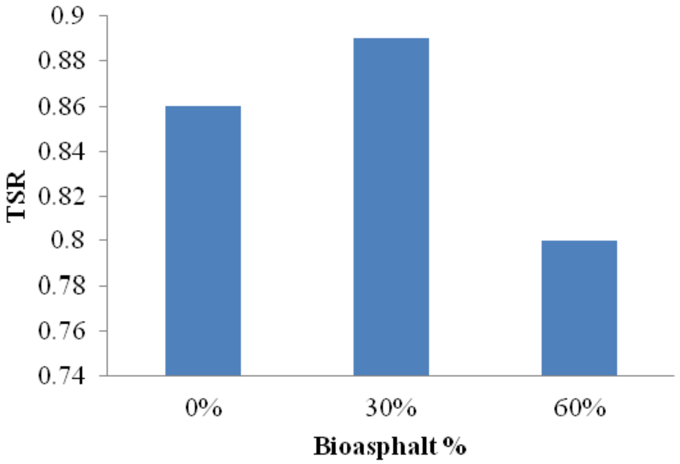


FIGURE 8 TSR of bioasphalt with PG 58-28.

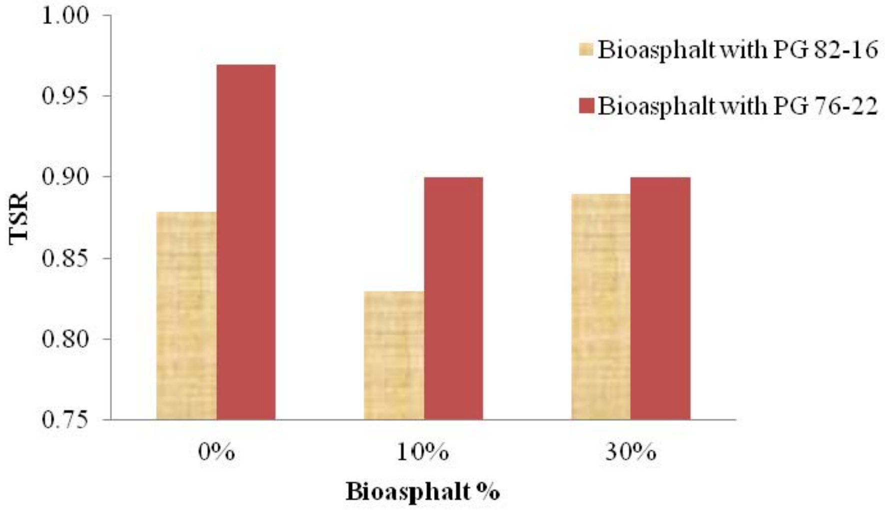


FIGURE 9 TSR of bioasphalt with PG 82-16 and 76-22.

SUMMARY OF FINDINGS

This study evaluated the effects of bioasphalt on the performance of binders (fatigue, rutting, and thermal cracking) and mixes in terms of fatigue, rutting, thermal cracking, and moisture susceptibility. The findings are summarized below.

Bioasphalt Binder

1. The addition of bioasphalt with traditional binder reduced the PG of the base binder, indicating an increased resistance to thermal cracking, but reduced resistance to rutting.
2. The addition of bioasphalt reduced the fracture energy at intermediate temperatures when compared to conventional asphalt under monotonic loading, indicating reduced resistance to fatigue cracking.
3. The addition of bioasphalt increased the J_{nr} value of the base binder, indicating higher susceptibility to rutting of the binder.

Bioasphalt HMA Mix

1. The addition of bioasphalt in the HMA reduced the dynamic modulus of the mix.
2. The flow numbers of the bioasphalt HMA mixes were lower than those of conventional mixes. This finding indicated that bioasphalt HMA mixes are more prone to rutting than conventional mixes.
3. The addition of bioasphalt in the HMA reduced the fracture energy and fracture work obtained from IDT testing at intermediate temperatures, indicating that the bioasphalt mixes are prone to fatigue failure when compared to control HMA.
4. The addition of bioasphalt in the HMA increased the thermal fracture energy, indicating an improved resistance to low-temperature thermal cracking. Bioasphalt mixes are highly ductile even at lower temperatures than conventional mixes.
5. All the bioasphalt mixes passed the minimum AASHTO TSR requirement (0.8).

The findings in this study are based on the bioasphalt made from waste cooking oil. Overall bioasphalt can be a promising candidate for low-temperature behavior. However, further modification of bioasphalt for higher temperature is required to increase its performance against rutting.

ACKNOWLEDGMENTS

The authors thank the National Science Foundation for providing the funds to conduct this research. In addition, the material support from United Environmental and Energy, LLC, New York, and POE Asphalt Paving Inc., Washington, is highly appreciated.

REFERENCES

1. Avello Bioenergy, Inc. Boone, Iowa. Available at http://www.avellobioenergy.com/en/products/bioasphalt/. Accessed August 2011.
2. United Environmental and Energy. Horsehead, New York. Available at http://www.unitedee.com/BioashpaltTechnology.html. Accessed August 2011.
3. Fini, E. H., S.-H. Yang, and S. Xiu. Characterization and Application of Manure-Based Biobinder in Asphalt Industry. Presented at the 89th Annual Meeting of the Transportation Research Board, Washington, D.C., 2010.
4. Williams, R. C., J. Satrio, M. Rover, R. C. Brown, and S. Teng. Utilization of Fractionated Bio Oil in Asphalt. Presented at the 88th Annual Meeting of the Transportation Research Board, Washington, D.C., 2009.
5. You, Z., J. M. Beale, E. Fini, S. W. Goh, and B. Colbert. Evaluation of Low Temperature Binder Properties of Warm Mix Asphalt, Extracted and Recovery RAP and RAS, and Bioasphalt. *Journal of Materials in Civil Engineering*, 2011.
6. U. S. Environmental Protection Agency. http://www.epa.gov/region9/waste/biodiesel/ questions.html. Accessed July 10, 2011.
7. AASTHO M320-10: Standard Specification for Performance-Graded Asphalt Binder. American Association of State Highway and Transportation Officials, 2010.
8. Johnson, C., H. Wen, and H. Bahia. Practical Application of Viscoelastic Continuum Damage Theory to Asphalt Binder Fatigue Characterization. *Journal of Association of Asphalt Paving Technologist*, 2009, Vol. 78, pp. 597–638.
9. D'Angelo, J., R. Kluttz, R. N. Dongre, K. Stephens, and L. Zanzotto. Revision of the Superpave High Temperature Binder Specifications: The Multiple Stress Creep Recovery Test. *Journal of the Association of Asphalt Paving Technologists*, 2007, Vol. 76.
10. AASTHO TP 70-10: Standard Method of Test for Multiple Stress Creep Recovery Test of Asphalt Binder Using Dynamic Shear Rheometer. American Association of State Highway and Transportation Officials, 2010.
11. Asphalt Institute. *Superpave Series No.2 (SP-2)*, Third Edition, 2001.
12. *Guide for Mechanistic–Empirical Design of New and Rehabilitated Pavement Structures*. NCHRP, Transportation Research Board of the National Academies, Washington, D.C., 2004.
13. AASHTO TP 70-10. Standard Method of Test for Multiple Stress Creep Recovery Test of Asphalt Binder Using Dynamic Shear Rheometer. American Association of State Highway and Transportation Official, 2010.

14. Witczak, M. W., K. Kaloush, T. Pellinen, M. El-Basyouny, and H. Von Quintus. Simple Performance Test for Superpave Mix Design. *NCHRP Report 465*, TRB, National Research Council, Washington D.C., 2002.
15. AASTHO T322: Standard Method of Test for Determining the Creep Compliance and Strength of Hot Mix Asphalt Using the Indirect Tensile Test Device. Association of American State Highway and Transportation Officials, 2010.
16. Wen, H., and Y. R. Kim. Simple Performance Test for Fatigue Cracking and Validation with WesTrack Mixtures. *Transportation Research Record: Journal of the Transportation Research Board*, *No. 1789*, Transportation Research Board of the National Academies, Washington, D.C., 2002, pp. 66–72.
17. Wen, H. Use of Fracture Work Density Obtained from Indirect Tensile Testing for the Mix Design and Development of a Fatigue Model. Paper presented at 91st Annual Meeting of the Transportation Research Board, Washington D.C., 2012.
18. Zborowski, A. Development of a Modified Superpave Thermal Cracking Model for Asphalt Concrete Mixtures Based on Fracture Energy Approach. Ph.D. dissertation. Arizona State University, December 2007.
19. AASTHO T283: Standard Test Method of Test for Resistance of Compacted Hot Mix Asphalt to Moisture-Induced Damage. Association of American State Highway and Transportation Officials, 2010.

Investigation of Rheology and Aging Properties of Asphalt Binder Modified with Waste Coffee Grounds

ADAM ZOFKA
ILIYA YUT
University of Connecticut

The environmental awareness and aging of the U.S. infrastructure call for alternative materials to modify or replace asphalt binders. There is a concern about the effect of modifiers on the binder susceptibility to oxidative age hardening. Coffee beans have been recognized for the antioxidant properties of their chlorogenic and caffeic acid components. Therefore this study has been initiated to investigate the effect of coffee bean modification on the rheology and aging properties of asphalt binder. The experimental protocol included mixing PG 64-22 neat binder with 2 to 8 wt% of either ground dry coffee beans or waste coffee grounds. The dynamic shear rheometer (DSR) was utilized to analyze temperature susceptibility of laboratory-aged neat and coffee-modified binders, whereas the attenuated total reflection Fourier transform infrared (FTIR) spectrometer was employed to track chemical changes in the coffee-modified binder samples subjected to standard Superpave laboratory aging procedures. Preliminary results indicated that wasted coffee grounds practically do not change temperature susceptibility of base binder. However, the oxidation rate of coffee-modified binders increases with an increase in concentration of waste coffee grounds after either short-term or long-term aging but does not exceed the oxidation rate of a base binder. It is concluded that coffee beans added to considered asphalt binder served as a solvent rather than as an antioxidant.

INTRODUCTION

An increasing environmental awareness in the United States has recently resulted in push for sustainable asphalt production and paving practices to reduce carbon emissions, increase cost effectiveness, and to eliminate health and safety hazards. On the other hand, durability and oxidation resistance remain major factors of satisfactory long-term performance of asphalt pavements. While research is in place to modify or even replace asphalt binders by alternative materials, there is a concern about the compatibility of a potential additive with an asphalt binder. Another concern is the effect of modifiers on the binder susceptibility to oxidative age hardening.

Hardening of asphalt binder is caused by oxidative aging. The principal cause of asphalt aging is the atmospheric oxidation of certain molecules with the formation of highly polar functional groups containing oxygen (*1*). Oxidation of asphalt is a chain reaction that occurs in presence of free radicals and results in formation of ketones, sulfoxides, and carboxylic acid salts (*2*). Asphalts are exposed to aging phenomenon during storage, mixing, transport, and construction, as well as during the entire service life of the pavement.

To evaluate hardening susceptibility of asphalt binders, the aging process is typically simulated under laboratory conditions using the following two procedures: (*a*) accelerated air blowing of asphalt binder under high temperature followed by (*b*) conditioning asphalt binder sample at elevated pressure and temperature. The former procedure—rolling thin film oven

(RTFO) aging—is performed at 163°C for 85 min, and simulates the effect of rapid oxidation that occurs during hot mixing and placing of asphalt mixes (*3*). The latter procedure, pressure aging vessel (PAV), which involves aging at 100°C and 2.1-MPa pressure for 20 h, is supposed to yield a level of asphalt oxidation similar to that reached after several years of field aging (*4*).

Hardening of asphalt binders can be quantified as a product of hardening susceptibility (*HS*) and an oxidation rate (r_{CA}) induced by either RTFO or PAV test as shown in Equation 1 (*5*). The *CA* parameter is usually measured as an integrated area under the infrared (IR) absorbance band centered around 1,700 cm^{-1} on the IR spectrum of a binder measured by a transmission IR spectrometer (*5*). The attenuated total reflection (ATR) mode of IR measurements requires normalization of *CA* to address uneven penetration of IR light into a binder sample (*6, 7*).

$$\frac{d\ln\eta_0^*}{dt} = \left(\frac{d\ln\eta_0^*}{d(CA)}\right) * \left(\frac{d(CA)}{dt}\right) = HS * r_{CA} \tag{1}$$

where

η_0^* = limiting viscosity (i.e., hardening);
t = time of oxidation; and
CA = carbonyl (C=O) band area as measured from FTIR spectrum.

Antioxidants adsorb free radical intermediates and inhibit other oxidation reactions with formation of nonradical products. They have been long used in fuel and motor oil industry to prevent auto-oxidation of gasoline and diesel (*8–10*). Antioxidants can be added to an asphalt binder to mitigate the effects of oxidative hardening. Such chemicals as hydrated lime and zinc derivatives of thiophosphates have shown to reduce aging (*10–12*). It should be noted that natural presence of oxidation inhibitors in a neat binder may slow down the aging process without presence of antioxidants (*13*).

Waste products from the agriculture and food industry have been increasingly the focus of research on alternative noncrude binders. The hydrocarbon nature of those products usually suggests their compatibility with petroleum binders. Recently, several studies examined the effect of bio-waste on oxidative age hardening of asphalt binders. Bio-oil from nonfood sources (e.g., oak wood and switchgrass) may increase aging index of bio-modified asphalt binders under RTFO and PAV aging conditions (*14*). On the other hand, waste cooking oil has shown to reduce binder viscosity, thus increasing resistance to thermal cracking in hot-mix asphalt mixture, while reducing their fatigue and rutting resistance (*15*). Most recently, the grape pomace (residue from red wine production) has been reported to decrease aging index of laboratory-aged binders, thus exhibiting antioxidant properties (*16*).

Roasted coffee beans have been recognized for the antioxidant capacity of their chlorogenic and caffeic acid components with regard to oxidation of foods and human body (*17*). On the other hand, caffeine can be an effective scavenger of hydroxyl radicals (OH) with lesser degree of success in scavenging oxygen and alkyl peroxy radicals (ROO and HOO)**,** which are most likely to be present in asphalt binder (*18*). Waste coffee grounds have been used for production of bio-fuels because of relatively high bio-oil content (*19*). It is also known that a popular U.S. coffee chain provides free waste grounds for gardeners. In knowing that about 16 billion pounds of waste coffee grounds can be available worldwide (*20*), it appears attractive to evaluate the feasibility of using waste coffee as an antioxidant and extender for asphalt binder. Therefore, this study has been initiated to investigate the effect of coffee bean modification on the rheology and aging properties of asphalt binder.

OBJECTIVES

To evaluate the feasibility of using coffee grounds as an extender and antioxidant of asphalt binder, the following objectives were established.

- Evaluate the effect of coffee beans on viscoelastic properties of asphalt binder aged in laboratory conditions.
- Compare the effects of coffee beans and waste coffee grounds on oxidation pathways in laboratory-aged asphalt binder.

EXPERIMENTAL PROTOCOL

Materials and Sample Preparation

In the beginning of this study, a base PG 64-22 binder was modified with 2 and 4 wt% of Java Merapi dry coffee beans supplied by an online vendor. The beans were manually ground into particles not greater than #4 U.S. sieves (4.78 mm). The fraction passing #8 sieve (2.36 mm) was used for mixing with base asphalt binder. When chemical composition of dry coffee beans was found to be similar to that of roasted and processed (waste) coffee grounds, it was decided to proceed with 4 and 8 wt% waste coffee grounds. The waste grounds (Eight O'clock Arabica) also had finer particle size with 100% passing #16 sieves (1.18 mm), which was expected to help the mixing process. Figure 1 shows the coffee products used in this study.

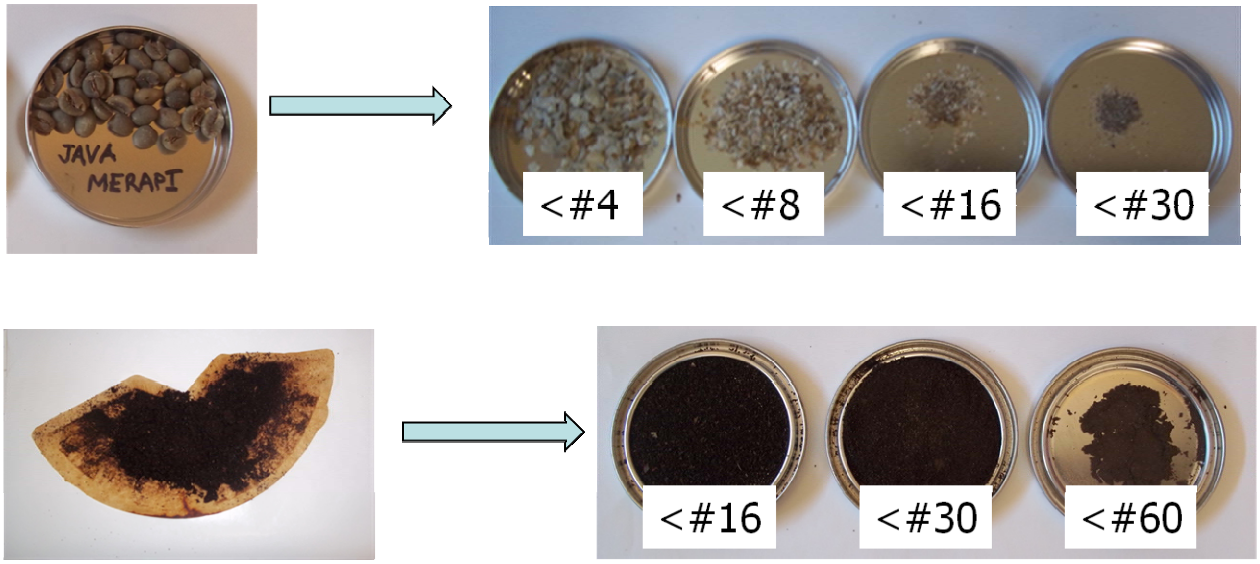


FIGURE 1 Gradation of dry coffee beans (top) and waste coffee grounds (bottom).

To prepare each batch of a coffee-modified binder, about half quart (~400 g) of neat binder were preheated in an oven to 140°C and placed into a heating jacket. The coffee additive (either ground dry beans or waste grounds) was stirred in gradually with a shear mixer at approximately 4,000 rpm. Then temperature was increased to 170°C and the blend was stirred for another hour. At the end of mixing, a modified binder blend was poured into smaller cans for aging and spectroscopic evaluation.

Spectroscopic Equipment and Testing Protocol

This study employed FTIR spectroscopy to compare chemical composition of coffee and asphalt binder and to determine oxidation rates in neat and coffee-modified binders under RTFO and PAV aging conditions. The infrared spectra of binder samples were collected using a compact FTIR spectrometer equipped with a single reflection diamond ATR accessory. About 1 g of binder was placed directly on the internal reflection element (IRE) and a fixed load was applied to a sample to ensure its full contact with the IRE. Twenty-four scans were averaged for each sample within the wave number range of 4,000 to 400 cm^{-1} at a resolution of 4 cm^{-1}, and the resultant averaged spectrum was recorded. Three replicates were probed from each binder sample.

Aging Protocol

The standardized aging cycle in this study included RTFO aging at 163°C for 85 min followed by PAV conditioning at 100°C and 2.1 MPa for 20 h. Aged binder samples were scanned by an ATR FTIR spectrometer and tested in a dynamic shear rheometer (DSR) as described next.

Rheological Testing

Standardized Superpave performance grading tests of binders was conducted with DSR. The dynamic shear modulus, G^*, and phase angle, δ, for original and RTFO-aged binder samples was determined at 64°C with application of at constant 12% strain with angular frequency of 10 rad/s. The 25-mm diameter plates with 2-mm final gap were used for original and RTOF-aged samples. The PAV-aged samples were tested at 25°C (corresponding to the specified low PG grade of –22°C) and at 1% strain with frequency of 10 rad/s. Two 8-mm plates with 1-mm final gap were used for the PAV-aged samples.

Spectroscopic Analysis

Qualitative Analysis (Fingerprinting)

A qualitative analysis of IR spectra in this study was conducted in three steps. First, the individual spectra of coffee beans and waste grounds were analyzed qualitatively to fingerprint major coffee components, i.e., caffeine, lignin, and chlorogenic acid. The coffee spectra were then compared with neat binder spectra to identify similar functional groups. Of a particular interest was presence of oxidized functional groups such as carbonyl (C = O) and sulfoxide (S = O), which are also the major products of the oxidation reaction in asphalts. Lastly, the IR spectra of neat binders and coffee-modified blends were compared to evaluate changes in absorbance because of oxidation of the components.

Figure 2 provides an insight on chemometric analysis of dry coffee beans' spectra within so called fingerprinting region between 1,800 and 600 cm^{-1} wave numbers. The characteristic absorbance bands associated with caffeine, lignin, and chlorogenic acid are determined from spectral databases and previous work (*21–23*). Figure 2 clearly shows that the spectra of coffee bean core and endocarp are identical, hence very similar and relatively small concentration of caffeine (identified at 1,701, 1,550, 1,373, and 773 cm^{-1}). The approximate chemical structures of coffee components are depicted in Figure 3. Based on those observations, no separation of core from endocarp is required when mixing coffee with binder.

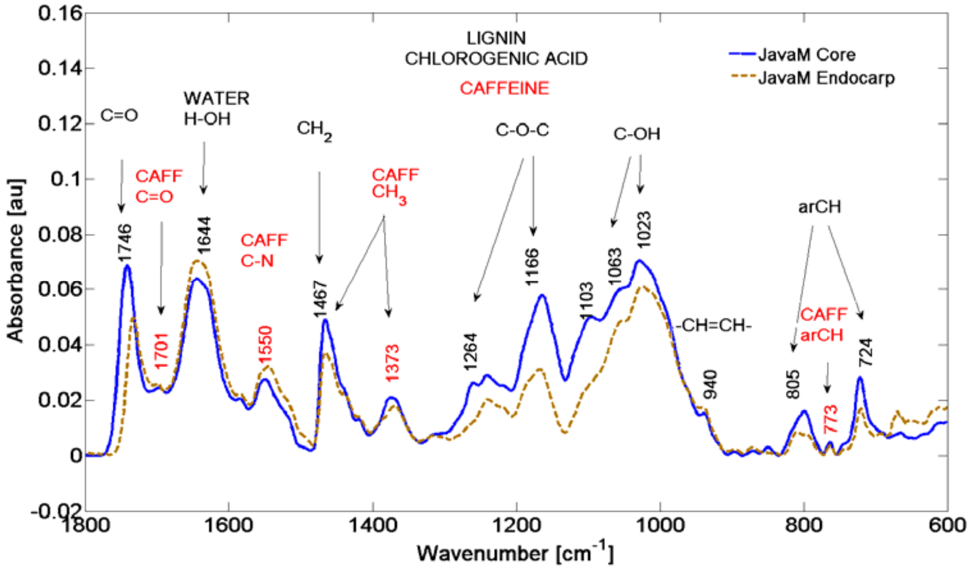
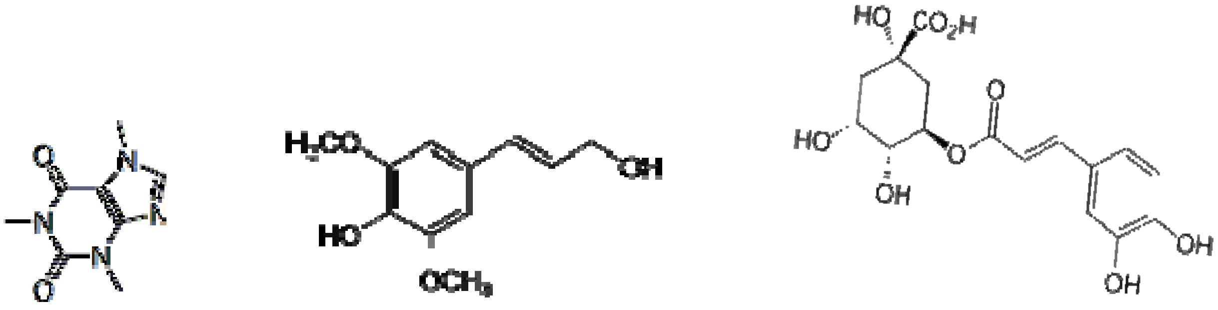


FIGURE 2 IR absorbance spectra of coffee bean components.



(a) (b) (c)

FIGURE 3 Typical chemical structure of coffee component: (*a*) caffeine (*22*), (*b*) lignin (*23*), and (*c*) chlorogenic acid (*22*).

Figure 4 superimposes IR absorbance spectra of dry coffee beans, waste coffee grounds, and neat PG 64-22 binder. The typical IR bands associated with aromatic carbons, methylene–methyl groups, and substituted aromatic hydrocarbons at 1,600, 1,460, 1,370, and 900 to 700 cm^{-1} are determined correspondingly from the previous work (*1*). The absence of caffeine from the processed coffee grounds can be derived from the absence of carbonyl peak at 1,700 cm^{-1}, while much lower moisture content in waste coffee is shown by the peak at 1,644 cm^{-1}.

A very important observation should be noted about the peak at 1,746 cm^{-1}. This peak is associated with aromatic ester which only occurs in chlorogenic acid. The identical peak heights at 1,746 cm^{-1} indicate that chlorogenic acid is not extracted from the coffee beans during coffee brewing. Taking into consideration much higher concentration of oxidized functionalities in chlorogenic acid as compared with lignin (Figure 3) one can expect it to be the major factor in the oxidation of coffee-modified blend.

The qualitative similarity between binder and coffee spectra in Figure 4 originates from bands associated with aliphatic hydrocarbons (1,467 and 1,373 cm^{-1}), 1,3-disubstituted aromatics (805 cm^{-1}) and long aliphatic chains (724 cm^{-1}). It can be anticipated, however, that olefinic components (900 cm^{-1}) and overall lower aromaticity of lignin and chlorogenic acid may result in a reduced viscosity of a coffee-modified binder blend.

Figure 5 superimposes three typical IR absorbance spectra. The bottom spectral line corresponds to an unaged neat binder. A solid and a dashed line in the middle of the chart depict spectra of 4-wt% modifications by coffee beans and waste coffee grounds, correspondingly. The top solid and dashed lines are the spectra of the coffee-modified binders after RTFO followed by PAV aging cycle.

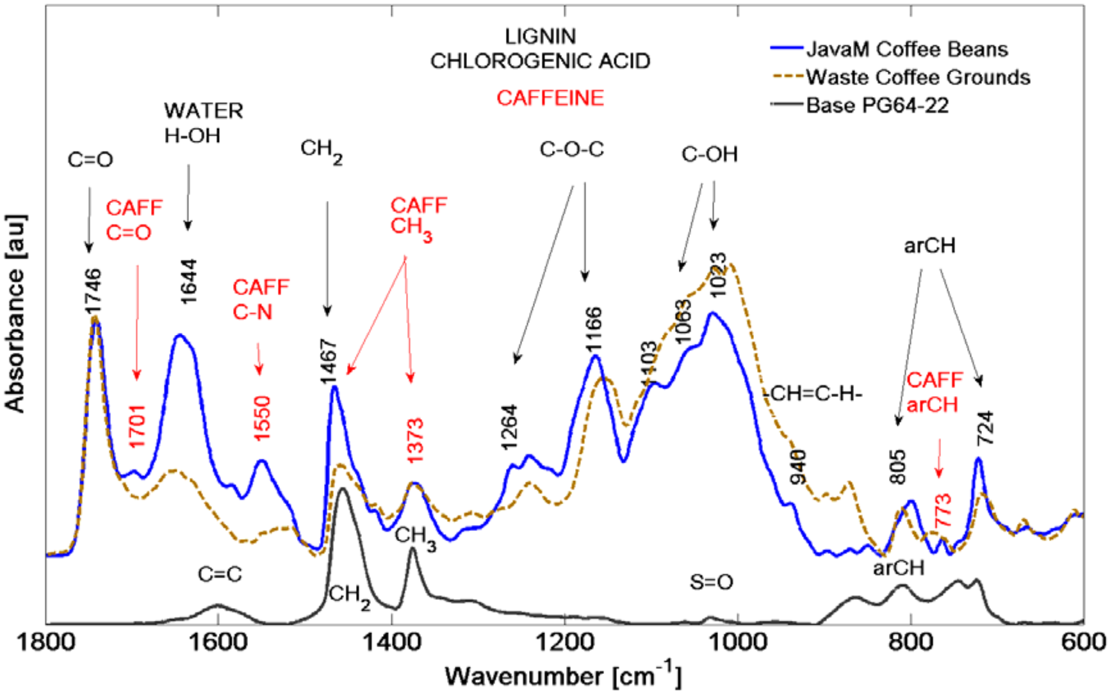


FIGURE 4 Superposition of the IR spectra of coffee beans, waste coffee grounds, and neat binder.

Close-ups on the region between 1,760 and 1,600 cm^{-1} in Figure 5 allow for tracking the changes in absorbance by the benzylic ketones in asphalt binders (C = O at 1,700 cm^{-1}) before and after mixing and aging. One can infer that binder become slightly oxidized because of mixing with either coffee beans, while no apparent oxidation occurs when mixing binder with coffee waste grounds. Further evaluation of the close-up on aged blend spectrum confirms the major effect of RTFO and PAV conditions on the carbonyl growth in the blend.

Change in the intensity of a characteristic absorbance peak at 1,746 cm^{-1} associated with aromatic ester in coffee products allow to track the concentration of coffee within a modified binder blend. No change in the intensity of C = O peak at 1,746 cm^{-1} because of aging leads to a conclusion that no degradation of coffee waste grounds occurs under RTFO and PAV conditions. On the other hand, slight degradation of coffee beans is suspected because of decrease in area under the coffee C = O peak.

The extent of sulfoxide formation in an aged binder is typically associated with the increase in absorbance intensity of the band centered on 1,030 cm^{-1}. Examination of the close-ups on that region in Figure 5 does not suggest any influence of coffee modification on the sulfoxide content in modified binder blend. Lastly, a remarkable identity of S = O peaks for coffee beans and waste coffee grounds after the full cycle of aging indicates no effect of coffee modification on sulfoxide formation during RTFO and PAV aging.

Semiquantitative Analysis

The oxidation paths in coffee-modified binder blends were determined based on computed carbonyl and sulfoxide indices as shown in Equations 2 and 3. The oxidation indices were

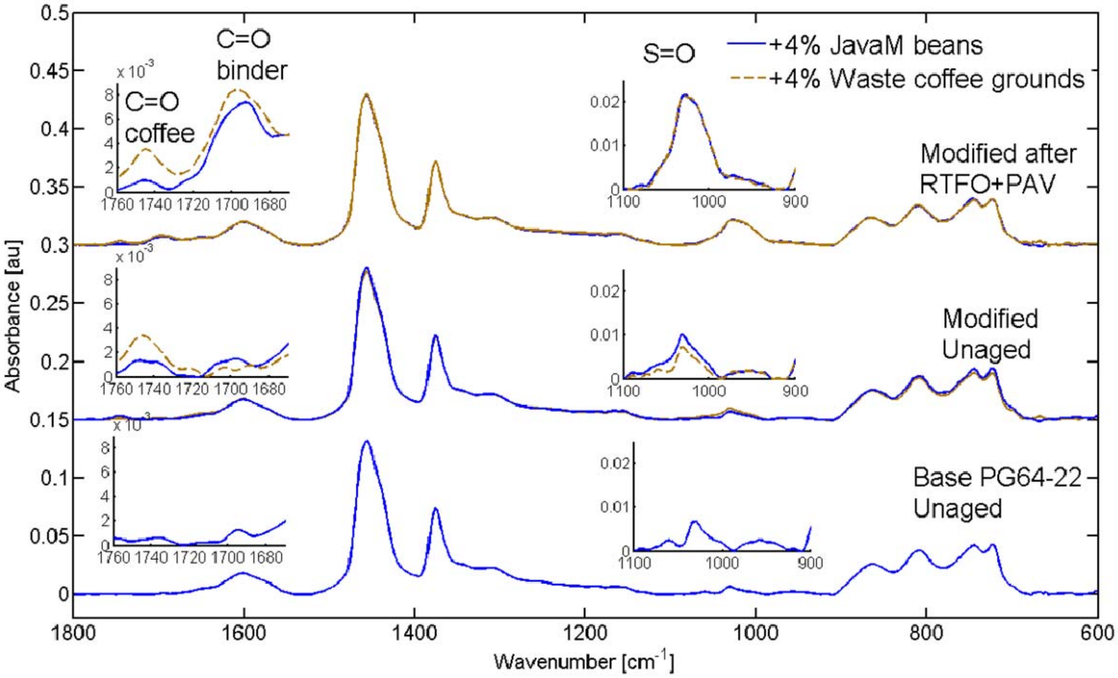


FIGURE 5 Superposition of the IR spectra of base and coffee-modified binders before and after blending and aging.

calculated as integrated areas under a carbonyl–sulfoxide peak normalized to the maximum absorbance band area within binder spectra, which corresponded to stretching vibrations of methylene ($–CH_2–$) and methyl ($–CH_3$) components of binder. The subscripts in Equations 2 and 3 denote integration limits. Lastly, the carbonyl oxidation rates (r_{CA}) were computed for RTFO- and PAV-aged binder samples as differential of carbonyl index over the duration of aging procedure.

$$\text{Carbonyl Index:} \quad I_{CO} = AR_{1720-1670}/AR_{3000-2750} \tag{2}$$

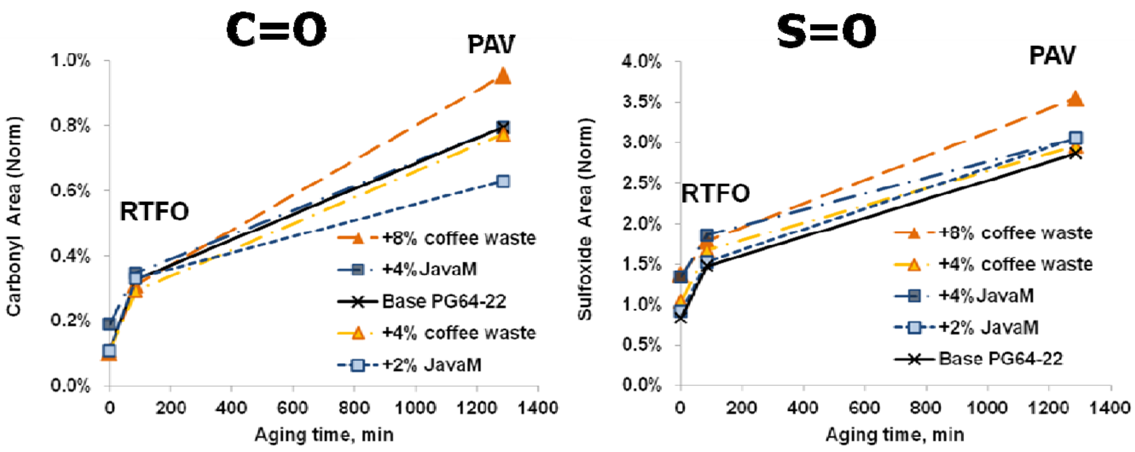
$$\text{Sulfoxide Index:} \quad I_{SO} = AR_{1080-980}/AR_{3000-2750} \tag{3}$$

Figure 6 illustrates dynamics of the carbonyl and sulfoxide formation because of RTFO and PAV aging. A visual evaluation of carbonyl trends on the left chart in Figure 6 indicates that oxidation occurs much faster in the RTFO apparatus than it does in PAV, which is an expected trend. However, the difference between oxidation slopes of the modified blends under PAV conditions appears to be much greater than the difference between RTFO-induced slopes. The sulfoxide trends on the right chart in Figure 6 seem to be identical for all blends under either RTFO or PAV conditions, except 4-wt% Java-modified blend, which might be an outlier. A quantitative analysis of the oxidation rates and hardening susceptibility is provided in one of the following sections.

Rheological Analysis of Hardening Paths

An analysis of rheology of coffee-modified binder blends was conducted based on the DSR measurements of G^* and δ. The parameters characterizing rutting and fatigue susceptibility were computed according to the Superpave performance grading specifications as follows:

- G*/sin δ for original and RTFO-aged binders to assess rutting resistance at high-service temperatures.



(a) (b)

FIGURE 6 Oxidation paths for (*a*) carbonyl and (*b*) sulfoxide formation.

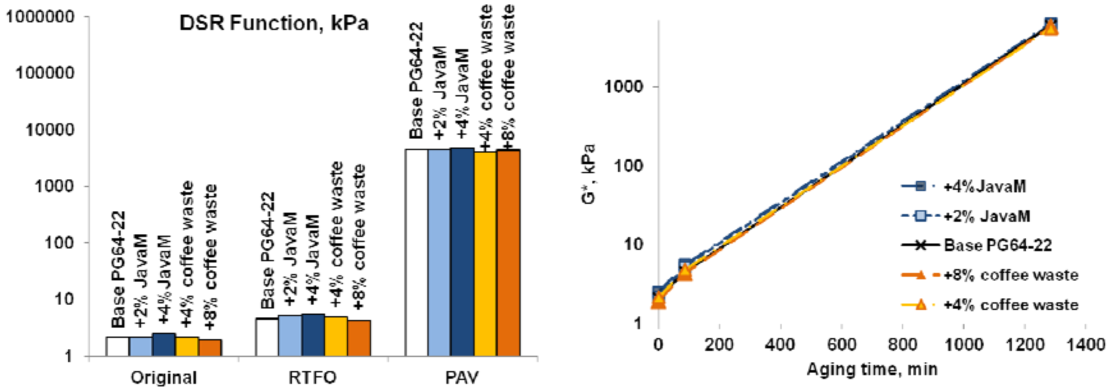
- G*/sin δ for PAV-aged binders to evaluate fatigue susceptibility at medium service temperatures.

A column chart on the left in Figure 7 compares DSR functions of coffee-modified blends with those of the base PG 64-22 binder. It can be observed that an increase in concentration of coffee beans results in a slight increase in viscosity of the unaged modified binder blend, while coffee waste grounds cause opposite effect when added to the base binder. During the short-term laboratory aging, the differences between blends viscosities seem to remain the same. However, those differences diminish after the long-term aging. The hardening paths depicted on the right in Figure 7 confirm that variation in viscosity of coffee-modified blends because aging is very small. Nevertheless, it is apparent that binders modified with coffee waste grounds exhibit consistently lower viscosity as compared with base and coffee beans-modified binders. This observation supports the hypothesis from spectroscopic analysis about the effect of caffeic oil on the viscosity of a resultant binder blend.

Analysis of Hardening Susceptibility

In order to quantify hardening susceptibility and to evaluate the actual contribution of oxidation in binders to change in their viscosity, aging parameters were computed as shown earlier (see Equation 1). Figure 8 illustrates ranking of binders based on their aging index, oxidation rate, and hardening susceptibility values. In terms of the increase in viscosity because of aging, it appears that hardening trends in coffee-modified binders are governed by hardening trend of their base binder (PG 64-22 in this study). On the other hand, an increase in oxidation rate because of the increase in coffee grounds content is obvious with a more pronounced effect under PAV aging conditions. Note that a high r_{CA} value for 2-wt% Java-modified binder after RTFO aging might be an outlier.

Examination of hardening susceptibility clearly shows exponential decay in *HS* values of the modified binder blends with the increase in either coffee beans or coffee waste grounds



(a) **(b)**

FIGURE 7 Comparison of (*a*) DSR functions and (*b*) G* values for coffee-modified binder blends.

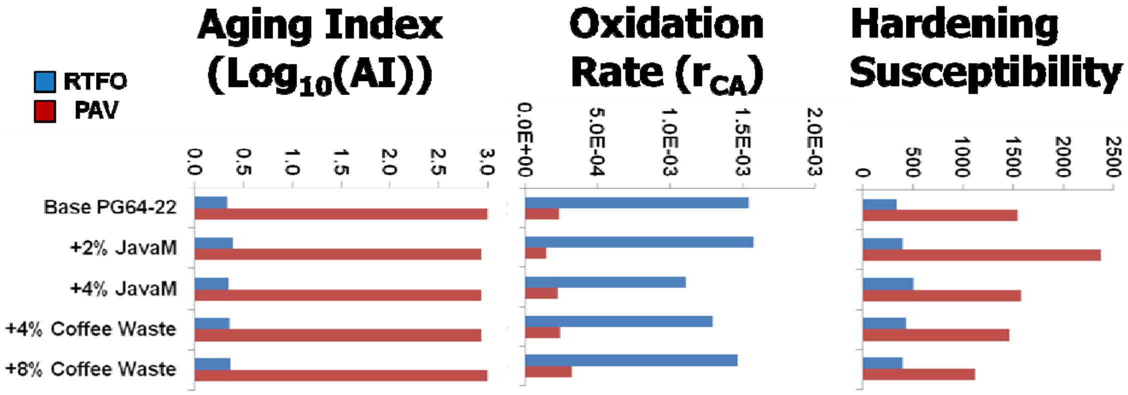


FIGURE 8 Aging parameters for coffee-modified binder blends.

content. Once again, such an effect is more pronounced under PAV conditions, while the RTFO-aged 2-wt% Java-modified binder stands out of trend. Overall, the trends in Figure 8 suggest that, although coffee does not exhibit antioxidation effect on aged binders, it clearly reduces its viscosity because of high oil content, thus leveling out hardening trends in coffee-modified binder blends.

CONCLUSIONS

The preliminary study presented in this paper evaluated the feasibility of using coffee waste grounds as an antioxidant in asphalt binders. Coffee waste grounds are available in the industrial quantities at little or no cost. Furthermore, coffee grounds are recognized for their antioxidant effect on bio-products. Oxidation trends in coffee-modified binder blends were investigated by means of FTIR spectroscopy, while their rheological properties were tested by DSR at high and intermediate temperatures.

Results show that coffee grounds fail to prevent oxidation of the considered base binder. Increase in concentration of coffee grounds, however, does not affect aging index of coffee-modified binder blends. This results in lower hardening susceptibility of blends with higher coffee grounds content. It is surmised for the moment that, because of high olefinic content and low aromaticity, coffee grounds work rather as a solvent for a hardened base binder, thus preventing the increase in viscosity because of oxidation during laboratory aging.

Finally, it should be emphasized that only in-situ long-term performance evaluation of any alternative binders can provide a final answer about their usability and practicality in asphalt pavements.

ACKNOWLEDGMENTS

The authors thank Connecticut Advanced Pavement Laboratory (CAP Lab) at the University of Connecticut (UConn) for providing DSR equipment. In addition, Alex Bernier (currently a master's student at UConn) is acknowledged for his help with aging tests in the CAP Lab. The FTIR equipment used in this study is partially sponsored by the SHRP 2 administration.

REFERENCES

1. Petersen, J. C. Quantitative Functional Group Analysis of Asphalts Using Differential Infrared Spectrometry and Selective Chemical Reactions: Theory and Application. In *Transportation Research Record 1096*, TRB, National Research Council, Washington, D.C., 1986, pp. 1–11.
2. Petersen, J. C., and P. M. Harnsberger. Asphalt Aging: Dual Oxidation Mechanism and Its Interrelationships with Asphalt Composition and Oxidative Age Hardening. In *Transportation Research Record 1638*, TRB, National Research Council, Washington, D.C., 1998, pp. 47–55.
3. AASHTO R 28: Standard Method of Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel. AASHTO, Washington, D.C., 2009.
4. AASHTO T 240: Standard Method of Test for Effect of Heat and Air on a Moving Film of Asphalt Binder (Rolling Thin-Film Oven Test). AASHTO, Washington, D.C., 2009.
5. Martin, K. L., R. R. Davison, C. J. Glover, and J. A. Bullin. Asphalt Aging in Texas Roads and Test Sections. *Transportation Research Record 1269*, TRB, National Research Council, Washington, D.C., 1990, pp. 9–19.
6. Jemison H., B. Burr, R. R. Davison, J. A. Bullin, and C. J. Glover. Application and Use of the ATR FTIR Method to Asphalt Aging Studies. *Petroleum Science and Technology*, Vol. 10, No. 4, 1992, pp. 795–808.
7. Yut, I., and A. Zofka. Attenuated Total Reflection (ATR) Fourier Transform Infrared (FT-IR) Spectroscopy of Oxidized Polymer-Modified Bitumens. *Applied Spectroscopy*, Vol. 65, No. 7, 2011, pp. 765–770.
8. Pedersen, C. J. Mechanism of Antioxidant Action in Gasoline. *Additives in Fuels*, Vol. 48, No. 10, 1956, pp. 1881–1884.
9. Mahoney, L. R., S. Korcek, S. Hoffman, and P. A. Willermet. Determination of the Antioxidant Capacity of New and Used Lubricants: Methods and Applications. *Industrial Engineering Chemistry Product Research and Development*, Vol. 17, No. 3, 1978, pp. 250–255
10. Barnes, A. M., K. D. Bartle, and V. R. A. Thibon. A Review of Zinc Dialkyldithiophosphates (ZDDPS): Characterization and Role in the Lubricating Oil. *Tribology International*, Vol. 34, 2001, pp. 389–395.
11. Arnold, T. S., J. Rozario, and J. Youtcheff. New Lime Test for Hot-Mix Asphalt Unveiled. *Public Roads*, Vol. 70, No. 5, 2007.
12. Ouyang, C., S. Wang, Y. Zhang, and Y. Zhang. Improving the Aging Resistance of Asphalt by Addition of Zinc Dialkyldithiophosphate. *Fuel*, Vol. 85, 2006, pp.1060–1066.
13. Petersen, J. C. A Review of the Fundamentals of Asphalt Oxidation: Chemical, Physicochemical, Physical Property, and Durability Relationships. *Transportation Research Circular E-C140*, Transportation Research Board of the National Academies, Washington, D.C., 2009.
14. Peralta J., M. A. Raouf, S. Tang, and R. C. Williams. Bio-Renewable Asphalt Modifiers and Asphalt Substitutes. In *Sustainable Bioenergy and Bioproducts* (K. Gopalakrishnan et al., eds.). Springer-Verlag, London, 2012, pp. 89–115.
15. Wen, H., S. Bhusal, and B. Wen. Evaluation of Waste Cooking Oil-Based Bioasphalt as an Alternative Binder. Presented at 91st Annual Meeting of the Transportation Research Board, 2012.
16. Calabi-Floody, A., and G. Thenoux. Controlling Asphalt Aging by Inclusion of Byproducts from Red Wine Industry. *Construction and Building Materials*, Vol. 28, 2012, pp. 616–623.
17. Nicoli, M. C., M. Anese, K. Manzocco, and C. R. Lerici. Antioxidant Properties of Coffee Brews in Relation to the Roasting Degree. *Lebensmittel-Wissenschaft und-Technologie*, Vol. 30, Academic Press Limited, 1997, pp. 292–297.
18. Leon-Carmona, J. R., and A. Galano. Is Caffeine a Good Scavenger of Oxygenated Free Radicals? *Journal of Physical Chemistry B*, Vol. 115, 2011, pp. 4538–4546.
19. Kondamudi, N., S. K. Mohapatra, and M. Misra. Spent Coffee Grounds as a Versatile Source of Green Energy. *Journal of Agricultural and Food Chemistry*, Vol. 56, 2008, pp. 11757–11760.

20. Tropical Products: World Markets and Trade. FTROP 2-06. Circular Series, Foreign Agricultural Service, U.S. Department of Agriculture, June 2006.
21. Pretsch, E., P. Buhlmann, and M. Badertscher. *Structure Determination of Organic Compounds: Tables of Spectral Data.* Springer, Berlin, 2009.
22. Spectral Database for Organic Compounds. National Institute of Advanced Industrial Science and Technology (AIST), Japan. http://riodb01.ibase.aist.go.jp/sdbs. Accessed Jan. 10, 2012.
23. Bykov, I. Characterization of Natural and Technical Lignins Using FTIR Spectroscopy. Master's thesis. Lulea University of Technology, 2008.

APPENDIX

Workshop Agenda

Alternative Binders for Sustainable Asphalt Pavements

January 22, 2012
91st Annual Meeting of the Transportation Research Board
Washington, D.C.

Sponsored by
Characteristics of Asphalt Materials (AFK20)
Characteristics of Nonasphalt Components of Asphalt Paving Mixtures (AFK30)

Pres. #	Presentation Title	Duration	Presenters
P12-5125	Considerations for Use of Alternative Binders in Asphalt Pavements: Material Characteristics	25	Robert Q. Kluttz Kraton Polymers E-mail: bob.kluttz@kraton.com
P12-5126	Alternative Binder from Micro-algae: ALGOROUTE Project	25	Emmanuel Chailleux Institut Français des Sciences et Technologies du Transport, France E-mail: emmanuel.chailleux@lcpc.fr Mariane Audo Institut Français des Sciences et Technologies du Transport, France E-mail: mariane.audo@ifsttar.fr Clémence Queffelec Université de Nantes, France E-mail: clemence.queffelec@univ-nantes.fr Olivier Lepine Alpha Biotech, France E-mail: olivier.lepine@algosource.com
P12-5126	Alternative Binder from Microalgae: ALGOROUTE Project	25	Jack Legrand Génie des Procédés – Environnement – Agroalimentaire (GEPEA), France E-mail: jack.legrand@univ-nantes.fr Bruno Bujoli Universite de Nantes, France E-mail: Bruno.Bujoli@univ-nantes.fr

Pres. #	Presentation Title	Duration	Presenters
P12-5127	High-Temperature Rheological Properties of Asphalt Binders Modified with Soy Fatty Acids	25	Joseph Seidel Purdue University E-mail: jseidel@purdue.edu John E. Haddock Purdue University E-mail: jhaddock@purdue.edu
P12-5128	Grape Pomace from Red Wine as Antioxidant to Improve the Age Hardening Resistance of Asphalt Binder	25	Alejandra Calabi-Floody Universidad de la Frontera, Chile E-mail: acalabi@ufro.cl Guillermo Thenoux Pontificia Universidad Católica de Chile E-mail: gthenoux@ing.puc.cl
12-4490	Development of a Rubber Modified Fractionated Bio-Oil for Use as a Noncrude Petroleum Binder in Flexible Pavements	25	Joana Peralta Iowa State University E-mail:joana@iastate.edu Ronald Christopher Williams Iowa State University E-mail: rwilliam@iastate.edu Marjorie Rover Institute for Transportation at Iowa State University E-mail: mrrover@iastate.edu
P12-5129	Organo-Montmorillonite Nanoclay, an Alternative Modifier to Sustain the Durability of Asphalt Pavement	25	Gang Liu Delft University of Technology, Netherlands E-mail: liugang102129@hotmail.com André Molenaar Delft University of Technology, Netherlands E-mail: a.a.a.molenaar@tudelft.nl Shaopeng Wu Wuhan University of Technology, China E-mail:Wusp@mail.whut.edu.cn M. F. C. Van de Ven Delft University of Technology, Netherlands E-mail: M.F.C.vandeVen@tudelft.nl

Pres. #	Presentation Title	Duration	Presenters
12-4297	Evaluation of Waste Cooking Oil-Based Bioasphalt as an Alternative Binder	25	Haifang Wen Washington State University E-mail: haifang_wen@wsu.edu Sushanta Bhusal Washington State University E-mail: sushanta.bhusal@email.wsu.edu Ben Wen United Environmental and Energy, LLC E-mail: supenbhusal@hotmail.com
P12-5131	Investigation of Rheology and Aging Properties of Asphalt Binder Modified with Coffee Berries	25	Adam Zofka University of Connecticut E-mail: azofka@engr.uconn.edu Iliya Yut University of Connecticut E-mail: iliya.yut@uconn.edu

THE NATIONAL ACADEMIES

Advisers to the Nation on Science, Engineering, and Medicine

The **National Academy of Sciences** is a private, nonprofit, self-perpetuating society of distinguished scholars engaged in scientific and engineering research, dedicated to the furtherance of science and technology and to their use for the general welfare. On the authority of the charter granted to it by the Congress in 1863, the Academy has a mandate that requires it to advise the federal government on scientific and technical matters. Dr. Ralph J. Cicerone is president of the National Academy of Sciences.

The **National Academy of Engineering** was established in 1964, under the charter of the National Academy of Sciences, as a parallel organization of outstanding engineers. It is autonomous in its administration and in the selection of its members, sharing with the National Academy of Sciences the responsibility for advising the federal government. The National Academy of Engineering also sponsors engineering programs aimed at meeting national needs, encourages education and research, and recognizes the superior achievements of engineers. Dr. Charles M. Vest is president of the National Academy of Engineering.

The **Institute of Medicine** was established in 1970 by the National Academy of Sciences to secure the services of eminent members of appropriate professions in the examination of policy matters pertaining to the health of the public. The Institute acts under the responsibility given to the National Academy of Sciences by its congressional charter to be an adviser to the federal government and, on its own initiative, to identify issues of medical care, research, and education. Dr. Harvey V. Fineberg is president of the Institute of Medicine.

The **National Research Council** was organized by the National Academy of Sciences in 1916 to associate the broad community of science and technology with the Academy's purposes of furthering knowledge and advising the federal government. Functioning in accordance with general policies determined by the Academy, the Council has become the principal operating agency of both the National Academy of Sciences and the National Academy of Engineering in providing services to the government, the public, and the scientific and engineering communities. The Council is administered jointly by both Academies and the Institute of Medicine. Dr. Ralph J. Cicerone and Dr. Charles M. Vest are chair and vice chair, respectively, of the National Research Council.

The **Transportation Research Board** is one of six major divisions of the National Research Council. The mission of the Transportation Research Board is to provide leadership in transportation innovation and progress through research and information exchange, conducted within a setting that is objective, interdisciplinary, and multimodal. The Board's varied activities annually engage about 7,000 engineers, scientists, and other transportation researchers and practitioners from the public and private sectors and academia, all of whom contribute their expertise in the public interest. The program is supported by state transportation departments, federal agencies including the component administrations of the U.S. Department of Transportation, and other organizations and individuals interested in the development of transportation. **www.TRB.org**

www.national-academies.org

TRANSPORTATION RESEARCH BOARD
500 Fifth Street, NW
Washington, DC 20001