FURFURAL MODIFIED ASPHALT OBTAINED BY USING A LEWIS ACID AS A CATALYST

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INTRODUCTION

Asphalt is solid or semi-solid at room temperature, becomes soft and starts flowing upon heating, and becomes hard and brittle at very low temperatures.

States have been facing problems such as cracking, rutting, and asphalt adhesion to aggregates in their asphaltic pavements for years. Many polymer additives have been used in asphalt to reduce these problems, but little work has been done using chemically modified products of asphalt to attempt to solve these serious problems of asphalt pavements[1-3]. The above mentioned problems decrease the life of the pavements, resulting in an increase of maintenance and/or replacement costs. There are two types of cracking which can occur in asphalt pavement; one related to load, and the other related to thermal stress. The load-related cracking is known as fatigue cracking and is defined as fracture under repeated or cyclic stress having a maximum value of less than the tensile strength of the material. The thermal cracking occurs due to pavement shrinkage at low temperatures causing the shrinkage stresses to exceed the tensile strength.

FHWA researchers have found furfural to be a suitable candidate for functional group modification of asphalt. The modified product shows improved performance as well as improved rheological properties.[4] The furan ring in the product was found to be the principal component responsible for the product high temperature stiffness, whereas the furan ring (with or without an aldehyde group) was also important in improving the product low temperature properties[2]. The nature of this reaction was determined by FHWA laboratories using different analytical instruments. Phenolic moieties present in asphalt were found to be reacting with furfural (in the presence of an acid as a catalyst) forming a polymeric material[3]. However, mix testing showed corrosive fumes (due to HCl) escaping from the furfural modified asphalt[5].

Thus, a chemically modified asphalt is needed which: has low creep stiffness, has less temperature susceptibility, can resist thermal stress to alleviate thermal cracking, can maintain a high stiffness at high temperatures to resist rutting, and is an environmentally accepted modified product. The major objective of this study was to obtain a furfural modified asphalt with the above properties using a non-polluting Lewis acid, para-toluene sulfonic acid (PTSA), as a catalyst for the reaction.

EXPERIMENTAL METHOD

Materials used: The asphalts[AAD-1(California Coast), AAV-1(North Alaskan Slope), and AAM-1(West Texas Intermediate)] used in this study were obtained from the Strategic Highway Research Program (SHRP) Material Reference Library (MRL), Reno, Nevada. The aggregate used was traprock screenings(#10 diabase) from Vulcan Materials Co. All reagents were of analytical grade from Baxter Scientific Products unless otherwise specified.

Furfural Reaction: 200 g of asphalt was placed in a 500-ml three-necked round-bottomed flask equipped with a mechanical stirrer and a thermometer. The asphalt was heated to 93^{0}C, followed by the addition of PTSA (0.07-0.12 milimoles/gram of asphalt) and then furfural (0.15-0.20 milimoles/gram of asphalt) drop wise with continuous stirring. The contents of the flask were then

heated for 1.5 hours at the same temperature.
Test Methods: Standard tests used to measure the properties of asphalts are given below:
Freeze-Thaw Pedestal Test:[6] The wet environment has an impact on the asphalt-aggregate bond. This bond can be weakened or destroyed if water penetrates into the pavement.
This test measures the water susceptibility of the adhesion of virgin and modified asphalt to the aggregate. The briquettes of the asphalt-aggregate mixture were made according to the Wyoming pedestal test developed by Plancher et al[6]. The samples in jars filled over the top of the briquette level with water were stored in a freezer at -10 to -12°C for 24 hours, cooled to the room temperature, stored in an oven at 60°C for 24 hours, and then examined for surface cracks or breakage. This cycle was continued until the failure of the briquets occurred due to repeated freeze-thaw cycling.
Test Methods:

1. Rolling Thin Film Oven Test (RTFOT), ASTM-D1754-87.
2. Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel(PAV), AASHTO PP1-93 (1A).
3. Test Method for Determining the Flexural Creep Stiffness of Asphalt Binder Using the Bending Beam Rheometer (BBR),AASHTO TP1-93.
4. Test Method for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR), AASHTO TP5-93.
5. Corbett Seperation Analysis, ASTM D-4124-86.
6. Thin Layer Chromatography (TLC)[3].
7. Fourier Transform Infrared (FTIR), & Stokes Data Analysis Method[3].

RESULTS AND DISCUSSION:
TLC results of the model polymer made by the interaction of phenol and furfural, using PTSA as a catalyst, shows more polarity in the model polymer than in phenol or furfural.
The IR spectrum (figure I) shows that the modified asphalt has more mono and poly substitution on the benzene ring as compared to the corresponding virgin asphalt.
Rheological Properties: Chemical modification of an asphalt with furfural was conducted using a method developed at the Federal-Highway Administration[4]. Figure II shows the continuous SHRP PG grading for virgin and Furfural-Modified asphalts using HCl as a catalyst. The rheological properties of the asphalts used (AAD-1, AAV, & AAM-1)[7], Fu-Modified using HCl and Fu-Modified asphalt using PTSA, are illustrated in figures *II, III, IV*, and *V*, respectively. Virgin asphalt AAV passes the criteria for stiffness at 57°C, and the modified binder passes at 63°C. The low temperature rheological data for both virgin and the modified binder pass the SHRP specification at -28°C. The useful temperature range (the sum of the high and low PG grades) for virgin binder AAV is 85°C; that for the modified binder is 91°C. The temperature difference of 6°C is equal to 1 PG grading and is a significant change. From an economic point of view, 1 PG grading will result in a significant cost savings, but the corrosivity of HCl is a major problem. To solve that problem, a new catalyst (p-toluene sulfonic acid, PTSA) was used. The use of PTSA (figure III) provided a modified asphalt product of AAV which showed PG 63-31 continuous PG grading and 94°C as the useful temperature range. The temperature difference between the virgin and the modified product of 9°C is equal to 1.5 PG grading and is slightly better than that of the HCl modified product. Figure IV demonstrates the rheological behavior of virgin AAM-1 and its Fu-modified binder. The continuous high temperature grading for the virgin binder and for the modified binder is at 67 and 78°C respectively. The low temperature grading for both virgin and the Fu-modified binders were found to be -23°C and -

30^0C respectively. The useful temperature range for the virgin binder is 90^0C; that for Fu-modified binder is 108^0C. The difference in the useful temperature range is 18°C (or 3 PG grades), which is extremely significant. Figure V depicts the rheological continous grading for the third asphalt used in this study, binder AAD-1. The virgin binder passes the high temperature stiffness specification at 62^0C; the modified binder passes it at 71^0C. The creep stiffness and slope for both the virgin and the modified binders pass the specification at -31^0 and -34^0C respectively. The useful temperature range is 90^0 and 105^0C for virgin and modified binder respectively, a 12°C range or 2 PG grades. Thus, these modifications are improving the PG grading simultaneously at both high and low temperatures, but the degree of improvement is asphalt source-dependent.
Moisture susceptibility was checked through the Wyoming freeze thaw pedestal tests and is shown in figure VI. The virgin asphalt AAV-1 failed after 4 freeze-thaw cycles, whereas Fu-modified by HCl and Fu-modifed by PTSA failed after 16 and 18 freeze-thaw cycles, respectively. This indicates that the modified binder is significantly (four times) less moisture susceptible than its corresponding virgin binder.

CONCLUSION: The use of furfural for asphalt modification in presence of a Lewis acid (catalyst) produces a product which is:

- Environmentally acceptable
- Easy to prepare.
- Economical.
- Less temperature and moisture susceptible.
- Improves both the high and low temperature rheological properties simultaneously.
- Asphalt source-dependent in terms of performance.
- Shows potential for higher fatigue and rutting resistance as compared to the corresponding virgin binder.

REFERENCES

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6. H. Plancher, G. Miyake, R. L. Venable and J. C. Petersen, "A Simple Laboratory Test to Indicate the Susceptibility of Asphalt-Aggregate Mixtures to Moisture Damage During Repeated Freeze-Thaw Cycling," Proceedings of the Canadian Technical Asphalt Association, Vol. 25, pp. 247-262, 1980.
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Figure I
Infrared Spectra of: a) Asphalt AAD-1 and b) Fu-Mod. AAD-1

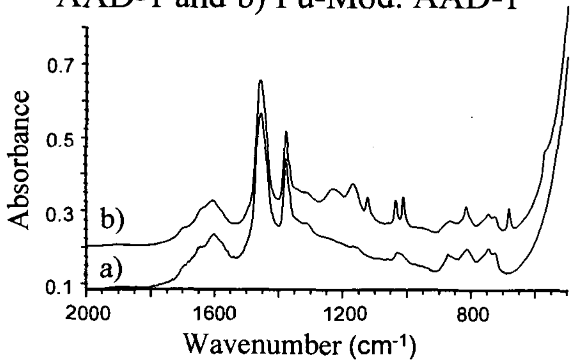

Figure II
PG Grades for Virgin (AAV) and Fu-Mod., Using HCl as the Catalyst

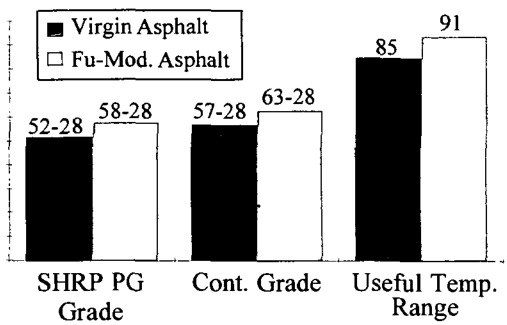

Figure III
PG Grades for Virgin (AAV) and Fu-Mod., Using PTSA as the Catalyst

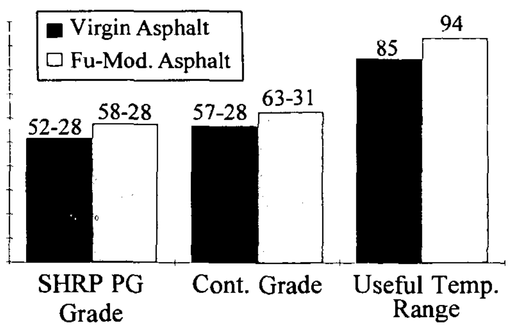

Figure IV

PG Grades for Virgin (AAM-1) and Fu-Mod., Using PTSA as the Catalyst

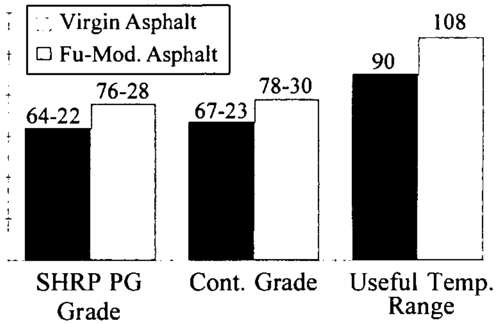

Figure V

PG Grades for Virgin (AAD-1) and Fu-Mod., Using PTSA as the Catalyst

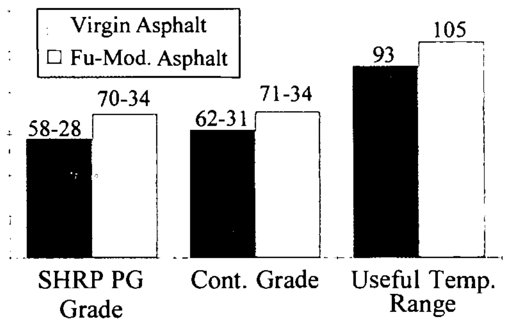

Figure VI

Comparison of Freeze-Thaw Pedestal Tests