Asphalt Mixtures Containing Chemically Modified Binders

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The properties of a mixture containing an AC-20 control asphalt binder were compared with those of mixtures in which the binder was modified with either 1.5 percent chromium trioxide (CrO_3), 6.0 percent maleic anhydride (MAH), or 0.75 percent furfural. Penetration and viscosity data of binders recovered from the mixtures indicated that the three chemically modified binders should be stiffer at high pavement temperatures and softer at low pavement temperatures than the AC-20 control asphalt. The permanent strains from a creep test were used to evaluate the susceptibilities of the mixtures to rutting. The three chemically modified binders decreased these strains by an average of 25 percent. However, this difference was not statistically significant because of the high variability of the test data. The three chemically modified binders provided improved low-temperature properties down to approximately −16°C (3.2°F) on the basis of diametral tests. All four mixtures showed equivalent data below this temperature. The MAH-modified mixture passed both engineering tests used to evaluate moisture susceptibility. The CrO_3, furfural, and AC-20 control mixtures each failed at least one of the tests. The AC-20 control mixture had a high amount of visual stripping, whereas all three modified mixtures showed no visual stripping. It was concluded that the poor engineering test results shown by the CrO_3- and furfural-modified mixtures were related to a loss of cohesion rather than a loss of adhesion. Except for the moisture susceptibility results, the three modified mixtures performed similarly.

A research study was recently performed by FHWA in which paving grade asphalts were modified through chemical reactions to determine whether binders with increased resistances to rutting, low temperature cracking, and moisture susceptibility could be produced (*1*). Various chemicals and processes were used to make asphalts more polar or more polymeric, or both. It was hypothesized that this would decrease the temperature susceptibilities of the asphalts and increase their adhesion to aggregates. The three reagents that provided the greatest improvements in binder properties were chromium trioxide (CrO_3), maleic anhydride (MAH), and furfural. The procedures for reacting these reagents with the asphalts and the quantities of each reagent used have been documented elsewhere. (*1*)

OBJECTIVE

The primary objective of the study documented in this paper was to show whether the improved binder properties provided by the three reagents were of sufficient magnitude to improve the engineering properties of mixtures. It was intended that this mixture study be limited and exploratory.

A secondary objective was to evaluate parts of the National Cooperative Highway Research Program (NCHRP) Asphalt-Aggregate Mixture Analysis System (AAMAS) (*2*). The AAMAS procedures for curing, gyratory testing, creep testing, and moisture susceptibility testing were evaluated. [The development of this system was continued by the Strategic Highway Research Program (SHRP), but the SHRP system was finalized after this study was completed. Only parts of the AAMAS were evaluated because it was believed that other parts would not be used by SHRP. The quantity of each chemically modified binder required to perform the entire AAMAS procedure would also be very time-consuming to make.]

MATERIALS

Binders

Four binders were evaluated in this study: (a) AC-20 control asphalt, (b) AC-5 asphalt modified with 1.5 percent CrO_3, (c) AC-5 asphalt modified with 6.0 percent MAH, and (d) AC-5 asphalt modified with 0.75 percent furfural. The AC-20 and AC-5 asphalts were from the same crude slate. Both were obtained from the Marathon Petroleum Company refinery, Detroit, Michigan.

The percentage of each reagent used was determined by modifying the AC-5 asphalt so that its absolute viscosity at 60°C (140°F) was as close as reasonably possible to that of the AC-20 control asphalt. However, duplicating the viscosity of the AC-20 control asphalt was difficult and could not be done in each case. The CrO_3-modified binder was an AC-20, the MAH-modified binder was an AC-30, and the furfural-modified binder was an AC-40. Standard physical properties of the binders are shown in Table 1.

Aggregates

A single blend of aggregates was used in the mixtures. It consisted of 45 percent 11.2-mm (7⁄16-in.) traprock coarse aggregate, 35 percent No. 10 traprock screenings, and 20 percent natural, angular quartz sand. The combined aggregate gradation in terms of percent passing was 12.5 mm, 100.0; 9.5 mm, 95.7; No. 4, 66.0; No. 8, 48.7; No. 16, 37.2; No. 30, 26.9; No. 50, 16.0; No. 100, 9.7; and No. 200, 6.5.

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TABLE 1 Physical Properties of the Binders

Marathon Petroleum Company AC-20 asphalt	Virgin	TFOT
Thin Film Oven Test, percent loss		0.14
Penetration, 25 °C (100 g, 5 s), 0.1 mm	78	47
Absolute Viscosity, 60 °C, dPa-s	1,923	5,171
Kinematic Viscosity, 135 °C, um^2/s	401	598
Specific Gravity, 25/25 °C	1.027	
Marathon Petroleum Company AC-5 asphalt	Virgin	TFOT
Thin Film Oven Test, percent loss		0.27
Penetration, 25 °C (100 g, 5 s), 0.1 mm	212	121
Absolute Viscosity, 60 °C, dPa-s	411	990
Kinematic Viscosity, 135 °C, um^2/s	195	285
Specific Gravity, 25/25 °C	1.017	
AC-5 asphalt with 1.5 percent CrO_3	Virgin	TFOT
Thin Film Oven Test, percent loss		0.57
Penetration, 25 °C (100 g, 5 s), 0.1 mm	91	56
Absolute Viscosity, 60 °C, dPa-s	1,717	5,437
Kinematic Viscosity, 135 °C, um^2/s	383	608
Specific Gravity, 25/25 °C	1.030	
AC-5 asphalt with 6.0 percent MAH	Virgin	TFOT
Thin Film Oven Test, percent loss		0.42
Penetration, 25 °C (100 g, 5 s), 0.1 mm	91	63
Absolute Viscosity, 60 °C, dPa-s	2,759	9,307
Kinematic Viscosity, 135 °C, um^2/s	533	860
Specific Gravity, 25/25 °C	1.029	
AC-5 asphalt with 0.75 percent furfural	Virgin	TFOT
Thin Film Oven Test, percent loss		0.51
Penetration, 25 °C (100 g, 5 s), 0.1 mm	73	71
Absolute Viscosity, 60 °C, dPa-s	3,973	4,401
Kinematic Viscosity, 135 °C, um^2/s	455	514
Specific Gravity, 25/25 °C	1.016	

(1.8)°C + 32 = °F dPa-s = P um^2/s = cSt mm/25.4 = in

This aggregate blend was used in the surface courses of the FHWA accelerated loading facility (ALF) pavements located at the Turner-Fairbank Highway Research Center. The ALF mixture is a high-quality mixture that is highly resistant to rutting. It is used in pavements subjected to high traffic volumes and high load levels, and it did not rut when tested by the ALF loading machine. By using the ALF aggregate blend, any effects that the modified binders would have on rutting would be conservative. However, it is expected that chemically modified binders would be used in premium mixtures because of the added expense associated with them.

MIXTURE TESTING PROGRAM

The mixtures were designed by the Marshall method. Specimens at the optimum binder content were then tested to determine their resistances to rutting, low temperature cracking, and moisture damage. The binders were extracted and recovered to determine the effects of heating during mixing, curing, and compaction on the properties of the binders. The tests performed were as follows:

- Marshall mixture design at 60°C (140°F) using 75 blows per side: optimum binder content, Marshall stability, Marshall flow, air voids (total), voids in the mineral aggregate (VMA), voids filled with asphalt (VFA), and density;
- Resistance to rutting: gyratory testing machine (GTM) at 60°C (140°F) [refusal, or ultimate, air void levels and gyratory stability index (GSI)], uniaxial compressive dynamic modulus at 40°C (104°F), and uniaxial compressive creep test at 40°C (104°F) (creep modulus and permanent strain);
- Resistance to low-temperature cracking: diametral Modulus (M_d) versus temperature and indirect tensile test at −8°C (18°F) (tensile strength, tensile strain at failure, and work to cause tensile failure);
- Resistance to moisture damage: tensile strength ratio (TSR), diametral modulus ratio (M_dR), percent visual stripping, and percent swell; and
- Extraction and recovery: penetration at 25°C (77°F), absolute viscosity at 60°C (140°F), and kinematic viscosity at 135°C (275°F).

MIXTURE DESIGN

A 75-blow Marshall mixture design was performed on each mixture to determine the optimum binder contents. The target mixing temperature was 152°C (306°F), and the target curing and compaction temperature was 143°C (290°F). The equiviscous principle of the Marshall method indicated that these temperatures could be used for all four mixtures.

The AAMAS study reported that kneading and gyratory compaction procedures produced specimens with engineering properties more similar to those of a compacted pavement than did Marshall hammer compaction (*2*). However, it was found through trial tests that the kneading compactor could not compact the mixtures to the 6 to 8 percent air-void level required by the test for moisture susceptibility, even with low tamps and pressures, unless a compaction temperature below 110°C (230°F) was used. The surface mixture used in the ALF pavements was also designed by the 75-blow Marshall method. For these two reasons, Marshall hammer compaction was used throughout most of this study. A GTM later became available and was used in the rutting study.

The AAMAS procedure specifies that after the binder and aggregates are mixed, the loose mixture is to be cured in a loosely covered pan in a forced draft oven at the compaction temperature (*2*). An oven-curing period of 4 hr was used in this study. AAMAS initially recommended this period but later changed it to 3 hr. AAMAS allows other curing periods if they are more simulative of the hot-mix plant production and placement time, and SHRP was recommending a curing period of 4 hr at 135°C (275°F) when this study was performed. This curing process is intended only to simulate the hardening that occurs during mixture production and placement and not long-term aging.

In most designs, mixtures are not cured, and they are compacted immediately after mixing. The current practice of using the equiviscous principle for choosing a compaction temperature may not be applicable when lengthy curing periods such as 4 hr are used. Lengthy curing periods significantly alter the viscosities of binders, and various binders will harden to various degrees. Without curing, the degree of aging that occurs during the short mixing time is considered to be approximately the same for all binders. Any small differences in the degrees of aging from binder to binder are assumed to have negligible effects on the choice of a compaction temperature.

Asphalt contents of 4.5, 5.0, 5.5, 6.0, and 6.5 percent by mixture weight were used in designing the AC-20 control mixture. After determining that the optimum asphalt content was 5.7 percent on the basis of a target air-void level of 3 to 5 percent, trial binder contents for designing the three modified mixtures were set at 5.2, 5.7, and 6.2 percent by mixture weight. One additional design using the five asphalt contents was performed on the AC-20 control mixture without curing to evaluate the effects of curing.

The Marshall design results are given in Table 2. An optimum binder content of 5.7 percent was chosen for all mixtures so that the amount of binder would not confound the analysis of the test data. The air-void levels for the four mixtures were similar: 3.8, 3.2, 4.0, and 3.2 percent for the AC-20 control, CrO_3, MAH, and furfural mixtures, respectively. The Marshall stabilities, VMA, and VFA of the four mixtures were statistically equal. The differences in Marshall flows were small and not significant in terms of expected differences in pavement performance. According to the mixture design data, the mixtures had equivalent properties. One benefit of having equivalent design properties and equivalent mixing and compaction temperatures is that these indicate that hot-mix plant temperatures, and probably most other construction practices, may not have to be modified.

During the designs, the binder modified with furfural bubbled when heated in its metal container. The binder was tested for water content but contained none. Free furfural was not found in the binder by either thin-layer chromatography or reverse-phase, high-performance liquid chromatography. Therefore, the furfural was completely reacted and not the cause of the bubbling. Stored binder corroded the inside surfaces of the container lids within 6 months. It was hypothesized that both effects were caused by the hydrochloric acid that was used as a catalyst in the furfural reaction. Additional studies in this area were initiated.

Table 2 shows that curing increased the binder content by approximately 0.4 percent by mixture weight. This increase was mainly the result of a 3 percent increase in binder absorption. Curing also increased the Marshall stabilities by

TABLE 2 Mixture Design Properties at the Optimum Binder Content

	AC-20 (Cured)	CrO_3	MAH	Furfural	AC-20 (No Curing)
Binder Content, % by mix weight	5.7	5.7	5.7	5.7	5.3
Maximum Specific Gravity	2.593	2.588	2.587	2.587	2.590
Density, Kg/m^3	2,491	2,501	2,482	2,502	2,486
Density, lbm/ft^3	155.6	156.2	155.0	156.3	155.3
Marshall Stability, N	19,750	18,745	17,828	18,505	14,902
Marshall Stability, lbf	4,440	4,214	4,008	4,160	3,350
Marshall Flow, mm	3.25	3.25	2.75	3.00	2.50
Marshall Flow, 0.01 in	13.3	12.5	11.2	11.8	10.3
Air Voids, percent	3.8	3.2	4.0	3.2	3.8
VMA, percent	15.3	14.9	15.6	14.9	15.1
VFA, percent	74.5	78.2	74.5	78.7	74.0

Marshall Design Blows = 75
Mixing Temperature = 154 °C (310 °F)
Compaction Temperature = 143 °C (290 °F)
Effective Specific Gravity of Aggregate = 2.856

more than 4448 N (1,000 lbf). Marshall flows increased around 0.75 mm (0.03 in.). Adding lengthy curing periods such as 4 hr to the Marshall design means that new specifications would have to be developed.

RESISTANCE TO RUTTING

The NCHRP AAMAS procedure was used to measure the resistance to rutting. In this procedure, specimens are first compacted and tested by the U.S. Army Corps of Engineers GTM. This gyratory procedure is a variation of ASTM D3387. The uniaxial compressive dynamic modulus and creep compliance tests were then performed on the compacted specimens. The diameter of each specimen was 10.2 cm (4.0 in.), and the heights after compaction and testing by the GTM were approximately 12.7 cm (5.0 in.). Two to three specimens per mixture were fabricated, depending on the amount of available binder and the variability of the test data.

GTM

To measure the resistance to rutting caused by shear susceptibility, the mixtures were evaluated by measuring the GSI using the GTM. The GSI is the ratio of the maximum gyratory angle to the minimum gyratory angle and is a measure of shear susceptibility at the refusal, or ultimate, density of the mixture. After the refusal density is reached, there is no reduction in air voids with additional revolutions. The gyratory angle, which is a measure of the magnitude of shear strain, does not increase significantly for stable mixtures, and thus the minimum and maximum angles will be virtually equal. The angle will increase when testing unstable mixtures. The GSI at 300 revolutions will be close to 1.0 for a stable mixture and will be significantly above 1.1 for an unstable mixture (*3*) (A more definitive failing GSI has not been established).

A vertical pressure of 0.827 MPa (120 lbf/in.^{2}), a 2-degree gyratory angle, and the oil-filled roller were used to compact the specimens. AAMAS states that the vertical pressure is the maximum anticipated tire contact pressure, and the angle is related to the maximum anticipated pavement deflection (*2*). The initial compaction temperature was 143°C (290°F). AAMAS initially compacts mixtures to a 5 to 8 percent air-void level, which is representative of in-place pavement air voids after construction. Specimens were compacted to approximately a 6 percent air-void level in this study.

After initial compaction, the specimens in their molds were placed in an oven at 60°C (140°F) for 3 hr. They were then compacted by the GTM at 60°C (140°F) using 300 revolutions. The average height of each specimen was measured at 0, 25, 50, 75, 100, 200, 250, and 300 revolutions. Heights, which are proportional to air-void levels, are used to verify that the refusal density has been reached. The relationship between air-void level and the number of revolutions can be calculated from these heights, and the bulk specific gravity of the specimen can be measured after GTM testing. This gives the compaction history of a mixture. A trace of the gyratory angle versus revolutions is also obtained to determine the maximum and minimum angles.

The test results are shown in Table 3. The refusal air-void levels and the GSIs for the four mixtures were equal. The GSIs were close to 1.0, indicating very little susceptibility to permanent deformation caused by shear.

The refusal air-void levels of 1.9 percent were significantly lower than the Marshall design air-void levels. It appears that the AAMAS GTM compactive effort is excessive for this mixture. Also, ALF pavement air-void levels for this particular aggregate blend have remained above 4.0 percent after they have been trafficked by the ALF loading machine.

The GTM is sensitive to increased shear susceptibility caused by an excess volume of binder in a mixture. The GTM may not be sensitive enough to measure small differences in shear susceptibilities caused by other factors, including the type of binder. Therefore, the AAMAS repeated load and creep tests were used to further evaluate the resistances of mixtures to rutting.

Compressive Dynamic Modulus and Creep Properties

Repeated load and creep tests were performed in compression on each specimen compacted by the GTM to determine the dynamic modulus, creep modulus, and the permanent deformation after the creep load was released (*2*). Testing was performed at 40°C (104°F) using a closed-loop servohydraulic MTS materials testing system.

Vertical compressive deformations were measured by averaging the outputs of two linear variable differential transducers (LVDTs), each having a gauge length of 7.620 cm (3.000 in.). Permanent strains were calculated from these deformations by dividing them by the LVDT gauge length.

A repeated load consisting of a 0.1-sec sinusoidal wave followed by a 0.9-sec rest period was applied to each specimen to determine the dynamic modulus at the 200th cycle. This modulus is used in many mechanistic pavement designs to represent the stress-strain characteristic of a mixture over the majority of its life.

The load or stress used in the repeated load test should provide linear viscoelastic properties. Trial tests showed that the chosen stress of 0.55 MPa (79.6 lbf/in.^{2}) did provide data in the linear range. This stress was approximately 15 percent of the compressive strength of the AC-20 control mixture, which was determined by performing strength tests on additional specimens. AAMAS specifies the stress to be 5 to 25 percent of the unconfined compressive strength of the mixture determined in accordance with ASTM D1074, with the exceptions that the test temperature is 40°C (104°F) and the loading rate is 3.81 mm/min per millimeter of specimen height (0.15 in./min per inch of specimen height) (*2*, ASTM D3387).

The creep test was then performed. The load was applied to each specimen for 60 min ± 15 sec and then released, and the deformation was allowed to recover for 60 min ± 15 sec (*2*). The creep moduli of the mixtures at 60 min of loading and the permanent strains at the end of the 60-min rest period were evaluated. Permanent deformations or strains are the primary inputs used by mechanistic pavement designs to predict rutting resistance.

The following equation was used to compute the dynamic and creep moduli (*2*):

$$E = \frac{\text{Stress}}{\text{Strain}} = \frac{P/A}{V/L}$$

TABLE 3 Resistance to Rutting

Test Temperature = 60 °C (140 °F)	AC-20	CrO_3	MAH	Furfural
Marshall Design Air Voids, Percent	3.8	3.2	4.0	3.2
GTM Initial Air Voids, Percent	6.2	6.2	5.9	5.9
GTM Refusal Air Voids, Percent	1.9	1.9 (NS)	1.9 (NS)	1.9 (NS)
GSI (maximum angle/ minimum angle)	1.05	1.05 (NS)	1.05 (NS)	1.05 (NS)
Test Temperature = 40 °C (104 °F)	**AC-20**	**CrO_3**	**MAH**	**Furfural**
Average Dynamic Modulus, MPa, at 200 cycles	666	1,056 (I)	939 (I)	981 (I)
Average Creep Modulus, MPa, at a loading time of 60 min	258	219 (NS)	218 (NS)	320 (NS)
Average Permanent Strain, cm/cm at a rest time of 60 min	0.00140	0.00108 (NS)	0.00108 (NS)	0.00099 (NS)

NS = No significant difference between control and modified binder.
I = Modification increased the test result.

MPa(145.04) = lbf/in^2 (1.8)°C + 32 = °F cm/2.54 = in

where

E = creep or dynamic modulus (Pa),
P = load (N),
A = loaded area (0.008107 m^2),
V = vertical deformation (cm), and
L = gauge length (7.620 cm).

The test data are shown in Table 3. The AC-20 control mixture had a significantly lower dynamic modulus at 40°C (104°F) compared with the three modified mixtures. There were no significant differences among the data for the three modified mixtures when compared with each other. (The results of statistical analyses that compare modified mixtures are not included in the tables.) The 33 percent average increase in dynamic modulus caused by the modifications was significant enough that it would be expected that the three modified mixtures should be more resistant to rutting. However, this expectation was not verified conclusively by the creep test. The permanent strains for the modified mixtures were, on an average, 25 percent lower than the strain for the AC-20 control mixture, but the variability of the test data was so high that the differences were not statistically significant. The creep moduli of the four mixtures were statistically equal. The usefulness of these moduli has not been established.

RESISTANCE TO LOW-TEMPERATURE CRACKING

The majority of low-temperature cracking studies use stiffness to compare the performances of binders or mixtures. High stiffnesses, or moduli, at cold temperatures are equated with low flexibility and an increased susceptibility to cracking. In this study, both the diametral modulus test and the indirect tensile strength test were used to evaluate low-temperature cracking.

Diametral Modulus Test

The log diametral modulus (M_d) versus temperature relationship of each mixture was determined by performing the diametral test at −32°C, −24°C, −16°C, −8°C, 0°C, 5°C, 16°C, 25°C, 32°C, and 40°C (−26°F, −11°F, 3.2°F, 18°F, 32°F, 41°F, 61°F, 77°F, 90°F, and 104°F), using three specimens per mixture compacted to the design air-void level (*4*). The M_d values of the mixtures were then compared at each temperature. Data above 16°C (16°F) are not needed to perform a low-temperature analysis. Higher temperatures were included because the test is easy and quick to perform. Both low- and high-temperature regions were then evaluated.

M_d values were measured using an apparatus manufactured by the Retsina Company of Oakland, California. This apparatus produces a total diametral modulus at a loading time of 0.1 sec by applying a vertical load on a diameter of a specimen and measuring the total horizontal deformation. This apparatus is marketed for measuring the resilient modulus of a specimen, but it actually measures a total modulus that includes elastic, viscoelastic, and permanent deformations (*5*). Deformations are measured in the horizontal, tensile direction, but the diametral theory assumes that the modulus in tension and the modulus in compression are equal. The M_d values reported in this study should not be considered absolute data because an assumed Poisson's ratio was used when calculating them. The following equation is used to calculate M_d (*2,5*):

$$M_d = \frac{10{,}000(P)(u + 0.2734)}{(t)(H_t)}$$

where

M_d = diametral modulus (Pa),
P = load (N),
u = Poisson's ratio (assumed as 0.35),
t = specimen thickness (cm), and
H_t = total horizontal deformation (cm).

The horizontal deformations were maintained within a range of 76 E-05 to 200 E-05 mm (30 E-06 to 80 E-06 in.) by varying the load. The test is virtually nondestructive in this range, and the same specimens can be tested at all temperatures (*5*). Specimens were tested at the lowest temperature first. The temperature was then raised to the next higher temperature. The specimens were cooled for 24 hr at the lowest temperature and for at least 4 hr for other temperatures.

The M_d values are shown in Table 4. There were no significant differences among the four mixtures at the lowest and highest temperatures. All three modified mixtures provided lower moduli at various intermediate temperatures, with an average decrease of approximately 30 percent in the temperature range of 0°C to 25°C (32°F to 77°F). The data indicate that the modified mixtures were more flexible at intermediate temperatures, but the effects on low-temperature cracking or high-temperature rutting are unclear. With respect to low-temperature performance, the data favor the modified mixtures down to approximately −16°C (3.2°F).

The diametral test cannot be performed above 40°C (104°F) because the diametral theory becomes invalid above this temperature. Specimens begin to fail in compression, whereas the theory requires that they fail in tension. Therefore, whether the modified mixtures would eventually become stiffer at temperatures above 40°C (104°F) could not be determined using this test.

The data for the three modified mixtures significantly differed from each other in only 3 of 30 *t*-test comparisons. This indicated that the modified mixtures had virtually equivalent M_d values at all temperatures.

Indirect Tensile Test

Indirect tensile tests were performed at a loading rate of 2.54 mm/min (0.10 in./min) (*4*). The specimens were tested at the design air-void level and at a reference temperature of −8°C (18°F). This temperature provides data in the brittle-ductile transition zone of asphalt mixtures. Additional research is

TABLE 4 Resistance to Low-Temperature Cracking

Average Diametral Modulus (M_d), MPa

Temperature °C (°F)	AC-20	CrO_3	MAH	Furfural
-32 (-25.6)	47,100	45,900 (NS)	43,000 (NS)	43,300 (NS)
-24 (-11.2)	39,300	39,500 (NS)	39,000 (NS)	37,800 (NS)
-16 (3.2)	36,700	33,000 (NS)	34,300 (NS)	31,100 (D)
-8 (17.6)	25,800	21,900 (D)	21,600 (D)	19,500 (D)
0 (32.0)	21,000	15,900 (D)	15,500 (D)	14,700 (D)
5 (41.0)	16,700	11,800 (D)	11,700 (D)	11,100 (D)
16 (60.8)	7,090	4,740 (D)	5,010 (D)	4,870 (D)
25 (77.0)	3,530	2,180 (D)	2,400 (D)	2,370 (D)
32 (89.6)	1,680	1,230 (D)	1,350 (D)	1,540 (NS)
40 (104.0)	730	660 (NS)	760 (NS)	870 (NS)

Average Indirect Tensile Test Data

Temperature = -8 °C (17.6 °F)	AC-20	CrO_3	MAH	Furfural
Tensile Strength, MPa	2.91	2.37 (D)	2.19 (D)	2.30 (D)
Strain at Failure, cm/cm	0.00140	0.00240 (I)	0.00254 (I)	0.00228 (I)
Work or Area, Pa	2,970	4,550 (I)	4,500 (I)	4,170 (NS)

NS = No significant difference between control and modified binder.
D = Modification decreased the test result.
I = Modification increased the test result.

MPa(145.04) = lbf/in^2 Pa/6895 = lbf/in^2 (1.8)°C + 32 = °F
cm/2.54 = in

needed to further develop this methodology because the results of the analysis can depend on what reference temperature is chosen.

Indirect tensile strength, tensile strain at failure, and the amount of work needed to cause tensile failure were evaluated. The work is the area under the stress-strain curve from the beginning of the test until failure. Higher strains at failure and higher amounts of work are associated with increased resistance to low-temperature cracking. These increases are usually accompanied by lower tensile strengths. Both the strains at failure and the amounts of work reported in this study should not be considered absolute data because an assumed Poisson's ratio was used when calculating strains.

The following equation is used to compute the indirect tensile strength of a specimen 10.2 cm (4.0 in.) in diameter (*2*):

$$S_t = \frac{614.2(P)}{t}$$

where

S = indirect tensile strength (Pa),
P = load (N), and
t = thickness (cm).

The following equation is used to compute the strain at failure, assuming a Poisson's ratio of 0.35 (*2*):

$$e_t = (0.205)(H_t)$$

where e_t is indirect tensile strain at failure and H_t is total horizontal deformation (cm).

The test data are shown in Table 4. *T*-tests indicated that the modified binders provided lower tensile strengths, higher tensile strains at failure, and higher amounts of work. The only discrepancy found was when the work data for the AC-20 control mixture and the furfural-modified mixture were compared. These data were not significantly different at the 95 percent level because of the high variability of the data for the furfural-modified mixture. The data were significantly different at the 93 percent level. Engineering judgment indicates that the furfural-modified mixture also required a higher amount of work to obtain failure. (There was not enough furfural-modified binder to fabricate additional specimens.) No significant differences were found when the three modified mixtures were compared.

Overall, the tensile test results indicated that the modified mixtures were more resistant to cracking at −8°C (18°F) than the AC-20 control mixture, but no modified mixture was better than another. The modified binders decreased the tensile strength by an average of 21 percent, increased the tensile strain at failure by an average of 72 percent, and increased the amount of work needed to cause tensile failure by an average of 49 percent. The modified binders decreased the M_d at −8°C (18°F) by an average of 19 percent.

RESISTANCE TO MOISTURE DAMAGE

The ALF aggregate blend used in this study is moderately susceptible to moisture damage and will visually strip in pavements if not treated with an antistripping additive. ALF mixtures that have not been cured and have not been treated generally have TSR and M_dR values of approximately 65 percent when tested by ASTM D4867, which was used to determine moisture susceptibility, and a percent visual stripping from 20 to 40 percent. Preliminary tests showed that the 4-hr curing period significantly increased the resistance of the AC-20 control mixture to moisture damage. The mixture passed the test. Therefore, it was decided to use uncured mixtures in this evaluation. If mixtures have to be cured to obtain engineering properties more similar to in-place pavement mixtures, the severity of the moisture-conditioning process must be increased. The ASTM test was not developed using mixtures cured for 4 hr.

Specimens compacted to approximately 7 percent air voids by the Marshall hammer were tested. Three unconditioned (dry) and three conditioned (wet) specimens were tested per mixture. Wet specimens were vacuum saturated with distilled water so that 55 to 80 percent of the air voids were filled with water, soaked in a 60°C (140°F) water bath for 24 hr, and tested at 25°C (77°F) along with the dry specimens. The optional freeze-thaw cycle of the ASTM method was not used. Past studies have shown that this step does not increase the level of damage when testing the ALF aggregates.

The diametral modulus test and the indirect tensile strength test were performed on each dry and wet specimen. Tensile tests were performed at a loading rate of 50.8 mm/min (2.0 in./min). The M_dR and TSR were computed for each mixture in terms of percents. A retained ratio is the average wet value divided by the average dry value.

The average percent visual stripping was also estimated for each mixture. Visual stripping is the percentage of area that is stripped on the basis of the total area of the split surface of the specimen.

The test data are shown in Table 5. A TSR below 80 percent, an M_dR below 70 percent, and visual stripping above 10 percent are suggested criteria for considering a mixture susceptible to moisture damage (*6*). The AC-20 control and CrO_3-modified mixtures had equal TSRs. Both were below 80 percent. The MAH- and furfural-modified mixtures had equivalent TSRs. Both were above 80 percent. The AC-20 control mixture and the CrO_3- and furfural-modified mixtures had M_dR values below 70 percent, and the M_dR of 39.6 percent for the CrO_3-modified mixture is very low. Only the MAH-modified mixture had an M_dR above 70 percent. Of all four mixtures, the MAH-modified mixture showed the most resistance to moisture damage.

The percent swell for each mixture, which is the average change in the volumes of the specimens caused by moisture conditioning, is also shown in Table 5. The swell of 1.3 percent for the CrO_3-modified mixture indicates that some internal damage probably has occurred. The swells for the other three mixtures are relatively low and have no practical significance.

The AC-20 control mixture failed both the TSR and M_dR tests as expected and had a high amount of visual stripping at 40 percent. The CrO_3-modified mixture also failed both tests. The furfural-modified mixture narrowly failed the M_dR test. However, none of the modified mixtures showed any visual stripping. It was concluded that the poor mechanical test results for these two modified mixtures were related to a loss of cohesion rather than a loss of adhesion. The binders were weakened by the moisture-conditioning process. The

TABLE 5 Resistance to Moisture Damage

	AC-20	CrO_3	MAH	Furfural
Tensile Strength, 25 °C (77 °F)				
Average Dry, MPa	0.600	0.492	0.471	0.427
Average Wet, MPa	0.441	0.361	0.419	0.363
Retained Ratio (TSR), percent	73.5	73.5	88.9	85.1
Diametral Modulus, 25 °C (77 °F)				
Average Dry, MPa	946	807	809	592
Average Wet, MPa	579	319	603	394
Retained Ratio (M_dR), percent	61.2	39.6	74.6	66.7
Average Visual Stripping, percent	40.0	0 (D)	0 (D)	0 (D)
Average Swell, percent by volume	0.6	1.3 (I)	0.3 (D)	0.3 (D)
Average Air Voids, percent	6.9	6.8	6.5	6.0

D = Modification decreased the test result.
I = Modification increased the test result.

MPa(145.04) = lbf/in^2

diametral modulus test was more sensitive to the damage in the binder compared with the tensile strength test, and it provided lower ratios. Reasons for these phenomena need to be investigated.

EXTRACTION AND RECOVERY

The binders were extracted and recovered to determine the effects of heating during mixing, curing, and compaction on the properties of the binders. Differences in degrees of hardening could affect mixture properties.

Mixtures were extracted by the centrifuge method and recovered by the Abson method. Trichloroethylene was used as the solvent. It was assumed that this solvent would not adversely affect the properties of the binders. Each mixture was allowed to digest in the trichloroethylene for 55 to 60 min at room temperature before it was centrifuged. A supercentrifuge was used to remove all dust from the solution.

Only one problem was encountered during recovery. The extracted solution containing the MAH-modified binder boiled out of the flask several times during the primary distillation process of the Abson method even though boiling chips were used. This phenomenon could not be controlled and a reason for it was unknown. If it is consistently found with asphalts modified with MAH, a different recovery process may be needed. It was assumed that the properties of the recovered binder were not adversely affected by this boiling action.

The data are given in Table 6. All three modified binders were significantly harder than the AC-20 control asphalt according to both viscosities. The penetrations at 25°C (77°F) for the AC-20 control asphalt and the binder modified with CrO_3 were equivalent. The penetrations for the other two modified binders were higher. On the basis of these data, all three modified binders should be stiffer at high pavement temperatures and softer at low pavement temperatures than the AC-20 control asphalt. This means that the modifications provided modified binders with desirable physical binder

TABLE 6 Recovery Results

	AC-20	CrO_3	MAH	Furfural
Penetration, 25 °C (100 g, 5 s), 0.1 mm	35	37	46	42
Kinematic Viscosity, 135 °C, um^2/s	973	1,370	1,714	1,362
Absolute Viscosity, 60 °C, dPa-s	17,041	56,055	61,971	53,774

(1.8)°C + 32 = °F dPa-s = P um^2/s = cSt mm/25.4 = in properties, even though the mixture curing process hardened the modified binders more than the AC-20 control asphalt according to both viscosities.

All four binders were significantly harder than was expected on the basis of properties for asphalt binders after production and placement in a pavement. The absolute viscosity of the recovered AD-20 control asphalt at 60°C (140°F) was almost 9 times the absolute viscosity of the original, unaged asphalt. A factor above 4 is excessive. There should also be some agreement between the thin film oven test properties in Table 1 and the recovered properties in Table 6. The data do not agree. The higher-than-expected degree of hardening indicates that the curing period should be reduced in any future study that uses these mixtures.

Excessive hardening could be expected on the basis of the work performed under the NCHRP AAMAS study. Although 3 hr of curing was finally specified by AAMAS, the required laboratory curing period based on the field data ranged from 0 to 13.5 hr and depended on the pavement project. Also, the curing period needed to match the laboratory and field viscosities did not always provide penetrations that were close to each other. A different curing period was often needed to match the penetrations. These findings indicate that the AAMAS laboratory curing procedure is very generalized, and it may be difficult to develop a standardized curing procedure on the basis of the field data.

CONCLUSIONS

Chemically Modified Binders

- The penetration and viscosity data of the binders recovered from the four mixtures indicated that the three chemically modified binders should be stiffer at high pavement temperatures and softer at low pavement temperatures than the AC-20 control asphalt.
- Tests performed to determine the effects of the modifications on the susceptibility to rutting were inconclusive. The primary measurements for evaluating this property were the permanent strains from the creep test. The three chemically modified binders decreased these strains by an average of 25 percent. However, the test data were so variable that this difference was not statistically significant.
- All three chemically modified mixtures had improved low-temperature properties down to approximately −16°C (3.2°F). The four mixtures had equivalent test results below this temperature. Some low-temperature cracking may be inhibited by the modifications.
- The MAH-modified mixture had the most resistance to moisture damage and passed both the diametral modulus and indirect tensile strength tests. The other three mixtures failed at least one of these tests. The AC-20 control mixture had a high amount of visual stripping, whereas all three modified mixtures showed no visual stripping. Therefore, any poor result shown by the modified mixtures was caused by a loss of cohesion rather than a loss of adhesion.
- When the mixture design and engineering test data for three modified mixtures were compared, very few differences were found. No modified binder was better overall than another. Differences in the retained ratios from the moisture susceptibility tests were the only exceptions to this finding.

NCHRP AAMAS Procedures

- The 4-hr mixture curing period excessively hardened the four binders.
- Adding lengthy curing periods to the Marshall design process would require the development of new specifications for stability and possibly for flow.
- Curing increased the resistance of the AC-20 control mixture to moisture damage to a level that did not match historic pavement performance. If a curing period is to be required by a design procedure, the severity of the moisture-conditioning process must be increased.
- Based on both Marshall compaction and the ultimate field densities of the ALF pavements, the AAMAS GTM compactive effort was slightly high.
- The 6 to 8 percent air-void levels required by the ASTM D4867 test for moisture susceptibility could not be obtained using a kneading compactor, even with low tamps and pressures.

RECOMMENDATIONS

Chemically Modified Binders

- The compositions of the fumes from the chemically modified binders and whether any harmful substances can leach from them need to be studied. All three binders had different odors, which were different from those of unmodified asphalt binders.
- The cost of manufacturing each chemically modified binder needs to be determined.
- How moisture conditioning affects the cohesive properties of chemically modified mixtures needs to be investigated.

NCHRP AAMAS Procedures

- Additional research is needed to develop curing procedures on the basis of field data. A uniform, standardized curing procedure is needed for use in research studies so that data from various studies and organizations can be compared. On the basis of data published in the AAMAS report, a standardized curing procedure may be difficult to develop.
- The current Marshall design practice of determining the compaction temperature from the viscosities of the unaged binder is probably not applicable when mixtures are cured. A standardized method of obtaining a curing and compaction temperature is needed when mixtures are cured.

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