

The Effect of Wax Modification on the Performance of Mastic Asphalt

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Abstract: The scope of this study is to evaluate the mechanical performance of the polymer modified mastic asphalt with 4% montan wax (Asphaltan A) additive. The impact of wax modification on binder, binder/filler mixtures, and mastic asphalt was investigated in the laboratory. Wax modified binder properties were determined using dynamic mechanical analysis (DMA), Fourier transform infrared (FTIR) spectroscopy and conventional tests (softening point, penetration, elastic recovery, breaking point, viscosity, and storage stability). The bending beam rheometer (BBR) was used for determining low temperature creep compliance and the tensile stress restrained specimen test (TSRST) for determining low temperature fracture. The fatigue cracking behavior of mastic asphalt was investigated using Superpave Indirect Tensile Test (IDT). Based on hot mix asphalt (HMA) Fracture Mechanics the influence of wax on the asphalt mixture resistance to fatigue and brittle cracking has been evaluated. The addition of wax to the polymer modified binder resulted in a viscosity reduction at higher temperatures, indicating a possible lower production and laying temperature as compared to asphalt without wax additive. DMA and BBR results showed some increase in stiffness and a more elastic response of the wax modified binder at medium and low temperatures. The TSRST fracture temperature was higher for the mastic asphalt containing wax, indicating a certain negative impact of wax modification.

Key words: Energy saving; HMA fracture mechanics; Low temperature performance; Superpave IDT.

Introduction

Mastic asphalt is most often used as wearing course for bridges and parking decks. Production, transport, and placing of mastic asphalt differ considerably from working with conventional asphalt concrete. Mastic asphalt is not compacted, but placed using screed pavers or manually. A major benefit of this material is that it is dense (no air void content), waterproof, and wear resistant. The binder content is high (compared to asphalt concrete), meaning better adhesion between binder and aggregate and reduced negative effect of aging.

Mastic asphalt binders (and mastics) normally have to be stiffer than for asphalt concrete to make the mastic asphalt resistant enough to rutting. Thus, hard paving grade bitumen is used in addition to high filler content. High filler content and optimum grading of coarser aggregates will stiffen the product and make the pavement resistant to deformation. Calcium carbonate filler normally is used in mastic asphalt, for better workability [1]. Since 1990's, development has been done on modification of mastic asphalt using polymers in Sweden [2, 3]. Polymer modified asphalts (PMAs) were developed to improve pavement performance. The main task of asphalt modification is to reduce rutting, fatigue cracking, and thermal cracking and, therefore, an increase of the aggregate durability and reduction of maintenance costs. PMAs are

blends of asphalt and one or more polymers, usually added in percentages ranging from 3 to 7% by weight, with respect to the bituminous phase [4].

Mastic asphalt mixing temperature must be kept within a certain range. Polymer modified mastic asphalt products (Gussasphalt) require even higher working temperatures. It may go up to +230°C or more, depending on the laying conditions. Temperature must be high enough for good workability, but not too high, as binder properties may then be affected in a negative way or polymer may degrade. If the mastic asphalt is heated too much (or for too long), the binder becomes brittle and the pavement more sensitive to cracking. Working at high temperatures is energy-intensive and will release more emissions of bituminous fumes and carbon dioxide compared to conventional hot mix asphalt works. This has become a problem, since harder requirements concerning allowed working temperatures/amount of emissions have been introduced [5-7].

Recently, several energy saving asphalt production techniques and processes have been developed, and warm mix asphalt (WMA) technology is currently of great interest to the asphalt industry as well as to researchers all over the world [8-14]. In particular, one way of reducing the asphalt mixture temperature, hence reducing the emissions is by using flow improving additives like wax [15-18]. Viscosity depressant additives which have shown significant effect on mastic asphalt are certain types of waxes. Adding 3% (by weight of binder content), normally is considered as sufficient.

Aiming to make polymer modified mastic asphalt more environment friendly, a joint Swedish project about wax as flow improver in mastic asphalt production was initiated a couple of years ago. The project involves laboratory testing of binder and asphalt mastic products as well as testing in the field [19, 20]. For Swedish conditions, mainly two types of waxes have been tried. These are FT-paraffin (Sasobit) and montan wax (Asphaltan A). Based on results from these studies, polymer modified mastic asphalt with montan wax additive is investigated presently focusing on low temperature performance and possible negative impact on

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crack susceptibility due to the addition of wax.

Influence of wax modification on rheological properties of polymer modified bitumen at high and medium temperatures were investigated as well using the Dynamic Mechanical Analysis (DMA). Conventional tests including softening point, penetration, elastic recovery, breaking point Fraass, viscosity, and storage stability were conducted to characterize the binder mixture. Chemical characterization was also done using Fourier Transform InfraRed (FTIR) spectroscopy to see the effect of adding wax and aging on binder and binder mixture. Bending Beam Rheometer (BBR) and Tensile Stress Restrained Specimen Test (TSRST) were used to study the behavior of the materials with wax additive at low temperatures.

The effect of wax additives on the resilient modulus, Poisson's ratio, creep compliance, and tensile strength of asphalt mixtures has been investigated with Superpave Indirect Tensile Test (IDT) [21, 22]. The effect of wax on fracture resistance of the asphalt mixtures on the field has been evaluated based on HMA Fracture Mechanics framework [23].

Methodology

The binder mixtures and mastic asphalt products used in this study were selected from earlier studies performed within a joint Swedish project about wax additive in polymer modified bitumen and coarse aggregate mastic asphalt [19, 20]. The materials used, sample preparation, and test methods are described in this chapter.

Materials

The polymer modified bitumen used is a 50/100-75 class product, Pmb 32, produced by Nynas. This binder is specially developed for use in mastic asphalt. Compared to standard bitumen, Pmb 32 shows higher resistance to low temperature cracking as well as to permanent deformation at higher temperatures. The product has been used in Sweden for many years with good results.

The wax additive is a montan wax product named Asphaltan A, produced by Romonta GmbH. The product is used mainly for mastic asphalt, with higher mixing and laying temperature than asphalt concrete.

The filler used contains mainly commercial filler (calcium carbonate product), and was mixed in production with approximately 10 % collected dust from the asphalt plant.

The bitumen/wax mixture was prepared in the laboratory by adding 4% wax by weight of approximately 240g of Pmb in 0.5 liter tins. The mixture was then heated for 30 min at 180°C. Finally, the binder mixture was placed in preheated moulds and homogenized in a mixer by shaking for 90s. Same procedure was followed for Pmb 32 containing no wax.

Aging of the binders was performed using the rolling thin film oven test (RTFOT, EN 12607-1) for 75 min at 200°C. The reason for using 200°C instead of 163°C, according to the standard procedure, is that mastic asphalt mixtures normally are produced in asphalt plants using higher mixing temperature compared to asphalt concrete mixtures. On the other hand, pressure aging vessel (PAV) long term aging was not performed in this study as mastic asphalt has no void content, and therefore should age very little over time.

Mixtures of filler and aged binder (with and without wax) were also prepared, using a ratio of 3:1. Mixing was carried out manually, using a stirrer. The mixing ratio is similar to that of the mastic asphalt product, with a filler content of 27-28% by weight of the aggregate and binder content of 8%. Mixtures were evaluated using the methods of analysis described in the following sections.

Coarse aggregate mastic asphalt was produced by NCC/Binab, using standard recipe/composition (BPGJA 8 with 8% binder content). One product was produced with Pmb 32, and another with Pmb 32 plus 4% (by bitumen weight) of wax additive Asphaltan A. Due to practical reasons at the plant, the wax was added to the asphalt mixture and not, as normally recommended, to the binder. Slabs were taken out during application work at an indoors parking deck. Specimens were then sawed from the different slabs in the laboratory and subjected to BBR, TSRST, and Superpave IDT testing.

Test Methods

The following standard methods were used to characterize the binder mixtures before and after aging:

- softening point (EN 1427),
- penetration at 25°C (EN 1426),
- elastic recovery at 10°C (EN 13398),
- breaking point Fraass (EN 12593),
- viscosity at 135 and 180°C (EN 13302), and
- storage stability at 180°C (EN 13399).

Fourier Transform InfraRed (FTIR) Spectroscopy

An FTIR spectrometer, Infinity 60AR (Mattson resolution 0.125cm^{-1}), was used to investigate functional groups of the binder mixtures, before and after aging. 5% wt solutions of binder samples were prepared in carbon disulphide. Scans were performed using circular sealed cells (ZnSe windows and 1mm thickness). All spectra were obtained by 32 scans with 5% iris and 4cm^{-1} resolution in wave numbers from 4,000 to 500cm^{-1} . Peaks of infrared (IR) absorbance from 750 to 680cm^{-1} were used as indication of amorphous and/or crystalline structures due to wax content. The peak at $1,705\text{cm}^{-1}$ shows bitumen carbonyl compounds and the peak at $1,030\text{cm}^{-1}$, sulfoxides. Finally, peaks at 965 and 700cm^{-1} represent the styrene-butadiene-styrene (SBS) polymers.

Dynamic Mechanical Analysis (DMA)

Both complex modulus and phase angle are functions of temperature and frequency which may be changed using additives like polymers or waxes. Comparative tests were performed on binder mixture samples as well as on mixtures of filler and aged binder (with and without wax).

DMA temperature sweeps were conducted in the total temperature range of -30 to +100°C using a dynamic shear rheometer (Rheometrics, RDA II). For the temperature range from -30 to +90 °C, parallel plates with diameter of 8mm and gap 1.5mm were used at a frequency of 10rad/s. For the temperature range of +10 to +100°C, plates with diameter of 25mm and gap 1mm were used, and the frequency was 1rad/s. The test started at lower

temperatures and was increased by $2^{\circ}\text{C}/\text{min}$. A sinusoidal strain was applied and values of actual strain and torque were measured. Dynamic shear modulus $|G^*|$, phase angle (δ), and $|G^*|/\sin\delta$ were calculated.

For performance grading of the binders, according to Superpave [24], time sweeps were carried out from $+70$ to $+88^{\circ}\text{C}$. The frequency used was 10rad/s and values of $|G^*|/\sin\delta$ were calculated.

Creep Test Using Bending Beam Rheometer (BBR)

Creep testing was performed on binder mixture samples, on mixtures of filler and aged binders and on mastic asphalt beams to see the effect of wax additive on the creep compliance of the polymer modified binder and asphalt. Tests were carried out at five different temperatures (-24 , -18 , -12 , -6 , and 0°C) using the bending beam rheometer (TE-BBR, Cannon Instrument Company). For each testing temperature, the rheometer was calibrated according to standards. At least two beams were tested for each material. Mastic asphalt beams were sawed from slab samples and trimmed, keeping the beam dimensions as similar as possible to the corresponding binder beam samples.

The sample beam (125mm long, 12.7mm wide and 6.35mm thick) was submerged in a constant temperature bath keeping it at each test temperature for 60min . The beam was placed on the sample support in the BBR to be tested and a seating load of 980mN was applied for 1s . Then the load was reduced to pre-load of 35 to 44mN for recovery of the sample for a period of 20s . After recovery period, a constant load of 980mN (100g) was applied for 480s . Creep stiffness (S), creep compliance $D(t)$ and creep rate (m) were determined. The BBR has a limitation of measuring up to 240s when automated. In order to take readings up to 480s , the rheometer was run manually and readings for load and deflection were noted for every 5s time interval. For the performance grading of the binders, according to Superpave, standard procedure was used [25].

Tensile Stress Restrained Specimen Test (TSRST)

A frequently used laboratory method for simulating low temperature cracking in pavements is the TSRST. The TSRST equipment used in this study was developed by Oregon State University [26, 27]. The tests were performed on specimens of polymer modified mastic asphalt with and without wax additive. The test specimen ($35 \times 35 \times 210\text{mm}$) was glued to two aluminium plates with epoxy. After the epoxy cured, the specimen/plate assembly was mounted in the load frame. The test specimen was kept at 2°C for 60min in the environmental chamber to ensure that the temperature was constant inside the specimen and the same as in the chamber. The cooling rate was $10^{\circ}\text{C}/\text{hr}$. The contraction of the specimen during cooling was measured using two linear variable differential transducers (LVDT). If the contraction exceeds 0.0025mm , a command is sent to the screw jack which stretches the specimen back to its original position. The test stopped when the thermally induced stresses in the specimen exceed its strength resulting in a fracture in the specimen. Test parameters obtained were fracture temperature, fracture strength, and transition temperature.

At the beginning of the test, a relatively small increase in the thermal stress can be observed due to relaxation of the asphalt

mixture. The induced stress then gradually increases with decreasing temperature, until the specimen breaks at a point where the stress reaches its highest value on fracture strength. The slope of the stress-temperature curve, $(\Delta S/\Delta T)$, increases as well until the temperature reaches a certain value, the transition temperature, where it becomes constant. The slope may play an important role in characterizing the rheological behavior of asphalt mixtures at low temperatures [27].

Superpave Indirect Tensile Test (IDT)

Resilient modulus, M_R , Poisson's ratio, ν , creep compliance, $D(t)$, and tensile strength, S_t were measured on polymer modified mastics asphalt with and without wax modification using procedures to carry out Superpave IDT test [21, 22]. Three samples were tested for each material and a trimmed average approach, as described in Reference [28] was used to obtain material parameters representative for each mixture. The specimen dimensions were 150mm in diameter and 40mm in thickness.

Initially, experiments were conducted at $+10$ and 0°C for asphalt mixtures with and without wax additives. However, it has been observed during IDT strength tests at these temperatures that specimens exhibit very ductile behavior - resulting in the deformations outside the measurement range before the fracture point. Thus it has been decided to perform the experiments at -5°C .

Resilient modulus test was conducted by applying a haversine load, each load cycle consisting of 0.1s loading application followed by a 0.9s rest period. In order to ensure the validity of linear viscoelasticity, the load magnitude was adjusted to keep horizontal deformations within range of 200 – 300 microstrain. The instantaneous and total resilient modulus and Poisson's ratio were then calculated according to [21, 22].

The creep compliance tests were performed on the same sample allowing it to recover for at least 10min . The sample was loaded with a constant load for $1,000\text{s}$. The load magnitude was chosen to result in horizontal deformation within the range of 200 to 750 microstrain by end of the test. The creep compliance was calculated as described in [28]. The creep compliance curve was then fitted with power law function:

$$D(t) = D_0 + D_1 t^m \quad (1)$$

where $D(t)$ is the creep compliance at time t , and D_0 , D_1 and m are creep compliance parameters; D_0 defines instantaneous elastic response and, D_1 and m define a slope of creep compliance.

The IDT strength test was conducted to determine the tensile strength and strain at failure of the mixture sample. Sample was loaded at a constant displacement rate of $50.8\text{mm}/\text{min}$ until the point of first fracture as defined in [28]. Relations proposed in [28] were used to calculate the tensile strength and the strain at failure. The stress-strain curve was recorded during the test and used to calculate mixture's fracture energy:

$$FE = \int_0^{\epsilon_f} \sigma(\epsilon) d\epsilon \quad (2)$$

where $\sigma(\epsilon)$ is a horizontal stress as a function of a horizontal strain and ϵ_f is a horizontal strain at the point of first fracture.

Table 1. Results Obtained from Conventional Test Methods.

Test	Pmb	Pmb 32+4% Wax
Original Binder	32	Wax
Softening Point (°C)	75	93
Penetration at 25 °C (dmm)	53	45
Breaking Point Fraass (°C)	-14	-11
Elastic Recovery at 10 °C (%)	72.5	53.4 ^a
Viscosity at 135°C (mPas)	1544	1394
Viscosity at 180°C (mPas)	258	192
Storage Stability after 72hrs at 180°C		
Δ Softening Point (°C)	0	0.5
After RTFOT at 200°C		
Softening Point (°C)	75	94
Penetration at 25°C (dmm)	23	24
Breaking Point Fraass (°C)	-9	-8
Elastic Recovery at 10°C (%)	55.5 ^a	52.2 ^a

^a Specimen Broke before Stretching to 200mm.

HMA Fracture Mechanics Framework

An HMA fracture mechanics developed recently in the University of Florida, USA provides a fundamental theoretical framework to predict crack initiation and propagation in asphalt pavements. According to HMA fracture mechanics, crack initiation in asphalt mixtures can be completely described by two distinct thresholds: the dissipated creep strain energy limit and fracture energy limit [29-31]. These thresholds were shown to be invariant of the mode and rate of loading [29-31]. Thus, combined with HMA fracture mechanics results from the Superpave IDT tests may be used to predict mixture's fracture performance in the field [23, 29-31].

The fracture energy, FE , threshold is calculated according to Eq. (2) and dissipated creep strain energy limit ($DCSE_f$) is determined as:

$$DCSE_f = FE - EE \quad (3)$$

where EE is the elastic energy defined as

$$EE = \frac{1}{2} S_t \epsilon_e \quad (4)$$

where S_t is the tensile strength of the mixture and ϵ_e is an elastic strain at failure, calculated as:

$$\epsilon_e = \frac{S_t}{M_R} \quad (5)$$

The $DCSE_f$ is a measure of how much micro-damage mixture can take before it results in a macrocrack initiation. In order to predict fracture performance of the mixture in the field, a so-called energy ratio criteria was proposed in [23]. Energy ratio is defined as:

$$ER = \frac{DCSE_f}{DCSE_{min}} \quad (6)$$

where $DCSE_{min}$ is a measure of how much damage will the material accumulate in the field during service life. For a given maximum

tensile stress in a pavement, σ_{max} , $DCSE_{min}$ may be calculated as [23, 32] :

$$DCSE_{min} = \frac{m^{2.98} D_1}{f(S_t, \sigma)} \quad (7)$$

$$f(S_t, \sigma) = 0.0299 \sigma_{max}^{-3.1} (6.36 - S_t) + 2.46 \cdot 10^{-8} \quad (8)$$

For a good field performance of the mixture $ER > 1$ is required. Generally, higher ER indicates better fracture resistance of the mixture. Presently, in order to evaluate the effect of wax additive on asphalt mixture's fracture resistance, the IDT results were introduced into Eqs. (3-8) and HMA fracture mechanics parameters were calculated. The influence of wax additive on mixtures resistance to fatigue fracture in the field has been evaluated for the case of $\sigma_{max} = 689 \text{ kPa}$ (100psi).

Results and Analysis

Addition of wax to the Pmb showed a reduction in viscosity, corresponding to a possible similar effect on production and laying temperature for the mastic asphalt. In addition to that, adding wax showed stiffening effect from about +100°C and downed to at least +5°C. This stiffening effect was demonstrated by decrease in penetration (at +25°C), increase in softening point, and by DMA temperature sweeps for the binder as well as binder/filler mixture, showing increase in complex modulus and decrease in phase angle.

In the following sections, results on binder, binder/filler mixture, and mastic asphalt performance, due to the addition of wax Asphaltan A are presented and discussed.

Conventional Characteristics

Results from conventional binder testing on Pmb 32 (with and without wax) are depicted in Table 1. The results show that adding wax definitely affects the binder within a broad temperature range.

Viscosity is reduced at high temperature (+135 and +180°C), indicating that production and laying temperature could be decreased by at least 10°C, using this type and amount of wax additive in the mix. Depending on the binder, a reduction of the temperature during production and placing of 10°C may reduce the emissions by 30 to 50% for mastic asphalt [33]. Because of the addition of wax it is possible to lower the mastic asphalt laying temperature, which is environmental friendly. In a recent study [34], a considerable increase in softening point and a decrease in penetration value was seen by adding montan wax in binder 160/220. As seen in Table 1, at temperatures from about +100°C and lower, a similar stiffening effect was achieved (in terms of penetration at 25°C and softening point) by addition of wax. This means that montan wax has stiffening effect on the binder. Elastic recovery at 10°C is decreased and Fraass breaking point is somewhat increased, indicating a certain negative effect on low temperature behavior. However, after aging both the binders show very similar results concerning penetration, elastic recovery and breaking point. Only softening point is still higher for the binder containing wax. As a whole, the wax modified binder was least affected by aging. Finally, the observed effect of wax modification

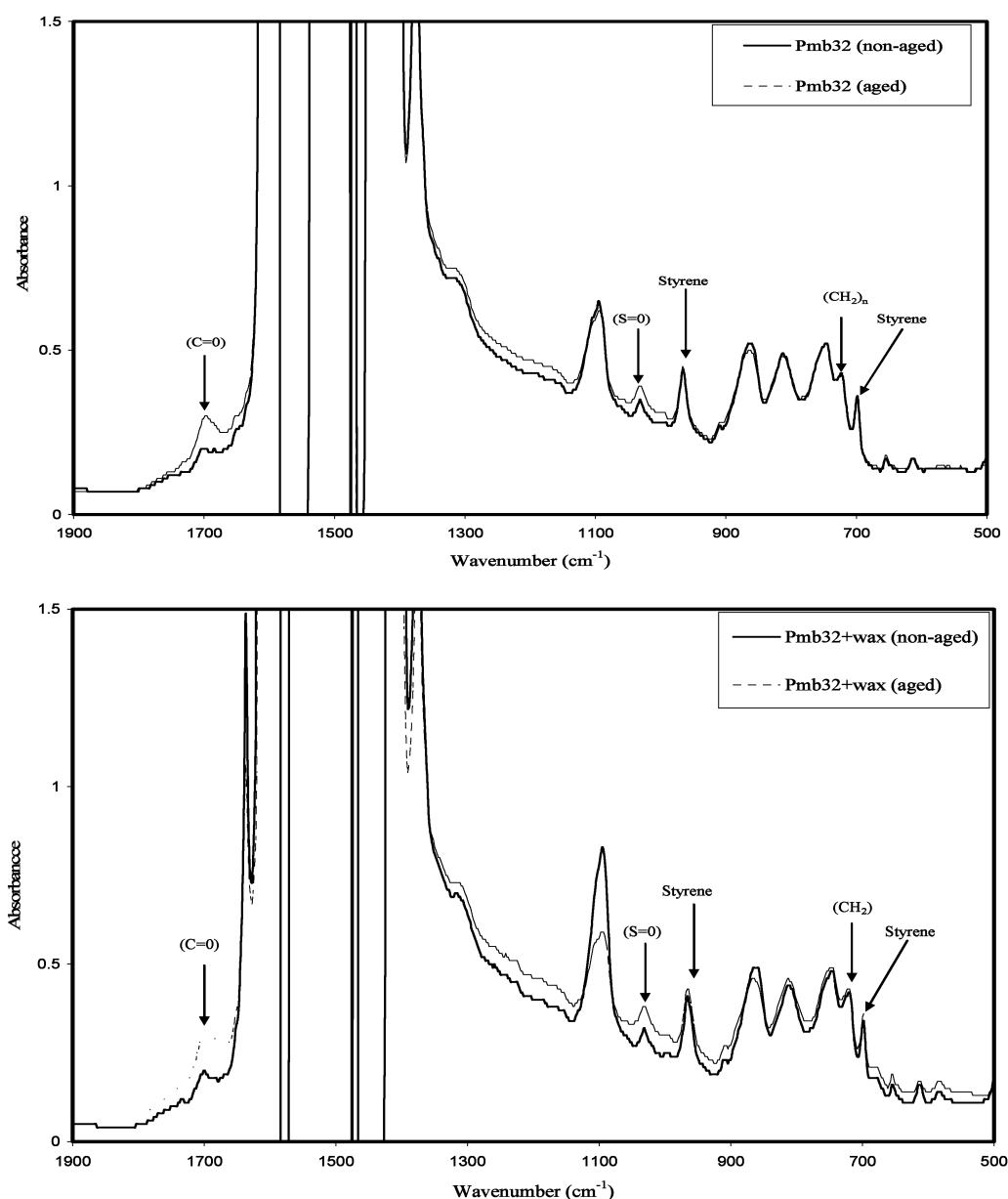


Fig. 1. FTIR Spectra of Pmb 32 and Pmb 32 with Wax, Before and After Aging.

Table 2. Chemical Characterization Using FTIR.

	Pmb 32			Pmb 32 + 4%Wax		
	Non-aged	Aged	AI ^a	Non-aged	Aged	AI ^a
C = O 1,705cm ⁻¹	1.13	2.61	2.31	1.20	2.48	2.07
S = O 1,030cm ⁻¹	0.79	1.07	1.35	0.8	1.04	1.30
(CH ₂) _n 750 to 680cm ⁻¹	0.94	0.95	1.01	1.37	1.26	0.92
SBS 700cm ⁻¹	1.16	1.16	1.00	0.93	0.95	1.02
SBS 965cm ⁻¹	3.03	2.83	0.93	3.37	3.02	0.90

^a Aging index (AI) determined by (IR_{aged}/IR_{non-aged})

on storage stability was negligible, within experimental scatter.

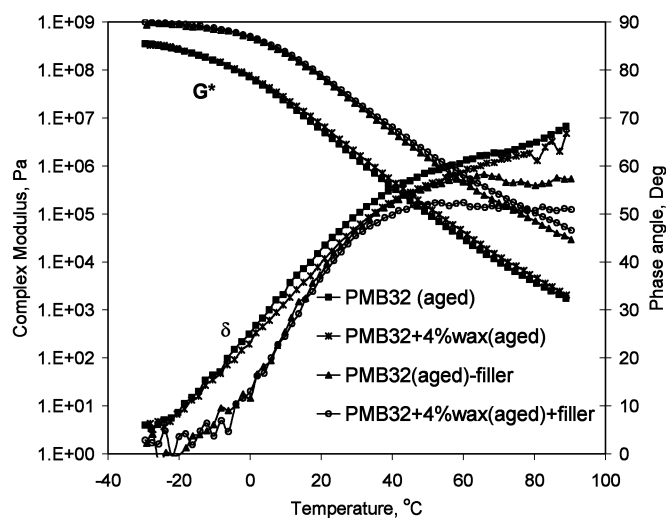
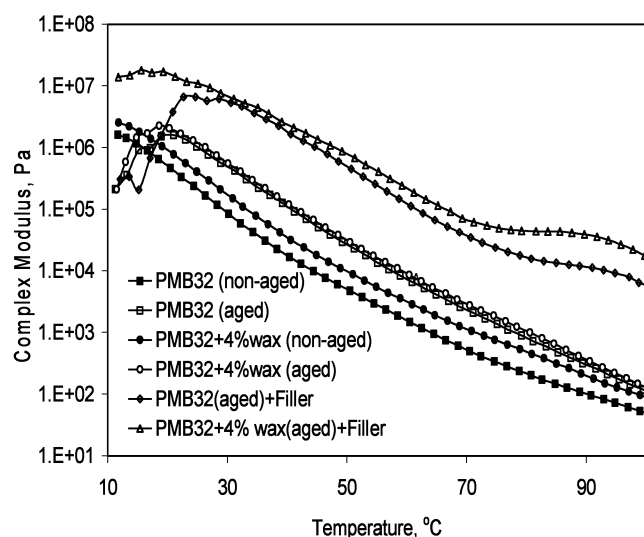
Limited Superpave binder testing was performed, using results from DMA (time sweep at frequency of 10rad/s) and BBR (S and m-value). Based on these results, the performance grade for Pmb 32 was estimated to be PG 76-28. Adding wax changed the grading to PG 88-22, indicating a quite large improvement on the rutting criteria and some negative impact on the resistance to thermal cracking.

Chemical Characterization by Fourier Transform InfraRed (FTIR) Spectroscopy

Fig. 1 presents the FTIR spectra obtained and Table 2 shows the FTIR spectra results. Adding wax to Pmb 32 did not show any increase in the sulfoxide absorbance at 1,030cm⁻¹ for neither non-aged nor aged mixture. Carbonyl absorbance at 1,705cm⁻¹ increased by

Table 3. BBR Test Results of Aged Binders, Binder/Filler Mixtures, and Mastic Asphalt Beams.

	Stiffness, S (MPa)					M-value						
	Temperature, °C											
Binders	-24	-18	-12	-6	0	-24	-18	-12	-6	0	LST	LmT
Pmb 32 ^a	503	281	124	-	-	0.234	0.308	0.359	-	-	-18.5	-19
(Pmb32 +4% Wax) ^a	532	311	160	-	-	0.202	0.256	0.299	-	-	-18	-12
Pmb32 ^a + Filler	2,753	2,061	1,158	641	276	0.13	0.214	0.288	0.357	0.438	-	-
(Pmb32+ 4% Wax) ^a + Filler	3,157	2,331	1,218	660	328	0.146	0.211	0.276	0.316	0.398	-	-
Pmb32 (Asphalt Mix)	6,654	5,465	4,053	2,885	1,386	0.057	0.095	0.179	0.265	0.359	-	-
Pmb32 + 4% Wax (Asphalt Mix)	6,715	5,836	4,729	4,288	2,046	0.066	0.098	0.133	0.203	0.291	-	-

^a After RTFOT at 200°C**Fig. 2.** Complex Modulus and Phase Angle as a Function of Temperature at 10rad/s for Binder Mixtures and Mixtures of Filler and Aged Binder.**Fig. 3.** Complex Modulus as a Function of Temperature at Frequency of 1rad/s for Binder Mixtures (Before and After Aging) and Mixtures of Filler and Aged Binder.

adding wax but decreased for the aged binder mix. As expected, IR absorbance for methylene groups with straight chains at 750 to 680 cm^{-1} was increased by addition of wax and not affected by aging.

Concerning absorbance representing SBS in Pmb 32, copolymer absorption for polybutadiene is shown at 965 cm^{-1} and for polystyrene at 700 cm^{-1} [35]. Adding wax had some minor effect on this absorbance, indicating possible chemical reaction between wax and polymer. In conclusion, addition of wax showed no negative influence on binder aging properties (aging index, AI).

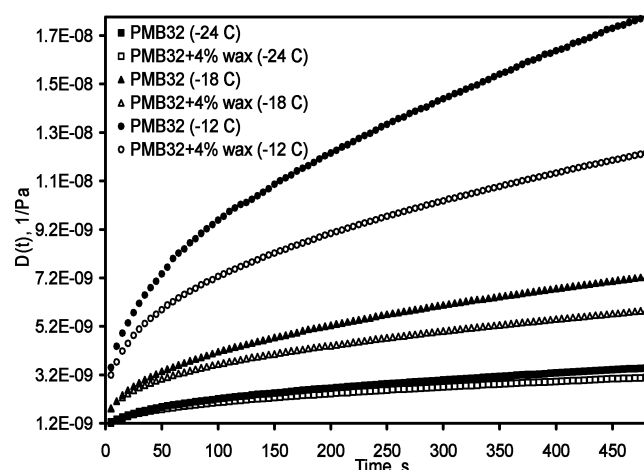
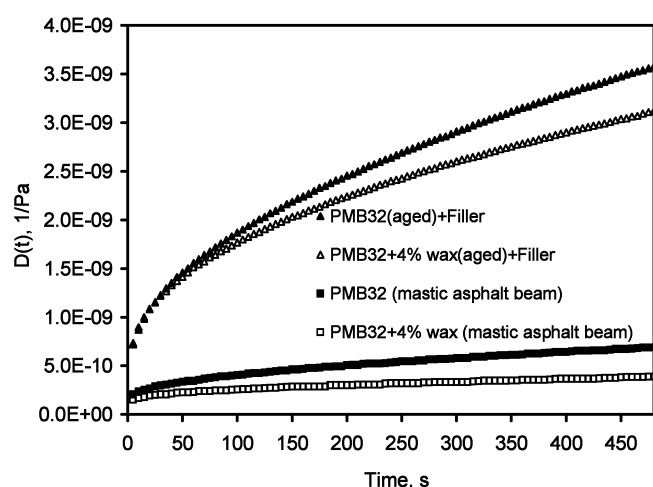
Dynamic Mechanical Analysis (DMA)

DMA temperature sweeps were performed over a wide range of temperatures (-30 to +100°C) for binder mixtures (with and without wax, before and after aging) as well as for mixtures of filler and aged binder. Results are shown in Figs. 2 and 3. Fig. 2 shows the temperature dependence (from -30 to +90°C) of complex modulus and phase angle for all mixtures tested in the study. One may notice in Fig. 2 that the wax modified binder mixtures showed much higher values of complex modulus as compared to the unmodified mixtures. However, we can correlate the results from viscosity (see Table 1) and say that wax modified binder mixtures will likely show a decrease in complex modulus at temperatures above 100°C or so, due to the fact that their viscosity values at higher temperatures (135 and 180°C) are lower than the unmodified binder. Highly polymer modified bitumens may exhibit four regions of modulus as a function of temperature: the glassy region, the transition region, a plateau region (corresponding to a phase angle maximum and minimum), and the flow region [36]. For binders containing wax, wax crystallization, and/or gel formation and melting may occur as well. For Pmb 32, having comparably low polymer content (approximately 4%), no evident complex modulus plateau is shown in Fig. 2. The polymer modification is simply indicated by an increase in elastic response (drop in phase angle) at temperatures higher than approximately +50°C, which can be seen in the Fig. 2. Adding wax to Pmb 32 showed noticeable increasing effect on complex modulus at medium and higher temperatures. This is more clearly illustrated in Fig. 3, showing a temperature sweep at 1rad/s. A similar effect of increase in complex modulus and decrease in phase angle was also seen when montan wax was added to binder 160/220 in a recent study [34].

A sharp decrease in complex modulus for temperatures below 25°C can be seen in Fig. 3 for aged binders and binder/filler mixture. It may be because of the samples being too stiff for the testing machine. Binder/filler mixtures around 80 to 90°C show a constant complex modulus and then again a decrease can be seen as temperature increases. It may indicate that binder started softening and stiffness might be due to the filler effect. Aging increased the

Table 4. Material Parameters from Superpave IDT.

Samples	M_R (GPa)	ν	D_0 (1/GPa)	D_1 (1/GPa)	m	$D(1000)$	$D'(1000)$	S_t (MPa)	ϵ_f (microstrains)
Mastic Asphalt with Pmb 32	18.298	0.291	0.0547	0.0386	0.5364	1.62	0.0008	5.05	1730
Mastic Asphalt with Pmb 32 + 4%Wax	20.218	0.273	0.0495	0.0198	0.5519	0.95	0.0005	4.35	1150

**Fig. 4.** BBR Creep Test at -24, -18, and -12°C on Aged Binder Mixtures.**Fig. 5.** BBR Creep Test on Binder/Filler Mixtures and Mastic Asphalt at -6°C. (For Clarity not All Test Temperatures Are Shown).

complex modulus for all mixtures, but the wax showed no noticeable negative influence on aging properties of the binder. Comparing binder/filler mixtures to binders, the filler mixtures obviously are much stiffer, i.e. the complex modulus is higher and the phase angle lower due to filler content. In general, the binder/filler mixture seemed less affected by the addition of wax additive, compared to the binder.

Creep Test Using Bending Beam Rheometer (BBR)

BBR tests were conducted at -24, -18, and -12°C for all test samples (binder mixtures, binder/filler mixtures, and mastic asphalt). Additional BBR analyses were performed also at -6 and 0°C for the binder/filler mixtures and mastic asphalt samples. Results of BBR low temperature parameters at a loading time of 60 s are indicated

in Table 3. The binder (Pmb 32 and Pmb 32 + wax) was aged in all cases.

For controlling the low temperature cracking propensity according to Superpave binder specifications, BBR creep stiffness must not exceed 300 MPa and the m -value must be limited to at least 0.300. Lower limit temperatures can be determined from BBR results at two or more different temperatures (Limiting stiffness temperature (LST) at which $S = 300 \text{ MPa}$ and Limiting m -value temperature (LmT) at which $m = 0.300$). This was done in the study based on test results at -12, -18 and -24°C. The results show that only LmT for Pmb 32 (after RTFOT) was significantly affected by the addition of wax, indicating a possible negative effect on low temperature performance. However, the m -value is the absolute value of the slope of the stiffness versus time on log-log scale [37]. It was included in the Superpave specification because it was established that materials with a longer relaxation time should dissipate stresses more slowly and therefore be more susceptible to thermal cracking. On the other hand, limiting temperatures are dependent on the source and grade of bitumen and polymer modification may not show beneficial effect. Especially for LmT, even negative effect has been found for polymer modification [38]. Also in the case of binder/filler mixtures, the BBR stiffness was somewhat increased by the addition of wax, at all temperatures tested, and the m -value mainly was decreased.

Fig. 4 shows creep compliance of binder mixtures at -24, -18, and -12°C, and Fig. 5 creep compliance at -6°C for binder/filler mixtures and mastic asphalt, indicating in all cases a decrease in compliance (increase in stiffness) due to wax modification for the test period of 480s. At very low temperature like -24°C, the impact of wax is small but increase with temperature and time.

The creep behavior of the binders at low temperatures is significantly different compared to filler/binder mixtures and mastic asphalt, and highly dependent on loading time. The loading time dependency is the key factor that shows difference between binders and their behavior in the pavements [39]. In order to measure creep compliance for as long loading times as possible, all test samples were subjected to creep in BBR for 480s. From Fig. 5, it is obvious that wax makes the binder and mastic asphalt stiffer hence possibly less resistant to cracking at low temperatures.

Tensile Stress Restrained Specimen Test (TSRST)

In TSRST, at least two specimens were tested for each mix. Stress temperature relationship is illustrated in Fig. 6 which shows that adding 4% wax to the polymer modified mastic asphalt had certain negative effect, increasing the fracture temperature by approximately 5°C, from -35 to -30°C. The fracture strength of the polymer modified mastic asphalt was around 6.7 MPa whereas that of polymer modified mastic asphalt containing wax was found to be 5 MPa. As it is seen in Fig. 6 the stress response of the wax modified

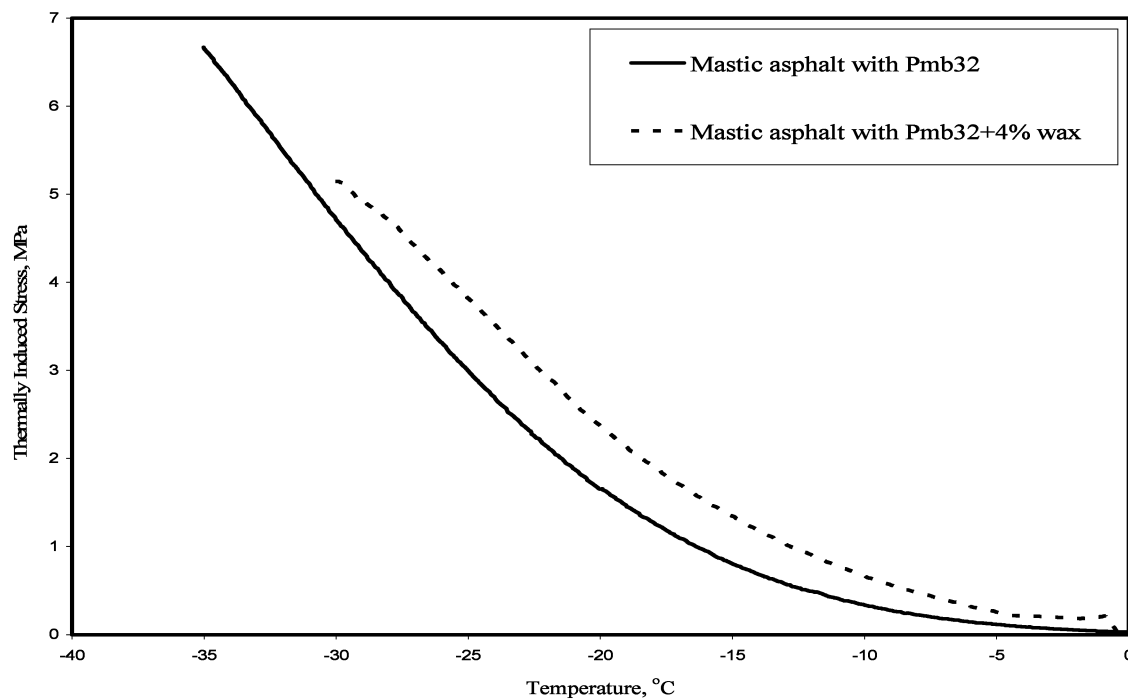


Fig. 6. TSRST Response of the Mastic Asphalt with and without Wax Modification.

Table 5. HMA Fracture Mechanics Parameters from Superpave IDT.

Samples	FE (KJ/m ³)	EE (KJ/m ³)	DCSE _f (KJ/m ³)	DCSE _{min}	ER
Mastic Asphalt with Pmb 32	6.0445	0.6685	5.376	1.0447	5.1166
Mastic Asphalt with Pmb 32 + 4%Wax	3.7274	0.5535	3.1738	0.5536	5.5944

mixture changed to linear at a higher temperature as compared to the one without wax. This indicates the transition temperature increased from -29 to -20°C due to the addition of wax, indicating a change from viscoelastic to elastic state at an earlier stage of the test procedure.

Superpave Indirect Tensile Test (IDT)

Resilient modulus (M_R), Poisson's ratios (ν), creep parameters, and tensile strength measured with SuperPave IDT are shown in Table 4 for asphalt mixtures with and without wax modification. One may observe in Table 4 that addition of wax resulted in stiffer mechanical behavior as compared with mixtures without wax modification. In particular, resilient modulus is approximately 10% higher for the mixture with wax additive. Furthermore, creep compliance was found to be reduced significantly by wax modification, in particular the creep compliance at 1000s, $D(1000)$, was approximately 50% lower and the creep rate at 1000s, $D'(1000)$, was approximately 40% lower as compared to the material without wax. These observations correlate well with results depicted in Figs. 2-4 as wax modification was found to stiffen binder significantly.

Tensile strength, S_t , and tensile strain at failure, ϵ_f , measured with Superpave IDT was found to be approximately 14 and 30% lower for the wax modified mixture. Results are in qualitative agreement with the observations from TSRST test discussed above, indicating a certain negative effect of wax modification on low temperature fracture performance. A quantitative difference between tensile strength measured with TSRST and IDT is expected as loading rates and stress states induced in two tests are completely different.

In Table 5, results from HMA fracture mechanics analysis of the IDT test data are summarized. Fracture energy (FE), elastic energy, dissipated creep strain energy limit (DCSE_f), and dissipated creep strain energy minimum (DCSE_{min}) are presented in Table 5 along with the energy ratio (ER). It may be seen that for the FE for the wax modified material is almost 20% lower as compared to the one without wax. This indicates that the wax modified mixtures is more susceptible to brittle cracking, i.e. crack initiation due to single application of high load, such as thermal induced cracking or fracture due to a single passage of a very heavy vehicle. However, the ER for wax modified mixture is roughly 10% higher implying that wax modified mixture has somewhat better resistance to fatigue cracking, i.e. fracture due to repeated traffic loading. This is due to the fact that wax modified mixture has significantly lower rate of creep, as depicted in Table 4. This means that the rate of damage accumulation due to repeated loading will be significantly lower as compared to the material without wax modification, cf. Eqs.(7, 8).

Thus in spite the fact that DCSE_f is lower for the wax modified mixture, it will take longer time to reach this threshold in the pavement.

Conclusions

The influence of wax additives on the mechanical behavior of polymer modified binders and asphalt mixtures have been investigated experimentally. Comparative tests were performed on polymer modified binder, mastics, and asphalt mixtures with and without 4% montan wax additive. In particular, it has been found that:

- Addition of 4% wax to the Pmb used in the study showed a viscosity reducing effect on the binder at higher temperatures, corresponding to a possible similar effect on production and laying temperature for the mastic asphalt used. Consequently, wax modification in this case can be used for reducing energy consumption, and emissions during production and placement.
- Wax modification resulted in no negative effect on the storage stability for the Pmb product under investigation.
- Adding wax had no negative influence on binder aging properties. In FTIR spectroscopy, no increase in sulfoxide absorbance or in carbonyl absorbance, due to wax, could be found.
- Stiffening effect due to wax modification was observed. For the bitumen/wax mixture, this was demonstrated by lower penetration value, higher softening point, and by an increase in complex modulus and decrease in phase angle at temperatures down to at least +5°C in DMA analysis. The same impact was shown for the binder/filler mixtures, indicating a slight increase in stability or resistance to rutting for the mastic asphalt, and possible negative effect on low temperature performance.
- Stiffening effects of wax additive at low temperatures, in terms of BBR creep stiffness. BBR testing was performed at different temperatures on binder, binder/filler mixture, and mastic asphalt from production. In all cases, adding wax increased the BBR stiffness to some extent. Similar stiffening effect has been observed in Superpave IDT tests performed on asphalt.
- The TSRST fracture temperature was 5°C higher for the mastic asphalt containing wax. Indicating a certain negative impact of wax modification on the low temperature fracture performance.
- From HMA fracture mechanics analysis of IDT results it has been shown that wax modified mixtures are more susceptible to brittle cracking, i.e. fracture initiation due to monotonically increasing load. However, the addition of wax slightly improved the resistance to fatigue fracture.

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