

Flow Characteristics and Viscosity Functions in Asphalt Binders Modified by Wax

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Abstract: Warm mix asphalt (WMA), obtained by means of special bitumen modifiers, such as wax or other organic additives, represents a promising technical solution to reduce the temperatures required for asphalt production and pavement construction. In this experience, an extended program of rheological analyses was carried out in order to evaluate the effects of different type of wax on bitumen viscous flow and dynamic properties at high pavement service temperatures. Five different organic additives, including both natural and synthetic waxes, were considered and eleven bitumen-wax blends were produced and studied using rheological testing. Viscosity measurements performed in the domain of the mixing and paving temperatures have shown essential changes in binders' rheological behavior mainly due to the crystallizing/melting properties of waxes. Changes in viscosity functions depended on the chemical structure of wax as well as on its physical characteristics. However, the viscosity of all blends at 120°C was lower than the viscosity of the base bitumen and the consequent reductions in mixing and compaction temperatures were quantitatively evaluated for all binders. The study of the flow characteristics of the bitumen-wax blends at high pavement service temperatures was carried out using complex viscosity master curves evaluated in the linear viscoelastic domain. Increasing resistance to viscous deformation referable to wax modifications was recorded by analyzing viscoelastic properties in the low frequency domain and different contributions were found with regard to each type of wax. For the polyamidic wax-modified binders, the results indicated the presence of a complex behavior characterized by the absence of a Newtonian region of flow. The final contribution of the experience is related to the development of wax modification of asphalt binders in order to produce WMA for pavement engineering applications.

Key words: Asphalt binders rheology; Linear viscoelastic behavior; Organic additives; Viscosity; Warm mix asphalt (WMA); Waxes.

Introduction

Background

The possibility of reducing the energy consumption and the atmospheric emissions during the manufacture of asphalt mixtures is related to a reduction of temperatures required in the course of mixing, laying, and compaction processes. The term *warm mix asphalt* (WMA) identifies innovative asphalt mixtures for paving technologies, which require lower energy consumption during the production processes. Several advanced techniques, aiming at producing warm asphalt mixtures, have been developed during the last years. The main goal of these techniques is to reduce the temperatures traditionally required for laying and mixing of bituminous materials, leading to a consequent decrease in cost, consumptions, and emissions. In addition to the immediate environmental and economical advantages, the development of the warm technique can induce further technological improvement: when the production temperature is the same adopted for the traditional hot mix asphalt (HMA), warm mixtures can also allow longer mixtures haul distances and longer construction season [1].

Nowadays, the warm asphalt technology involves a large group of very different technical solutions, including process technology

modification, water-based technologies, and viscosity reducing organic additives [2]. In this group, some promising technical solutions involve procedures based on mixtures modification with opportune additives, able to foam bitumen, such as zeolite, or to fluidify bitumen, such as synthetic or mineral-derived waxes. In particular zeolites are crystalline hydrated aluminum silicates which present a micro-porous structure able to contain water. The warm techniques involving zeolite are based on the concept that when zeolites are heated in the mixing plant their internal water can microscopically foam the bitumen [1, 3]. The foaming process create a volume expansion of bitumen which results in an improvement of the aggregate coating also at lower temperatures than the ones required for HMA manufacture [1].

The case of waxes is quite complex. The term wax is still used with a broad significance and it is generally applied to several wax-like materials found in nature, as well as hydrocarbons, acids, amides, alcohols, and esters with waxy character [4]. Moreover, certain synthetic compounds, such as the polyethylene waxes, which in their chemical structure are similar to waxes and have waxy physical characteristics, are technically used as wax substitutes and consequently can be included in the wax concept [5]. In the petroleum industry, the word wax is generally used to characterize the paraffinic crystallizing materials with a melting point higher than 25°C, which are often present in crude oils of different origins [4]. Waxes should be thus considered as natural constitutive components of all petroleum products, included bitumen. Petroleum wax classes are generally recognized also in bitumen and are usually classified as paraffin waxes, microcrystalline waxes, and amorphous waxes [6]. Paraffin waxes are macrocrystalline and are mainly composed of n-alkans, while bitumen microcrystalline

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waxes are defined as aliphatic hydrocarbon compounds with branched chains which crystallize as small needles [7]. When branched carbon chains are predominant in the internal structure we have the amorphous waxes. Hence, in general we can distinguish between paraffin waxes ($<C_{45}$, melting point $< 70^{\circ}\text{C}$, macro-crystalline) and non-paraffin waxes ($>C_{45}$, melting point $> 70^{\circ}\text{C}$, micro-crystalline or amorphous) but it was demonstrated that wax are not the only crystallizing compounds in bitumen. In fact also some aromatics and molecules with polar functional groups may crystallize upon cooling [8].

Because wax in bitumen has not still a univocal definition, opinions about their effects on bitumen quality have varied over the years [4]. In pavement engineering, waxes were traditionally considered detrimental because of the influence on asphalt physical properties related to their crystallizing and melting properties. Hence, during the past years several studies were carried out about the determination of wax content in bitumen and its influence on bitumen and asphalt mixtures properties [6, 9-12]. With regard to field performances, it was traditionally hypothesized that wax in bitumen can soften bitumen at high service temperature, affecting the rutting resistance of pavement, and can increase pavement stiffness and its sensitivity to thermal cracking when low temperatures occur. Moreover, the role of waxes in reduction of bitumen adhesion and fatigue resistance is often considered as negatively important [13].

Nowadays, the need of a decrease in costs and emissions in industrial plants and the consequent development of warm asphalt technologies are leading to a re-examination of the role of wax in road construction. The same melting/crystallizing phase transitions, characteristics of waxes and traditionally considered as harmful for the integrity of pavement structures, are now considered of decisive importance to reduce bitumen viscosity at the production temperatures avoiding at the same time a resistance reduction at service temperatures. However it is important to observe that effects related to the presence of waxes in bitumen must be considered as dependent on the chemical composition and on the internal structure of wax. In particular, the amount of heteroatoms, alicyclic and aromatic compounds, as well as molecular distribution and carbon chain branching, greatly influence the wax properties. As a consequence, according to the results of Edwards et al. [14, 15], waxes with different chemical composition differently affect bitumen thermo-rheological behavior. This fact is of primary importance in pavement technology since the different types of wax are produced as bitumen modifiers to be use in WMA [16]. In this category we found particular types of wax, such as Montan wax and Fischer-Tropsch (FT) paraffin obtained from industrial processes that, because of their particular characteristics, were recently proposed and commercialized as bitumen flow improvers. Montan wax is a combination of non-glyceride long chain carboxylic acid esters, free long-chain organic acids, long-chain alcohols, and other organic compounds with a complicated structure that derive from fossilized vegetables and are obtained by solvent extraction of certain types of lignite and brown coal [16].

Differently, full synthetic waxes proposed as bitumen modifiers are a product of the FT synthesis. In this industrial process, the coal or the natural gas (methane) is partially oxidized to carbon monoxide (CO) and is then reacted with hydrogen (H_2) under

catalytic conditions in order to produce a mixture of hydrocarbons compounds having molecular chain lengths of C_5 to C_{120} plus carbon atoms [1]. Final products of the FT process are synthetic naphtha, kerosene, gasoil and waxes. The resulting synthetic waxes are characterized by carbon chain lengths ranging from C_{40} to C_{120} (higher than the bituminous paraffin wax), consequent higher molecular weight ($> 1600\text{g/mol}$) and fine microcrystalline internal structure [16]. In consequence of these characteristics, the FT waxes have particular physical properties, different from those of the petroleum macro-crystalline paraffin; if compared with the paraffin waxes, the synthetic waxes have a higher melting point (generally $> 90^{\circ}\text{C}$) due to the longer carbon chains and a reduced brittleness at low temperatures caused by the smaller crystalline structure [6]. Hence, during the last years, as a consequence of the increasing interest in warm asphalt technologies, many researchers have investigated the use of the FT wax in asphalt with special regard to their influences on bitumen basic rheological and conventional properties and asphalt semi-empirical characteristics [12, 17-20]. Moreover, Hurley and Prowell conducted an extended laboratory experience focused on the volumetric and mechanical properties of warm asphalt mixtures produced with Sasobit FT waxes. This experience showed that wax improves the compactability of the mixtures and does not affect their rutting potential and their resilient modulus [1, 21]. The results available in literature confirm that the use of waxes in WMA can be considered as a promising technical solution. Therefore, the definition of the effects of different types of wax on bitumen flow characteristics by means of testing procedures involving the whole domain of mixing, paving and high service temperatures was the starting part of this work.

Objectives

As mentioned above, the use of wax as bitumen additive can represent a way to build asphalt pavements at lower temperatures than those traditionally required. However, despite their benefits on mixing and compaction processes, the presence of wax in bitumen can also provide some side effects on asphalt viscoelastic properties, including the increase of pavement susceptibility to high temperature typical damages (rutting and permanent deformation). In addition, it is known that several types of wax are commercially available to be used in WMA and also that different types of wax can produce different effects on bitumen rheology. Therefore, the purpose of this study was to investigate the effects of different types of wax on the various aspects related to bitumen flow and viscoelasticity. The main objectives were consequently outlined as follows:

- analyze flow characteristics of bitumen-wax blends at high temperatures, highlighting the relations between different types of wax and recorded viscosity functions;
- provide a quantitative evaluation of the reduction in asphalt mixtures mixing and compaction temperatures which derive from wax modification;
- study the influence of wax on the binder viscoelastic behavior at high pavement service temperatures;
- evaluate the potential resistance to non-reversible deformation of binders modified by wax.

Experimental Program

Materials

A 50/70 traditional bitumen, referred in the text as B, derived from a vacuum refinery process and five different organic additives designed for WMA technology were selected for the investigation. In addition to the base bitumen B, ten different bitumen-wax blends were then studied.

These blends were produced in laboratory from the addition of controlled quantities of five types of wax to the same base bitumen B. Two different percentages, 3.0 and 6.0%, were used for each wax. The blends preparation involved a previously standardized methodology. A bitumen sample of $300 \pm 5\text{g}$ was heated in a ventilate oven at $160 \pm 5^\circ\text{C}$ for 30 minutes and subsequently placed on a heating plate. Pre-weighted waxes were carefully added to bitumen and subsequently the blends were mixed for 15 minutes at $160 \pm 5^\circ\text{C}$. Lastly, the obtained binders were split into appropriate amounts to prepare samples for all the conventional characterizations. The ring and ball softening point procedure was done according to the EN 1427, the penetration was measured at 25°C according to the EN 1426 and the penetration index was consequently calculated (Table 1).

A previous phase of the experimental investigation was carried out in order to provide a basic characterization of the wax additives. Results of Fourier Transform Infrared (FTIR) spectroscopy revealed that the five selected wax can be included into two different categories. Waxes W, B, and N have an ordinary paraffinic structure while waxes A and L are different from the others and reveal a polyamide-like structure. The differential scanning calorimetry (DSC) analyses were then carried out in order to discriminate wax additives on the basis of their thermal behavior.

The conventional properties, the DSC waxes melting range, and the composition of the obtained blends are also listed in Table 1.

The procedure used to prepare the samples for the rheological measurements was referred to the EN 12594. Wax-modified binders were treated as polymer-modified bitumen (PMB), thus reheating and homogenization were carefully carried out at a controlled temperature ($160 \pm 5^\circ\text{C}$) in order to obtain reproducible results [22]. Special attention was then paid to the thermal history and to the storage conditions of the test samples (1 hour at $25 \pm 0.5^\circ\text{C}$) because

of their influence on rheological measurements [23].

Rheological Methods

The rheological properties of the asphalt binders modified with waxes were determined by means of static and dynamic mechanical methods consisting on continuous stress and oscillatory testing modes.

Rheometrical measurements were carried out using a dynamic shear rheometer (DSR). The parallel plate testing system consisting of 25mm diameter plates with 1.00 or 2.00mm testing gap was used. The selection of the testing geometry was based on the general testing conditions with regard to the expected materials' stiffness. The samples were placed on the bottom plate, squeezed out between the two plates and trimmed off from the edge of the plates using a hot spatula. Once these operations were executed, the gap was set as required in order to guarantee the correct geometry of each samples. The temperature during the DSR tests was controlled by means of a Peltier conditioning system with a maximum admitted deviation of $+0.01^\circ\text{C}$. Due to the influence of the temperature on the rheological measurements, the specimens were subjected to a 30-minute thermal conditioning period before each test which the aim of guaranteeing a constant temperature during the whole experiment. In order to avoid errors due to the instrument's sensitivity, the torque applied was higher than the minimum suggested by the instrument producer (min. torque = $0.5\mu\text{Nm}$).

To investigate the behavior of wax-modified binders in the whole range of the operative temperatures, the experimental program is composed by two phases. The first phase focuses on the study of the flow properties at the mixing and compaction temperatures while the evaluation of the linear viscoelastic behavior at the service temperatures is the subject of the second phase.

Viscosity of binders was measured using rotational rheological tests to evaluate the bitumen flow curves at different temperatures, from 80 to 160°C with steps of 10°C . For each temperature, the measure was extended for 4 minutes in order to evaluate the influence of the transient thixotropic effects.

In the entire temperature range investigated, the measurements were performed in strain-controlled mode using shear rates from $1 \cdot 10^{-2}$ to $1 \cdot 10^3 \text{ s}^{-1}$.

Table 1. Wax Characteristics and Conventional Properties of Asphalt Binders.

Binder	Additive Type [-]	Additive Melting Range (DSC) [$^\circ\text{C}$]	Additive Content [%]	Pen. @ 25°C [dmm]	Soft. Point [$^\circ\text{C}$]	Pen. Index (IP) [-]
B	-	-	-	55	50.7	-0.8
B-3W	W - Fischer-Tropsch wax	90÷118	3.0	33	78.4	3.0
B-6W	W - Fischer-Tropsch wax	90÷118	6.0	26	95.5	4.6
B-3L	L - Partial synthetic amid wax	138÷148	3.0	31	100.5	5.5
B-6L	L - Partial synthetic amid wax	138÷148	6.0	24	115.9	6.3
B-3N	N - Fossil ester wax	70÷89	3.0	33	57.7	-0.4
B-6N	N - Fossil ester wax	70÷89	6.0	29	68.1	1.2
B-3A	A - Modified brown-coal derivative	140÷148	3.0	32	103.8	5.9
B-6A	A - Modified brown-coal derivative	140÷148	6.0	28	116.8	6.7
B-3B	B - Modified brown-coal derivative	63÷115	3.0	30	85.6	3.8
B-6B	B - Modified brown-coal derivative	63÷115	6.0	26	97.0	4.7

Mixing and compaction temperatures were determined as equi-viscous temperatures. Because of the impact of the non-Newtonian characteristics, particular attention was paid to the selection of the reference viscosity values. In relation to the findings of the experiences reported in literature 0.17 ± 0.02 and $0.28 \pm 0.3 Pa \cdot s$ evaluated in correspondence of a shear rate equal to $6.8 s^{-1}$ were selected as reference values for mixing and compaction temperatures respectively [24-26].

The flow behavior of asphalt binders at high pavement service temperature was studied in terms of complex viscosity (η^*) and phase angle (δ) using stress-controlled frequency sweeps from 1 to $100 rad/s$. According to the results of SHRP [27], Marasteanu and Anderson [28], and Airey et al. [29], the extension of the linear viscoelastic domain was previously checked by performing stress sweeps tests and the limit of the linear viscoelastic (LVE) response was identified as the stress amplitude where the shear complex modulus (G^*) is decreased to 95% of its initial value. Linear viscoelastic conditions were consequently established and shear stress amplitudes from 50 to $10^4 Pa$ were selected according to the test temperature ($10^\circ C$ – $90^\circ C$). Dynamic mechanical data were subsequently analyzed and used to generate master curves of shear complex viscosity (η^*) and phase angle (δ) at a reference temperature of $60^\circ C$. Assuming the materials as thermorheologically simple, the time-temperature superposition (TTS) principle without vertical shift factors was applied and the Williams-Landel-Ferry (WLF) equation was then used to fit the trend of the horizontal shift factors (a_T).

Results and Discussion

High Temperatures

The analysis of flow characteristics of asphalt binders at high temperatures provides essential information about binder behavior during asphalt mixing, compaction, and paving processes. In this phase of the experimental program, the viscosity of wax-bitumen blends was studied as a function of shear rate, time, and temperature in order to provide a qualification of binders rheological behavior at high temperatures and to evaluate the reference equi-viscous temperatures for mixing and compaction operations.

The results of the high temperatures characterizations are initially presented in terms of viscosity-shear rate relationships at different temperatures. Moreover, are discussed the time-dependency and the temperature-dependency of the viscosity.

In Fig. 1, the viscosity functions obtained at the lowest test temperature ($80^\circ C$) for binders modified by wax W (3.0 and 6.0%) are presented and compared to the viscosity of the base bitumen B. As expected, at $80^\circ C$ the base bitumen B behaves as a Newtonian fluid, its viscosity remains constant over the entire domain of the shear rates investigated (0.01 – $100 s^{-1}$) and the Eq. (1), where η is the viscosity, γ is the shear strain, t is the time, and η_0 is the univocal steady-state viscosity, can be used to describe the entire viscosity-shear rate relationship.

$$\eta \left(\frac{d\gamma}{dt} \right) = \eta_0 \quad (1)$$

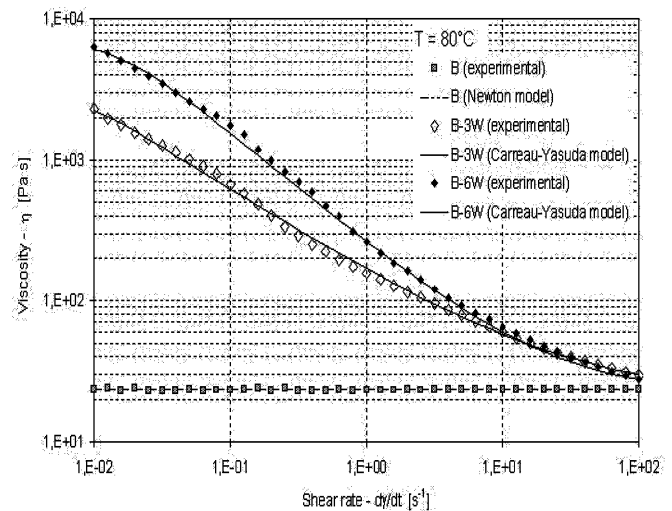


Fig. 1. Viscosity Curves at $80^\circ C$ for Binders B, B-3W, and B-6W.

The situation is opposite when the base asphalt is modified by the synthetic wax W (Fig. 1). In this case, the rheological behavior becomes non-Newtonian and the Eq. (1) cannot still be applied to fit the recorded viscosity functions. In particular the presence of the synthetic wax (W) leads to a non-linear viscosity-shear rate relationship with no horizontal asymptote even in the low frequency region. Due to this evidence no steady state seems to be achieved in the range of the shear rates investigated and a non-linear model, such as the Carreau-Yasuda model (Eq. (2)), well describe the flow behavior of the base bitumen when it is modified with the wax W.

$$\eta \left(\frac{d\gamma}{dt} \right) = \frac{\eta_0 - \eta_\infty}{\left[1 + \left(\lambda \cdot \frac{d\gamma}{dt} \right)^a \right]^{\frac{n-1}{a}}} + \eta_\infty \quad (2)$$

In Eq. (2), η is the viscosity, γ is the shear strain, t is the time, η_0 is the steady-state viscosity, and n , λ , a , and η_∞ are fitting parameters.

This same assumption can be successfully considered for both the binders B-3W and B-6W. However, as Fig. 1 depicts, the viscosity trend is strongly influenced by the wax content: higher values of viscosity and a steeper slope appear when the content of wax is increased, denoting, in these conditions, increasing shear susceptibility.

Similar results were obtained for other waxes but the observations discussed above for the case of wax W were not identically the same for all the other blends. At this regard, Fig. 2 illustrates the viscosity-shear rates dependency obtained for blends with the 6.0% of waxes L, A, B, and N.

As it can be observed, the rheology of the blend changes in relation to different modifications and each viscosity trend should be retained as referable to each singular wax. Hence, in order to describe the rheological behavior of wax-modified binders, it is not possible to set aside from the type of wax.

The first main difference is that shear-dependent behaviors were recorded for all modifiers with the exception of the wax N. If the behavior of the base bitumen is assumed as Newtonian (Eq. (1)), no

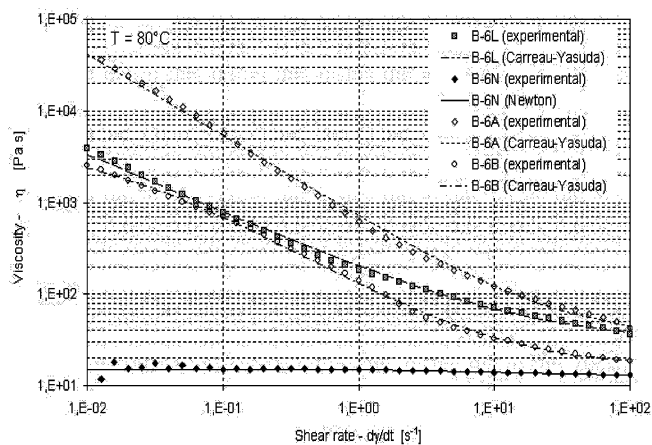


Fig. 2. Viscosity Curves at 80°C Obtained for the Binders Modified with 6.0% of Different Waxes (B-6L, B-6N, B-6A, and B-6B).

Table 2. Viscosity Parameters at 80 and 120°C.

Binder	T = 80°C		T = 120°C	
	Newton η [Pa·s]	Carreau-Yasuda η_0 [Pa·s]	Newton η [Pa·s]	Carreau-Yasuda η_0 [Pa·s]
B	$2.56 \cdot 10^1$	-	$1.04 \cdot 10^0$	-
B-3W	-	$2.83 \cdot 10^3$	$8.25 \cdot 10^{-1}$	-
B-6W	-	$7.38 \cdot 10^3$	$6.30 \cdot 10^{-1}$	-
B-3L	-	$3.66 \cdot 10^4$	$7.92 \cdot 10^{-1}$	-
B-6L	-	$9.11 \cdot 10^3$	-	$4.59 \cdot 10^1$
B-3N	$1.81 \cdot 10^1$	-	$8.49 \cdot 10^{-1}$	-
B-6N	$1.57 \cdot 10^1$	-	$6.96 \cdot 10^{-1}$	-
B-3A	-	$2.12 \cdot 10^4$	$8.22 \cdot 10^{-1}$	-
B-6A	-	$1.68 \cdot 10^5$	-	$1.44 \cdot 10^1$
B-3B	-	$2.82 \cdot 10^3$	$8.20 \cdot 10^{-1}$	-
B-6B	-	$4.53 \cdot 10^3$	$5.81 \cdot 10^{-1}$	-

changes in this sense are recorded by adding the wax N. In this case only a vertical shifting of the curve was recorded and the only effect produced by wax N is a reduction of η_0 . In other words, due to the chemical composition of N and to its consequent low melting range from DSC (Table 1), the behavior of binders B-3N and B-6N at 80°C is still Newtonian and it is identified by a lower steady-state viscosity than the one recorded for the base bitumen. As it was expected, due to the higher melting range, the same assumption is clearly not true for the other blends. In such cases the behavior becomes non-Newtonian as already discussed for binders modified by wax W but the curves denote different characters. Nevertheless, it is important to observe that all binders show a similar general shape of the viscosity function, lacking of the low frequency shoulder observed at the same temperature for ethylene-vinylacetate (EVA) and poly(styrene-butadiene-styrene) (SBS) modified bitumen by Stastna et al., [30]. This fact leads to identify the absence of a first Newtonian region in the measurement within the shear rate interval. As a consequence, the viscosity shear-dependence can be described by means of the Carreau-Yasuda model as already shown for B-3W and B-6W but the fitting parameter η_0 is not representative of the materials zero-shear viscosity, intended as an intrinsic material property. Steady-state viscosities and η_0 from Carreau-Yasuda evaluated at 80 and 120°C are however reported in

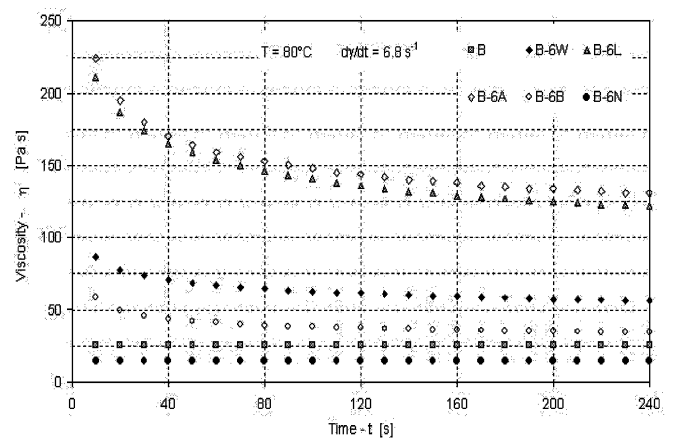


Fig. 3. Viscosity-Time Functions at 80°C.

Table 2 in order to identify a quantitative comparison between the different modifiers and their relative content.

As indicated by values in Table 2, different behaviors were obtained for the same binder when the test temperature was increased from 80 to 120°C. At this temperature, all binders except for B-6L and B-6A showed a Newtonian behavior. Because of the not completely reached melting of the polyamide-like waxes L and A (T_{melt} (DSC) = 148°C) the blends B-6L and B-6A still behave as non-Newtonian fluids. It is interesting to note that binders B-3L and B-3A behave differently. The viscosity of all other binders at 120°C is constant and lower than the viscosity of B ($1.04 \text{ Pa}\cdot\text{s}$) over the investigated shear rate range ($1 \div 10^3 \text{ s}^{-1}$). This recorded viscosity reduction agrees with the entity of the wax content and it is maximum for blend B-6B ($\eta = 0.581 \text{ Pa}\cdot\text{s}$). In order to assess the optimum mixing and compaction temperatures related to this recorded reduction in viscosity coefficients, the tests were repeated at different temperatures. For each fixed temperature, the tests were performed at 6.8 s^{-1} . The evidence of a change in bitumen rheology referable to wax is also well remarked by the time-dependent behavior (Fig. 3).

According to the previous observations about the shear rate dependency, the entity of the time-dependence is relative to the type and to the content of wax. Therefore, at 80°C, the base bitumen B does not exhibit a time-dependency, while similar thixotropic trends were observed for all blends except B-3N and B-6N. The most important time-effect was recorded for the polyamide-based blends B-6L and B-6A, remarking in these cases the existence of a stronger and more complex interaction established between wax and bitumen.

In order to investigate the contribute of waxes at the typical asphalt mixing and compaction conditions, the steady-state viscosities, evaluated after 240s of loading time, were plotted versus the test temperatures.

In Fig. 4 the viscosity-temperature trends obtained for the base bitumen B are compared to the ones obtained for binders modified by wax N (Fig. 4) and binders modified by wax L (Fig. 5).

As shown in Figs. 4 and 5, two different shapes for viscosity-temperature functions were observed depending on the type of wax. In Fig. 4, the linear trend observed when wax N was added to the bitumen denotes the presence of a vertical shifting only. In these cases, according to the previous experiences [31, 32], the

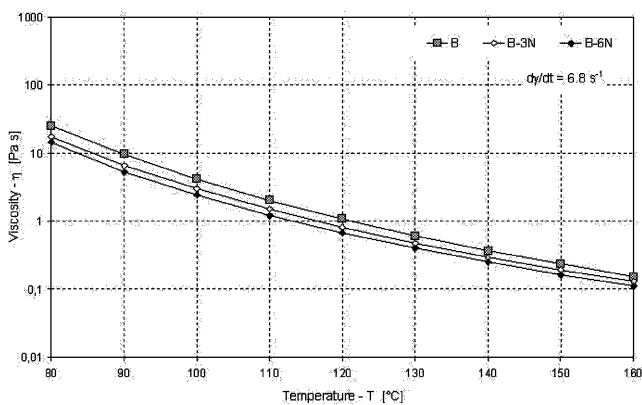


Fig. 4. Viscosity-Temperature Functions Observed for Binders B, B-3N, and B-6N.

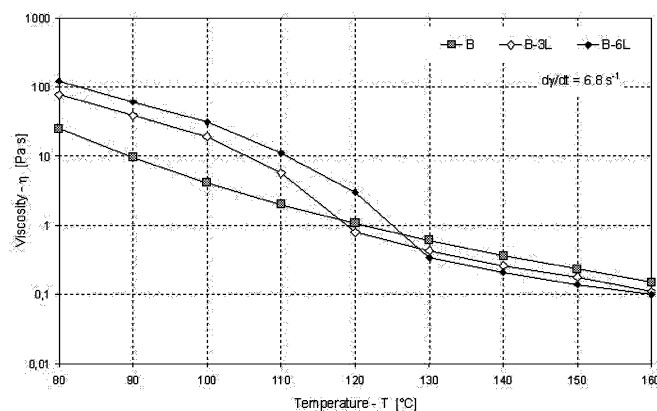


Fig. 5. Viscosity-Temperature Functions Observed for Binders B, B-3L, and B-6L.

viscosity-temperature relationships were described by means of the classical Arrhenius equation:

$$\eta(T) = A \cdot e^{\frac{E_f}{RT}} \quad (3)$$

where η is the viscosity, T is the temperature measured in Kelvin degrees, E_f is the flow activation energy, R is the universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and A is a fitting parameter.

In Fig. 5 is recorded an evident change of slope in the η - T trend related to location of the wax melting point. As a consequence, in this second case, the Arrhenius equation cannot still be applied to the entire range of test temperature and the viscosity reduction was recorded only for temperatures which were higher than the one of the wax melting point. It is interesting to observe that the temperature required for recording the discontinuity was dependent on the wax content.

For the sake of brevity, data obtained for wax W, A, and B are not presented here. However, no particular variations from the trend shown in Fig. 5 were recorded in those cases.

Table 3 summarizes the recorded mixing and compaction temperatures and the relative reductions (ΔT_{mix} and ΔT_{comp}) calculated with regard to T_{mix} and T_{comp} recorded for the base binder B.

Dynamic Analysis at Pavement Service Temperatures

Table 3. Optimum Mixing and Compaction Temperatures.

Binder	T_{mix} [°C]	T_{comp} [°C]	ΔT_{mix} [°C]	ΔT_{comp} [°C]
B	156.8	146.5	-	-
B-3W	152.3	141.5	4.5	5.0
B-6W	149.2	138.1	7.6	8.4
B-3L	150.4	140.1	6.4	6.4
B-6L	146.1	133.9	10.7	12.6
B-3N	153.0	142.0	3.9	4.5
B-6N	149.3	138.3	7.5	8.2
B-3A	151.3	140.7	5.5	5.9
B-6A	147.0	134.9	9.8	11.6
B-3B	153.6	142.9	3.2	3.6
B-6B	147.8	136.5	9.0	10.0

According to the continuous developments in asphalt binders characterization, rotational and complex viscosity evaluated for limit conditions of stress and time or frequency (zero-shear viscosity) is related to a prediction of asphalt performance at high service temperatures [31, 33-38]. As a consequence, in this phase of the experimental program, binders viscosity from dynamic mechanical analysis are evaluated at pavement service temperatures in order to define the influence of wax on binders damage behavior related to resistance to viscous flow and non-reversible deformation.

Dynamic mechanical data are reported in terms of shear complex viscosity $\eta^*(\omega)$ and phase angle $\delta(\omega)$ at a reference temperature of 60°C (Figs. 6, 7, and 8). In Fig. 6 is reported the behavior of the base binder B; similar behaviors were obtained for binders modified by wax N. The trend reported in Fig. 7 is representative of the data recorded for binders modified by paraffinic wax (W and B) while Fig. 8 depicts the representative data of binders modified by polyamide-like wax (L and A).

As Figs. 6, 7, and 8 depict, the influence of wax is still important at service temperatures. For the base bitumen (Fig. 6) we have a well known behavior: in this case, when the frequency tends to be zero and the strain amplitude is internal to the linear region, the phase angle approaches values near to 90°, identifying the achievement of a steady-state. In these conditions, also the delayed elastic response tends to be zero and the material stiffness is univocally represented by the viscous component (G_v). The bitumen behavior is therefore described by the viscous asymptote of the master curve and the steady-state viscosity (η_∞) approaches the theoretical zero-shear viscosity of the material (Eq. (4)).

$$\omega \rightarrow 0 \Rightarrow \frac{|G^*|}{\omega} \approx \frac{|G'|}{\omega} \rightarrow \frac{|G_v|}{\omega} = \eta_0 \quad (4)$$

In Eq. (4), ω is the radial frequency, G^* is complex modulus, G'' is the loss modulus, G_v is the viscous component of the modulus, and η_0 is the zero-shear viscosity.

For binder B, the above-mentioned conditions are verified and the complex viscosity evaluated at the lowest test frequency (1.0 rad/s), which can be already considered the zero-shear viscosity of the material. Differently, the same conditions are not verified for bitumen modified by waxes. Experimental data confirms results obtained from viscosity analyses at high temperatures, demonstrating that wax modification provides essential changes in

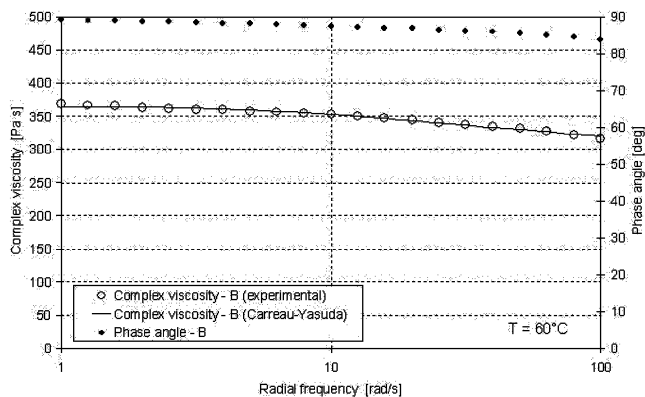


Fig. 6. Complex Viscosity η^* and phase angle δ at 60°C from Dynamic Mechanical Analysis (DMA) for Binder B.

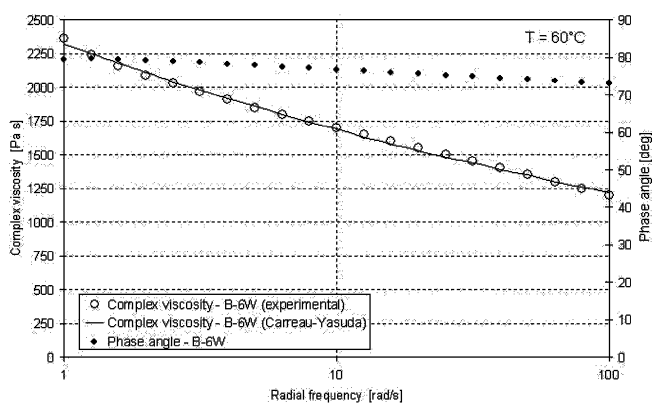


Fig. 7. Complex Viscosity η^* and phase angle δ at 60°C from DMA Analysis for Binder B-6W.

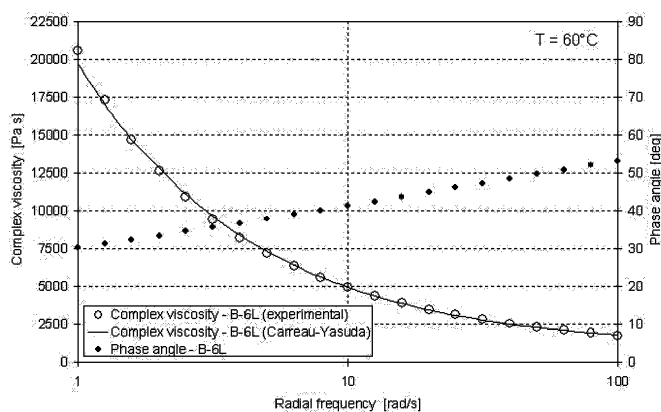


Fig. 8. Complex Viscosity η^* and phase angle δ at 60°C from DMA Analysis for Binder B-6L.

binders' behavior. In particular, for the paraffinic modified binder B-6W, the trend obtained does not allow the identification of the steady-state region, which probably is shifted towards lower loading frequencies (Fig. 7). This assumption agrees with the values recorded for the phase angle, quite far from 90°. A more radical change was found in the case of the modification by polyamide waxes. In this case, the curve describing the function $\eta^*(\omega)$ for B-6L, deviates its trend in the low-frequency domain, where the gradient becomes elevated and the asymptote rotates from the horizontal position to a sub-vertical position (Fig. 8). A similar essential change

Table 4. Experimental Low-Shear Viscosity and Models Parameters.

Binder	G^*/ω [Pa.s]	G''/ω [Pa.s]	η_0 (Cross) [Pa.s]	η_0 (Carreau-Yasuda) [Pa.s]
B	369	369	377	366
B-3W	2168	2096	-	6439
B-6W	2362	2321	9613	5483
B-3L	918	900	150310	1877
B-6L	20608	10382	-	1139900
B-3N	510	509	-	557
B-6N	1151	1138	-	2323
B-3A	1050	1028	11275	2280
B-6A	4691	3935	-	43850
B-3B	735	730	-	1178
B-6B	547	546	692	548

was also recorded by the inversion of the trend of δ . Contrary to the regular trend obtained for the base bitumen, the phase angle of B-6L at 60°C increases with increasing frequency, as occurs for some binders modified by elevated contents of radial or linear SBS. A similar trend does not allow the achievement of theoretical conditions needed to define η_0 and the fitting model cannot be applied correctly to estimate it. However, according to the objectives of this paper related to a material comparison and qualification for engineering applications, it was assumed that the fitting parameter with the non-linear models can represent a useful performance indicator related to a quantification of material resistance to viscous deformation. Table 4 includes η^* at low frequency from experimental data (ratio between G^* or G'' and ω) and the η_0 parameter from fitting models. During the analysis, both the Carreau-Yasuda model and the Cross model (Eq. (5)), were considered.

$$\eta^*(\omega) = \frac{\eta_0 - \eta_\infty}{1 + (K\omega)^\mu} + \eta_\infty \quad (5)$$

However, the Cross model, successfully applied to different PMB by Sybilski [37], does not allow in this case the definition of a finite value for η_0 , pointing out a difference between the effects of wax and the effects of polymers on bitumen viscosity.

As expected, the different methods provide similar values only for the base bitumen ($\eta_0 \approx 370 \text{ Pa.s}$). Nevertheless, it is important to note that G^*/ω and G''/ω ratios lead to very similar values for all binders with the only exception of B-6L and B-6A. This fact indicates that, for paraffinic modified binders, δ is not so far from 90° (also in accordance with trend in Fig. 7). As a consequence, for these binders we can hypothesize the existence of a Newtonian plateau located at quite lower frequencies than 1.0 rad/s . On the contrary, for the other two binders there is a general disagreement between experimental and fitting data and, moreover, between G^*/ω and G''/ω . This occurs because δ is not approaching 90° and the existence of a steady-state viscosity value independent on the shear rate cannot be guaranteed. Master curves of complex viscosity generated from data recorded at different temperatures seem to strengthen this assumption (Fig. 9).

As it can be observed in Fig. 9, it is confirmed that for small frequencies binders modified by paraffinic wax reach the horizontal

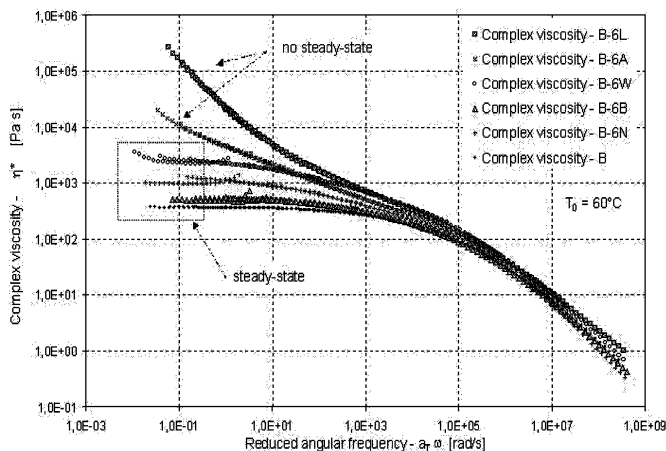


Fig. 9. Comparison between Complex Viscosity Master Curves Obtained for Blends with 6.0% Wax.

asymptote as well as the base binder B; this indicates the achievement of a steady-state flow.

On the contrary, the complex viscosity of B-6L and B-6A still depend on the radial frequency in the region of the reduced frequencies lower than the 1.0 rad/s (higher test temperatures), where their curves diverge from the others. As a consequence we can assume that the great stiffening and elastic ($\delta < 90^\circ$) effects exhibited by B-6L and B-6A at lower frequencies are certainly indicative of a stronger interaction between wax and bitumen that occurs in case of polyamide waxes and that probably originated a structured network similarly to the phenomena described by Polacco et al. [39] for EVA and SBS modified bitumen. Due to this interaction, a zero-shear viscosity value does not exist in this case and the viscosity at 60°C still increases also when frequency tends to be zero, as already shown by elastomer-modified binders characterized by a continuous polymer-rich phase [31, 40].

At higher radial frequencies, the complex viscosity of both modified binders approaches the viscosity obtained for B and no particular effect of wax can be recorded. The stiffening contribute of wax is therefore highly dependent on the rate of loading and it becomes null when the shear rate exceeds a certain threshold. This result should be related to a transient modification of the internal material structure that becomes irrelevant for certain loading conditions. However, the recorded behavior is of special interest in pavement engineering because the trend of η^* in the low frequency domain can be used to identify the asphalt resistance to viscous flow as related to pavement permanent deformation [31, 33, 34].

A quantitative evaluation of the complexity in thermo-rheological behavior caused by the polyamide-like wax was also offered by the peculiar trend of the horizontal shift factors (Fig. 10). The shift factors obtained for B-6L are similar to those obtained for B only in the region of low temperatures. On the contrary, at high temperatures there is a shifting between the two curves. This fact indicates the presence of a minor translation in the reduced frequency domain related to a difference in thermal susceptibility. Moreover, Fig. 10 shows that a_T of B-6L follows a quite different trend from the WLF equation, successfully applied to the base bitumen B.

Other than the rheological and rheometrical aspects discussed above, some general observations related to wax role in pavement

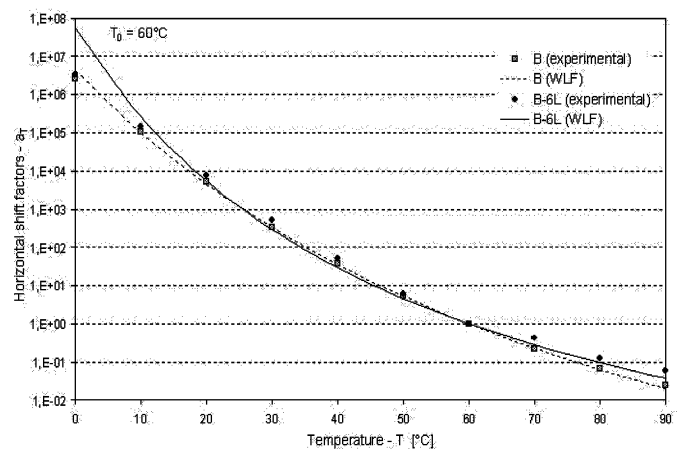


Fig. 10. Comparison Between the Horizontal Shift Factors Obtained for the Unmodified Bitumen B and Blend B-6L.

performance at high temperatures can be outlined from the DMA results. Differently from the data recorded at mixing and paving temperatures, all waxes, included N, produce a stiffening effect at 60°C and higher values of η_0 were always obtained as a consequence of wax addition. Furthermore, wax content does not seem to be important any longer at service temperatures for all the paraffinic-modified binders. B-3W and B-6W, as well as B-3B and B-6B, have similar viscosity values at 60°C . This fact leads to observe that, in case of paraffinic wax, wax content does not produce important effects on bitumen rheology at service temperatures.

Conclusions

Flow characteristics and viscosity functions of bitumen modified by different types of wax were studied in the domains of mixing, paving, and high pavement service temperatures by means of several rheological tests.

With regard to the objectives of the study and according to the experimental results, different rheological and engineering findings can be outlined. The first general conclusion is that different materials with own peculiar rheological behaviors can be obtained by blending a base bitumen from oil refinery plant with a wax modifier. In particular, by observing the recorded viscosity functions, different effects were found out for each different wax and the obtained experimental results allowed correlating the rheology of wax-modified binders to the characteristics of wax. As a consequence, the nature of wax and its consequent physical characteristics were found to be of decisive importance.

Furthermore, the effect of each singular wax was found as strongly dependent on test temperature. As expected, the strongest effects were found for lower temperatures than the wax relative melting point. In this region the polyamide-like waxes produced more important changes. When they were added to the base bitumen, an increase in viscosity was recorded especially in the low shear rates region, where the base and the paraffinic-modified binders reached the horizontal plateau of the steady-state flow. This change in bitumen rheology was supposed as related to the existence of a transient network originated by the interaction between bitumen and polyamide wax.

For higher temperatures than the wax relative melting point, the change in rheology was different and mainly related to a reduction of viscosity with respect to the base bitumen. As a consequence of these reductions, a general drop in the theoretical mixing and paving temperatures was recorded for both paraffinic and polyamide-like wax.

Low-shear viscosity evaluated within the domain of high service temperatures increases after wax modification, denoting, with respect to analysis methods based on damage behavior characterization, an improved resistance to viscous flow and non-reversible deformation in asphalt pavement. In this context as well, polyamide waxes lead to a more complex behavior of asphalt binders, resulting in the impossibility of determining a zero-shear viscosity value according to its theoretical definition. Nevertheless, in this case we can hypothesize a higher improvement in performances at high pavement service temperatures.

Implications of findings to field work are related to the evaluation of the quantitative reduction in compaction temperatures. Moreover, it can be stated that both paraffinic and polyamidic wax modification provide longer mixtures haul distances and longer construction season if the production temperature is the same used for HMA.

Finally, the obtained results can provide some indications to select the most appropriate wax modifier for a given pavement engineering application, by tacking into account the required performances.

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