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ORIGINAL ARTICLE

Effect of warm mix asphalt chemical additives on the mechanical performance of asphalt binders

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Abstract Warm mix asphalt (WMA) has become very popular in asphalt pavement construction because it allows reducing both energy consumptions and carbon emissions. WMA can be obtained by using different types of additives and can be produced, applied, and compacted at temperatures 20–40 °C lower than hot mix asphalt. WMA additives allow reducing the working temperatures without compromising the final performance of the asphalt concrete. Many WMA additives are available on the worldwide market and some of them reduce the viscosity of asphalts binder (organic additives or foam) whereas others do not act on this sense (chemical additives). This study focuses on the effect of chemical additives on the performance of asphalt binders for WMA production. To this purpose, a neat bitumen, a polymer modified bitumen (PMB) and two different chemical additives were selected. All the binders were characterized through conventional tests, DSR, MSCR, FTIR and microscopic analysis. The result clearly showed that the influence of the chemical additives on the neat bitumen is negligible or non-existent. On the contrary, significant changes were observed in the modified bitumen properties. Specifically, chemical additives reduce the viscosity temperature susceptibility of PMBs in the temperature range between 80 and 140 °C, increase the rutting resistance potential and the elastic response of PMBs at high temperatures. Moreover, a morphological inspection supported the modifications observed in the rheological properties of PMBs.

Keywords Warm mix asphalt · WMA additives · Viscosity · Rheology · DSR · Morphology

1 Introduction

In order to minimize environmental impacts of asphalt pavement construction, industry has developed Warm Mix Asphalt (WMA) that allows asphalt paving at reduced temperatures, thus reducing energy consumption and CO_2 emission. WMA also increases possibility for long haul distance, for an extended paving season and for a more flexible in situ working procedure (e.g. night-time applications and extended-time workability).

WMA mixtures are produced at temperatures approximately 20–40 °C lower than traditional Hot Mix Asphalt (HMA), thanks to physical–chemical changes in the bituminous binders during the mixing process [1, 2]. Lowered production temperatures

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achieved by WMA are obtained through several techniques [3], which can be divided into three main groups: foaming technologies [4], organic additives [5] and chemical additives [6].

Chemical additives usually need to be added to the bitumen before its batching into the asphalt mixer, even if they can be also employed as emulsion. These additives are used to facilitate the wetting of aggregate particles at lower production temperatures because they work as surfactants and adhesion promoters, reducing the surface tension of the binder. Thus, chemical additives interact at the aggregate surface in order to modify and control the internal friction of the mix and to improve the workability of the asphalt mixture [3]. Silva et al. [7] highlighted that the addition of chemical additives does not provide considerable alterations of the binder performance and does not significantly change the rheological characteristics of neat bitumens. Several authors showed that the viscosity of the neat bitumen remains almost unaltered after the incorporation of surfactant-type additives [6, 8, 9], even if they allow obtaining a reasonable workability and adequate in situ compaction efforts [10]. In this sense, specific studies pointed out that improvements in terms of WMA mixtures workability may be related to increases in lubricity (reduction of mixture internal friction) rather than decreases in viscosity, as the lubrication effect reduces the effort required to move aggregates during compaction [11, 12].

Despite these benefits, the lower binder aging provided by lowered manufacturing temperatures of WMA mixtures could suggest that these mixes may provide lower rutting performance than HMA. However, it has been shown that, in general, rutting potential is influenced by the additive type and dosage [3]. As regards the use of chemical additives, WMA mixtures generally provide lower rutting performance than HMA when produced with neat bitumens [6, 10, 13, 14] whereas no significant differences are observed in the case of polymer modified bitumens (PMBs) [6].

In general, PMB is obtained by adding polymers to a bituminous binder in order to enhance its performance and durability. The combination of warm technologies with polymer modification could be beneficial to obtain products with improved properties. Since these binders are characterized by a ternary system (bitumen/polymer/additive), a further aspect that needs to be taken into account is the possible interaction between all the components that could also negatively affect the bitumen/polymer compatibility and compromise both binder and asphalt mixture properties. In this sense, morphological analysis allows a better understanding of the mutual interaction among all the components involved and also detects differences in the rheological properties, as morphology and rheological characteristics are strongly related [15, 16]. At present, there are very few investigations aimed at evaluating these aspects, especially involving WMA chemical additives and PMBs.

A further aspect for PMBs is that they usually require higher working temperatures than neat bitumens, in order to gain proper mixture workability. This could suggest that PMBs may not be suitable for WMA production. Nevertheless, in situ investigations [17, 18] recently showed that styrene–butadiene–styrene (SBS) polymer modified bitumen combined with chemical additives provides adequate performance when used for the production of mixtures at reduced temperatures.

The main objective of this paper is to evaluate the effects of WMA chemical additives on binder performance. To achieve this scope, two bitumens and two types of chemical additives were studied through physical, rheological and chemical property measurements. Specifically, conventional tests (penetration, Ring & Ball softening point), viscosity and rheological measurements with Dynamic Shear Rheometer (DSR), as well as microscopic and Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance (FTIR-ATR) analyses, were performed.

2 Materials

Two bitumens (Table 1) were selected for the laboratory investigation: a neat 70/100 penetration-grade bitumen (coded as 70/100) and a polymer modified bitumen (coded as PMB, containing 3.8% SBS by bitumen weight). The 70/100 pen is regularly used in Europe for road construction whereas the PMB is usually employed in the construction of Italian highway pavements.

Two different commercial chemical additives (coded as A and B) were investigated and their properties are summarized in Table 2. Each chemical additive was added to both the original bitumens (70/

Table 1 Main properties of the bitumens

	Standard	Unit	70/100	PMB
Penetration (25 °C; 100 g; 5 s)	EN 1426	0.1 mm	84	54
Ring & Ball softening point	EN 1427	°C	45.4	71
Elastic recovery (25 °C; 5 cm/min)	EN 13398	%	–	89
Dynamic viscosity @ 135 °C	EN 12595	Pa s	–	1.24
Kinematic viscosity @ 135 °C	EN 12595	cSt	345	–
Fraass breaking point	EN 12593	°C	−16	–
Mass loss after RTFOT	EN 12607-1	%	–	0.05
Penetration after RTFOT	EN 1426	0.1 mm	54	27
Ring and Ball softening point after RTFOT	EN 1427	°C	51.1	77

Table 2 Basic characteristics of the WMA chemical additives A and B

	A		B	
Physical form at 25 °C	Colorless liquid		Dark amber liquid	
Density at 25 °C	≈ 1.0		0.97	
Viscosity (Pa s)	0.45	at 15 °C	1.735–3.22	at 10 °C
			0.35–0.645	at 30 °C

100 and PMB) at a dosage of 0.4% by bitumen weight, and four WMA binders (coded as 70/100_A, 70/100_B, PMB_A and PMB_B) were obtained. The WMA binders were prepared in laboratory by using a portable mixer operating at a high stirring rate (700 rpm). The blending conditions (temperature and time) were carefully selected in order to minimize additional aging effects. Specifically, a prefixed amount of chemical additive was blended with the hot bitumen (i.e. 160 °C for 70/100 and 170 °C for PMB) for 10 min.

3 Experimental program and test procedures

A series of laboratory tests were performed, including conventional tests (pen, Ring & Ball softening point), viscosity, dynamic shear rheometer (DSR) rheological characterizations, microscopic analysis (morphology) and Fourier transform infrared spectroscopy (FTIR).

Penetration (25 °C) and softening point were measured according to EN 1426 and EN 1427, respectively.

Viscosity was measured by using a Brookfield rotational viscometer, following the test procedure standardized by EN 13302-2. A shear rate equal to 10 s^{-1} and five temperatures (105, 120, 135, 150 and 165 °C) were considered. Moreover, complex viscosity η^* was calculated by using oscillatory measurements carried out with DSR. A constant strain amplitude of 0.5%, a constant angular frequency of 10 rad/s and fifteen temperatures, ranging from 0 to 140 °C (with a step of 10 °C), were applied. A plate diameter of 8 mm and a gap equal to 2 mm were used for tests between 0 and 30 °C and a plate diameter of 25 mm and a gap equal to 1 mm were employed for tests between 30 and 140 °C. Two replicates were performed for each testing condition.

Frequency sweeps in plate–plate configuration were performed with a DSR, allowing the complex modulus G* and the phase angle δ to be investigated. The tests were performed over a range from 0.1 to 10 Hz under isothermal conditions, and at nine temperatures ranging from 0 to 80 °C (with a step of 10 °C). All the tests were conducted in a control strain of 0.5%, and within the linear viscoelastic range of the materials. Two replicates were carried out for each testing condition.

In order to evaluate the binder rutting behavior, the DSR device was also used to perform Multiple Stress Creep Recovery (MSCR) tests, according to EN 16659–2016. Parallel plate geometry with a plate diameter of 25 mm and a gap of 1 mm was employed. During the test, the specimen is subjected to 10 creep-recovery cycles with a creep loading time of 1 s and a recovery time (with no loading) of 9 s for each cycle. The temperature and the stress dependency of the binders were evaluated by performing MSCR tests at four temperatures (58, 64, 70 and 76 °C) and two stress levels (0.1 and 3.2 kPa). Specimens were conditioned at the test temperature for 20 min before testing. Two replicates were performed for each testing condition.

The experimental program of the rheological tests is summarized in Table 3.

During the microscopic investigation, two light sources were used: ultraviolet (UV) for fluorescence and white light for transmitted structures. The same sample preparation procedure was followed for all the samples tested, as the morphology results are highly temperature-dependent [16]. Specifically, specimens were prepared by pouring a small drop of hot binder on a glass plate at a specific temperature (i.e. 160 °C for 70/100 and 170 °C for PMB) and the morphology measurements were performed at room temperature. Furthermore, in order to reduce the orientation effects suffered by the sample during the conditioning and spreading, the observation of the sample was focused on the original drop central area.

In FTIR-ATR, a very small amount of binder was directly placed on a ATR crystal (ZeSe) and the IR reflection from the specimen was measured between a wavenumber of 400 and 4000 cm^{-1}. The amounts of aromatic, carbonyl and sulfoxides compounds were calculated by respectively measuring the areas of IR bands at about 1600, 1700 and 1030 cm^{-1}.

4 Results and analysis

4.1 Conventional tests

As expected, PMB shows lower penetration and higher softening point values than 70/100 (both with and w/o additives). As it can be seen in Table 4, 70/100 pen shows a decrease in penetration with the addition of chemical additives (both A and B), whereas penetration does not show significant variation when these additives are added to PMB. As far as the softening point is concerned, both additives led to a slight increase in softening point for 70/100 pen whereas a not univocal trend is observed for PMB with additives. Nevertheless, according to European specifications (EN 1426 and EN 1427), no significant differences can be point out between the original bitumens and the WMA binders (except for penetration of 70/100 pen), as the variations observed are included in the repeatability and reproducibility ranges (Table 4). These data are in agreement with the results obtained in several studies [9, 10], when similar surfactant additives were used.

4.2 Viscosity

Figure 1 shows Brookfield viscosity as a function of the temperature, for all the binders studied (with and w/o chemical additives). Results confirm that the viscosity decreases as the temperature increases and that the PMB provides higher viscosity values than 70/100.

As far as the influence of the chemical additives is concerned, it can be observed that their presence has no relevant impact on the viscosity values of the 70/100 pen, whereas it is evident a slight increase in viscosity for PMBs, especially for chemical additive A.

Table 3 Experimental program

Test type (–)	Temperature (°C)	Frequency (Hz)	Shear rate (s^{-1})	Angular frequency (rad/s)	Stress level (kPa)
Viscosity	105–165	–	10	–	–
Oscillatory test (*)	0–140	–	–	10	–
MSCR	58–76	–	–	–	0.1 and 3.2
Frequency sweep	0–80	0.1–10	–	–	–

(*) only for PMBs

Table 4 Results of penetration tests, Ring & Ball tests and respective variations

Binder code	Penetration @ 25 °C (0.1 mm)	Δ_{Pen} (0.1 mm)	Δ_{Pen} (%)	R&B (°C)	$\Delta_{\mathrm{R\ \&\ B}}$ (°C)
70/100	81	0.0	9.95	45.8	0.0
70/100_A	73	–8.0	–0.90	46.2	0.4
70/100_B	67	–14.0	–9.05	47.0	1.2
PMB	33	0.0	1.02	75.0	0.0
PMB_A	32	–1.0	–2.04	75.8	0.8
PMB_B	33	0.0	1.02	72.2	–2.8

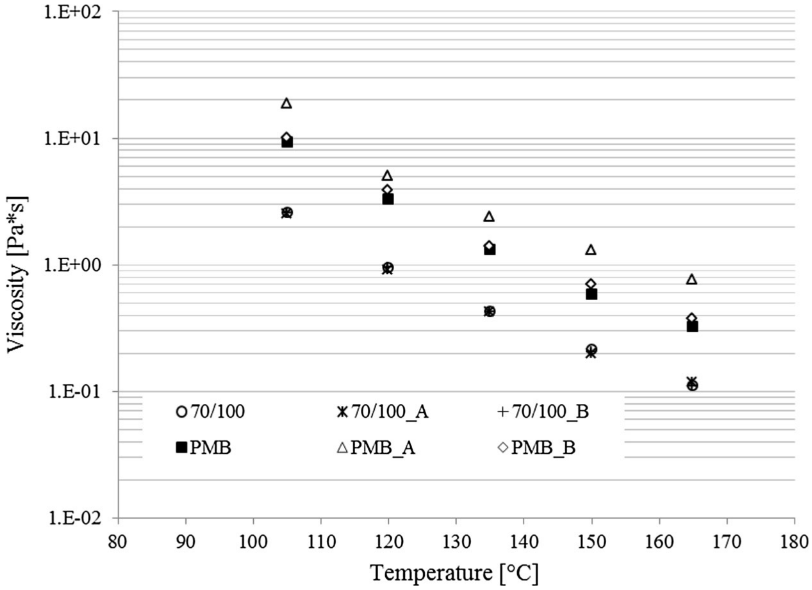


Fig. 1 Brookfield viscosity vs temperature at a shear rate of 10 s^{-1}

In order to better understand the effect of chemical additives on viscosity (especially when PMBs are used), the influence of the shear rate on the viscosity results was also investigated. To this end, the complex viscosity η^* was calculated as the ratio between the norm of the complex modulus G^* and the corresponding angular frequency ω, as follows:

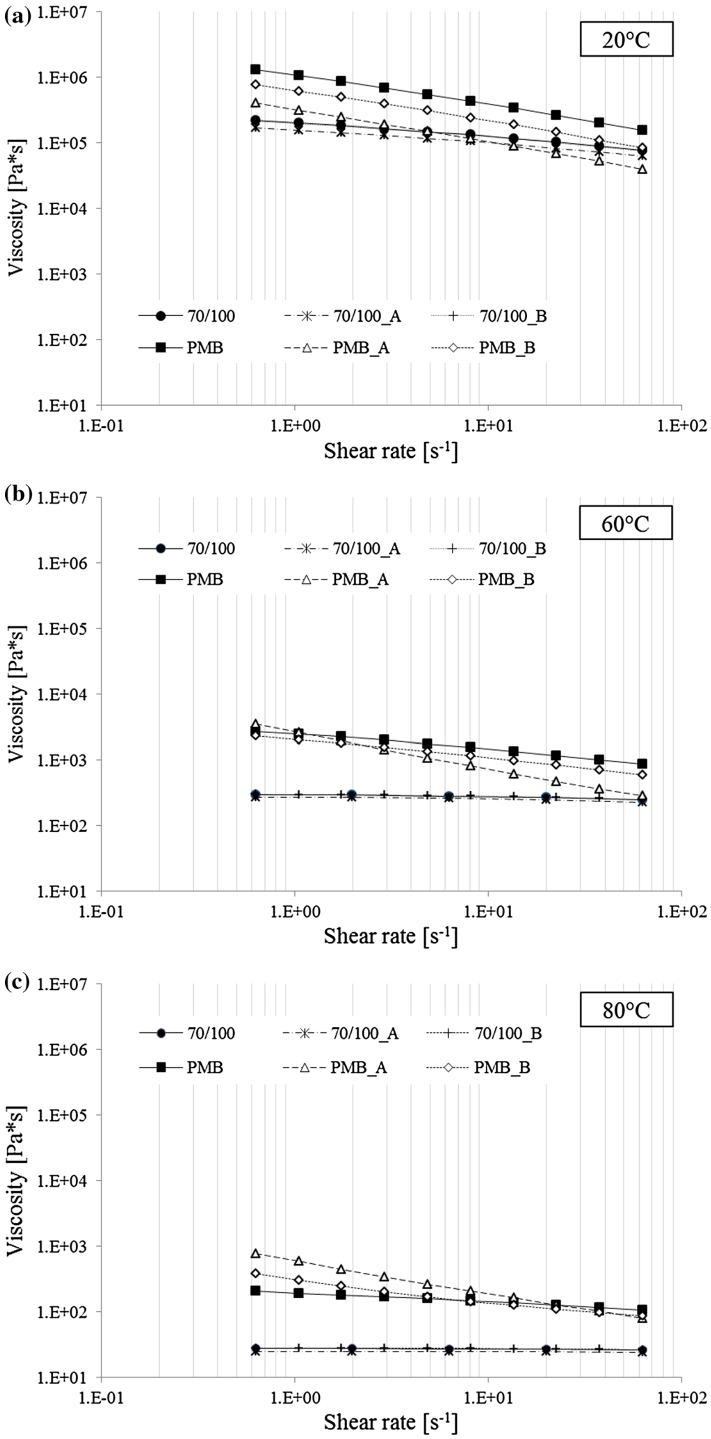
$$|\eta^*(\omega)| = \frac{|G^*|}{\omega} \tag{1}$$

Three temperatures were considered: 20, 60 and 80 °C. The chosen lower temperature at 20 °C was intended to compare viscosity results with the morphology analysis performed at room temperature. Viscosity at 60 °C is the parameter usually used for the evaluation of the performance of HMA pavements during summer (a low viscosity can induce distresses such as rutting). Finally, 80 °C can be useful for the evaluation of the viscosity trend with shear rate and temperature.

Figure 2, where the complex viscosity η^* is represented as a function of the shear rate for different temperatures, shows that 70/100 pen, both with and w/o additives, behaves as Newtonian fluid at the highest temperatures investigated, as the viscosity does not vary with the shear rate.

On the other hand, the PMB shows a shear thinning behavior characterized by a decrease in viscosity with increasing shear rate. Analogous trends are very evident when chemical additives are added to the modified bitumen. Specifically, an increase in the shear thinning behavior is detected for PMB_A and PMB_B with respect to PMB, especially at higher

Fig. 2 Viscosity as a function of shear rate at 20 °C (**a**), 60 °C (**b**) and 80 °C (**c**)



temperatures, where the shear rate dependence for the PMB (w/o additives) tends to reduce. However, the influence of the chemical additives is strongly affected by the temperature and by the interaction between bitumen, polymer and additive. In fact, at 20 °C, for each shear rate, PMB_A and PMB_B show lower viscosity values than PMB (Fig. 2a), in opposition to the Brookfield viscosities behavior observed for

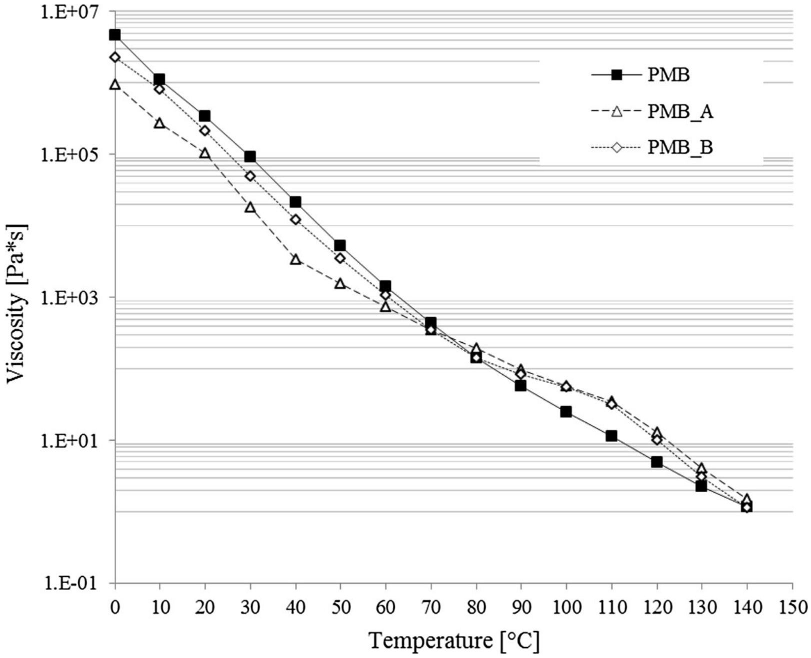


Fig. 3 Complex viscosity vs temperature at shear rate of 10 s^{-1} for PMBs

temperatures greater than or equal to 105 °C (Fig. 1). At 60 °C and at low shear rates, a slight reversal of trend can be detected for PMB_A, which shows higher viscosity values compared to PMB (Fig. 2b). This trend becomes more evident at 80 °C (Fig. 2c) where, at shear rates lower than 20 s^{-1}, both PMB_A and PMB_B provide higher viscosity values than PMB, approaching the Brookfield viscosity behavior (Fig. 1).

In order to detect the temperature at which this reversal of trend occurs for a shear rate equal to 10 s^{-1} (used during Brookfield viscosity investigation), a further analysis was performed by considering the temperature susceptibility of PMBs viscosity in a wide range of temperatures. Figure 3 shows that the viscosity gradually decreases with temperature for PMB (containing 3.8% of SBS). On the contrary, the addition of chemical additives provides a reduced slope (plateau region) around 80 °C and a rapid decrease in viscosity when the temperature exceeds 110 °C. This behavior is similar to the behavior detected by Lu and Isacsson [19] for PMBs with high SBS content (equal or higher than 6%), allowing to observe that the addition of chemical additives at PMBs produces viscosity modifications similar to the addition of a higher amount of polymer. When the temperature reaches about 80 °C, the addition of the chemical additive probably allows the polymer to become more soluble in and more interactive with the bitumen, reducing the variation of the viscosity with temperature (plateau region) [19]. Thus, the chemical additives investigated reduce the viscosity temperature susceptibility of the PMB in the temperature range between 80 and 140 °C.

Modifications provided by the chemical additives in the complex viscosity-temperature diagram can also be detected in the rheological behavior of PMBs. Figure 4 shows that for PMB the viscosity decreases steadily as the phase angle increases demonstrating that the binder behavior passes from viscoelastic to purely viscous ($\delta = 90°$) with increasing temperatures, as observed by several researchers [19, 20]. The addition of chemical additives provides different rheological behavior depending on additive type. Specifically, an elasticity-dominant region can be detected for PMB_A which reaches phase angle values of about 40°, analogously to what happen when higher SBS contents are considered [19]. On the contrary, PMB_B shows an intermediate trend for low temperature values till a phase angle of about 60° and then behaves similarly to PMB_A.

Both Brookfield and complex viscosity results allow to state that chemical additives do not affect

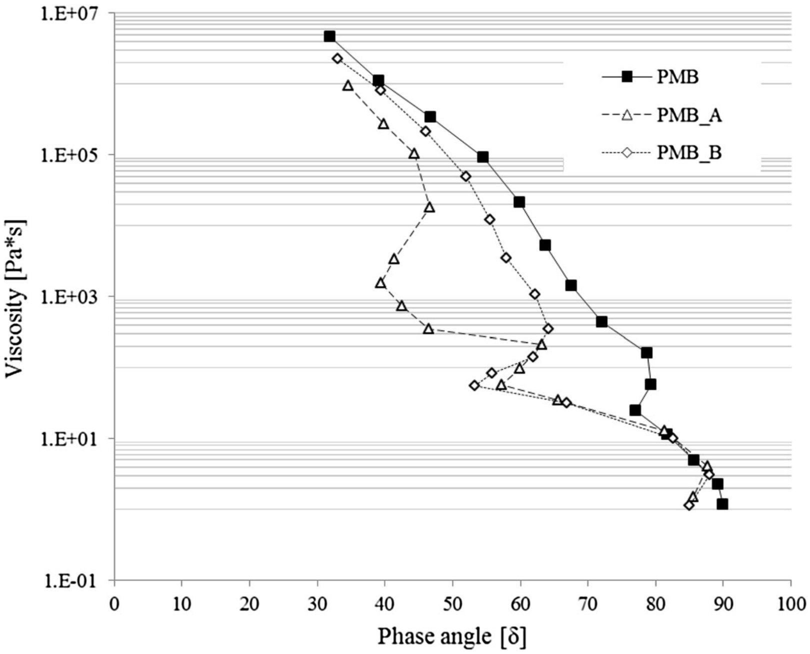


Fig. 4 Complex viscosity vs phase angle at shear rate of 10 s^{-1} for PMBs

the viscosity of neat bitumens but strongly influence the viscosity of PMBs.

4.3 Rheological characterization

4.3.1 Results of MSCR tests

The MSCR tests were carried out in order to investigate the effect of chemical additives on the rutting behavior of the material studied. The non-recoverable compliance (J_{nr}) is chosen as an indicator of rutting resistance and is expressed as the ratio between the permanent strain after the recovery phase and the applied stress during creep loading. For each stress level (0.1 and 3.2 kPa) and for each of the ten cycles, the parameter $J_{nr,i}$ was calculated and the average non-recoverable creep compliance J_{nr} was computed as the mean of ten $J_{nr,i}$ values. Figure 5 shows the results in term of average J_{nr} at a stress level of 3.2 kPa as a function of the test temperature.

As expected, for all materials tested, J_{nr} increases as the test temperature increases confirming that a higher viscous flow behavior is provided at higher temperatures, leading to higher permanent strain under the same stress.

As far as the influence of the chemical additives is concerned, the addition of A slightly increases J_{nr} values compared to 70/100 pen, whereas the addition of B has no significant effects on its rutting behavior. On the contrary, PMB_A and PMB_B showed an improved resistance to permanent deformation compared to PMB, demonstrating that both chemical additives may be able to decrease rutting potential in terms of non-recoverable creep compliance (J_{nr}), when PMBs are considered. This is in agreement with Morea et al. [6], who reported similar results with two chemical tensioactive additives.

As far as the difference between the two additives is concerned, the additive A performs better than additive B in terms of permanent deformations, according to the softening point results (Table 4).

A further characterization of the permanent deformation resistance of binders can be performed through the ratio between the average non-recoverable creep compliance J_{nr} and the total creep compliance J_{TOT}, evaluated immediately before the removal of the applied stress, as proposed by Santagata et al. [21]. This parameter provides information on the elastic/plastic characteristics of the material. Specifically, the ratio J_{nr}/J_{TOT} is equal to 0 whether the material completely recovers the accumulated strain whereas is equal to 1 whether it is unable to recover any accumulated strain. Figure 6 shows the J_{nr}/J_{TOT} percentages as a function of the temperature, for all materials tested. The 70/100 pen, with or w/o additives, is characterized by a J_{nr}/J_{TOT} value close

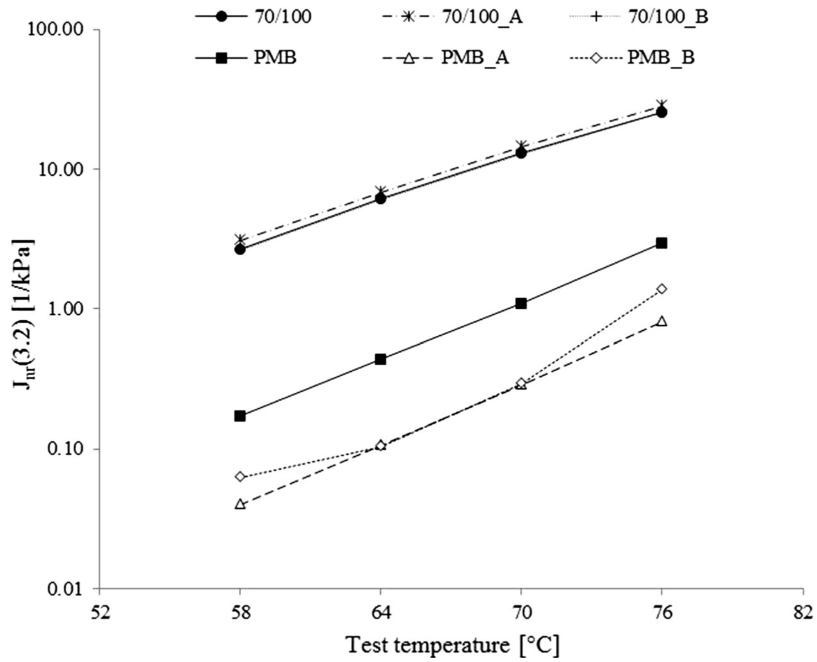


Fig. 5 Non-recoverable creep compliance of binders at 3.2 kPa

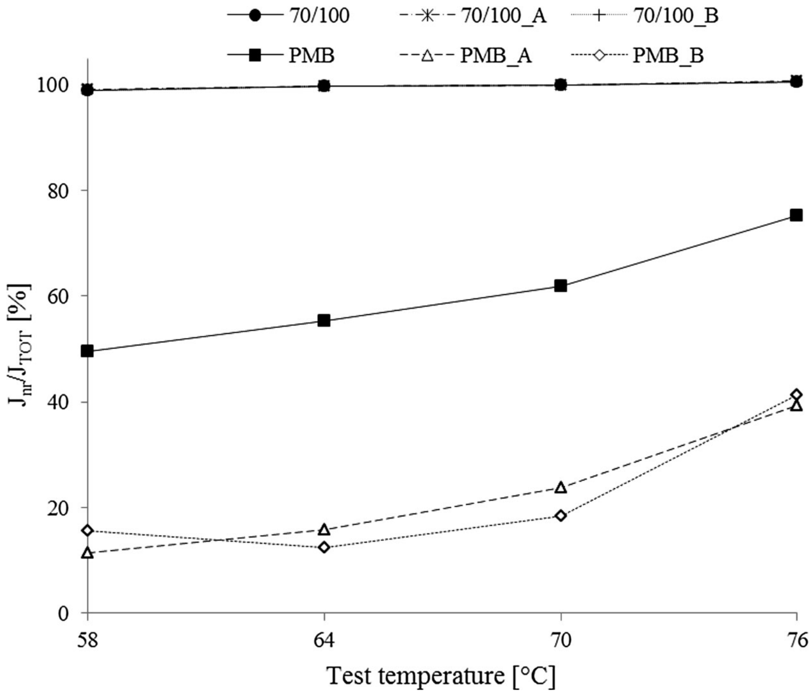
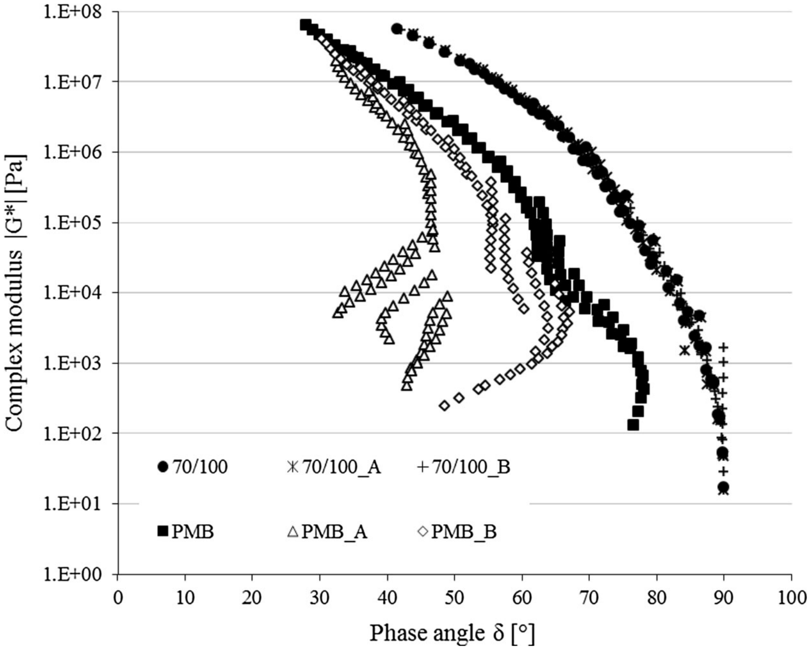


Fig. 6 Values of J_{nr}/J_{TOT} of binders at stress level of 3.2 kPa

or equal to 100%, for all testing temperatures. On the contrary, a marked decrease of J_{nr}/J_{TOT} can be observed when the chemical additives are added to the PMB. This is a further confirmation that when polymer modified bitumens are used, the chemical additives can be able to improve the deformation recovery after a creep phase, thus decreasing rutting potential.

Fig. 7 Black diagrams of binders tested



4.3.2 *Results of frequency sweep tests*

Viscoelastic properties of bituminous materials can be examined through frequency sweep tests by measuring the complex modulus G^* and the phase angle δ. The Black diagram G^*-δ, can be fruitfully used to analyze the experimental results as it allows presenting all the rheological data in only one plot, regardless of frequency and temperature. Moreover, it can be employed for controlling the application of the Time Temperature Superposition Principle (TTSP) and the thermo-rheological simplicity [22].

The Black diagram for 70/100 pen (Fig. 7) shows that all the measured data are almost described by a unique curve, characterized by high G^* values at high frequencies (low temperatures) and a more viscous behavior at low frequencies (high temperatures). This indicates a time–temperature equivalency and a thermo-rheologically simple behavior, which remains almost unchanged by adding chemical additives to the original bitumen (70/100_A and 70/100_B binders).

On the contrary, it is not possible to get a single smooth curve for PMB (Fig. 7) as it depicts the typical behavior of polymer modified bitumens [22], which usually show a thermo-rheologically complex behavior. The PMB rheological behavior can be divided into two domains: above and below a complex modulus value of approximately 10^5 Pa. At high frequencies (low temperatures, high G^* values), the Black diagram curve is similar to the 70/100 pen curve but with lower phase angles, showing a more elastic response. Below the complex modulus threshold of 10^5 Pa (low frequencies, high temperatures), an increase in δ occurs displaying an increased viscous response.

When chemical additives are added to the PMB, the rheological behavior significantly changes. At high complex modulus values, the Black diagram curves of PMB_A and PMB_B show a horizontal translation towards lower phase angles (more elastic response), especially for the additive A. Diversely, at low frequencies (low G^* values) a less viscous behavior is observed as a decrease in the phase angle occurred. Lower phase angles at low frequencies and/or high temperatures are beneficial when the resistance to permanent deformation is considered [23], as confirmed by the MSCR results (Fig. 5). The shape of the Black curve for PMB_B shows a high elastic component even at low frequencies (low G^* values), suggesting a rubbery-like behavior for phase angles between 50° and 70° and complex moduli between 10^2 and 10^4 Pa. This increased elastic response is probably due to an entangled polymer network, as suggested by Lu and Isacsson [19]. On the contrary, the Black diagram for PMB_A shows a much weaker rubbery-like behavior, with evident branching and discontinuous waves in the bottom part of the curve (low frequencies). According to previous experimental studies [15, 16, 22], this is due to a structural modification or to a bitumen phase transition, probably caused by the separation between the bitumen and the polymer in the presence of the additive.

To summarize, Fig. 7 show that the presence of the two chemical additives studied does not imply any change on the rheological properties of the 70/100 pen, whereas it has a remarkable influence on the viscoelastic response of PMB. This phenomenon may be mainly related to the morphological characteristics of the materials that can be detected through a microscopic analysis, as suggested in [15].

4.4 Microscopic analysis

Since the rheological properties of PMBs are strongly influenced by the polymer morphology, the microstructure of these binders with and w/o additives was also studied through the microscopic analysis. Figure 8 shows images of PMB binders observed at room temperature with two different light sources: UV fluorescence and white light.

In the fluorescence microscopy, it is generally assumed that the polymer swells with aromatic compounds from the bitumen, exhibiting a higher fluorescence to UV than the bitumen phase [15]. For this reason, when observed with a fluorescence microscope, the polymer-rich phase appears much lighter than the bitumen-rich phase. The fluorescence images in Fig. 8 show that PMBs are composed by two phases: a lighter SBS-rich phase and a darker bitumen-rich phase. The small polymer spheres are spread homogenously in a continuous bitumen phase, even if PMB_A displays very small polymer droplets.

With the white light source, bituminous samples were further investigated in a transmit mode. As shown in the micro images in Fig. 8, the polymer-rich and bitumen-rich phases appear red and dark, respectively. It is evident that morphology of the PMB changes considerably when the WMA additives are added. The PMB morphologies are also largely dependent on thermal history [15], thus affecting the rheological properties significantly. This probably explains the large differences in the rheological measurements shown in Fig. 7.

4.5 FTIR

The chemical additive effect could be assessed by analyzing specific functional groups, such as aromatic C=C at 1600 cm^{-1}, carbonyl C=O at 1700 cm^{-1} and sulphoxide S=O at 1030 cm^{-1}.

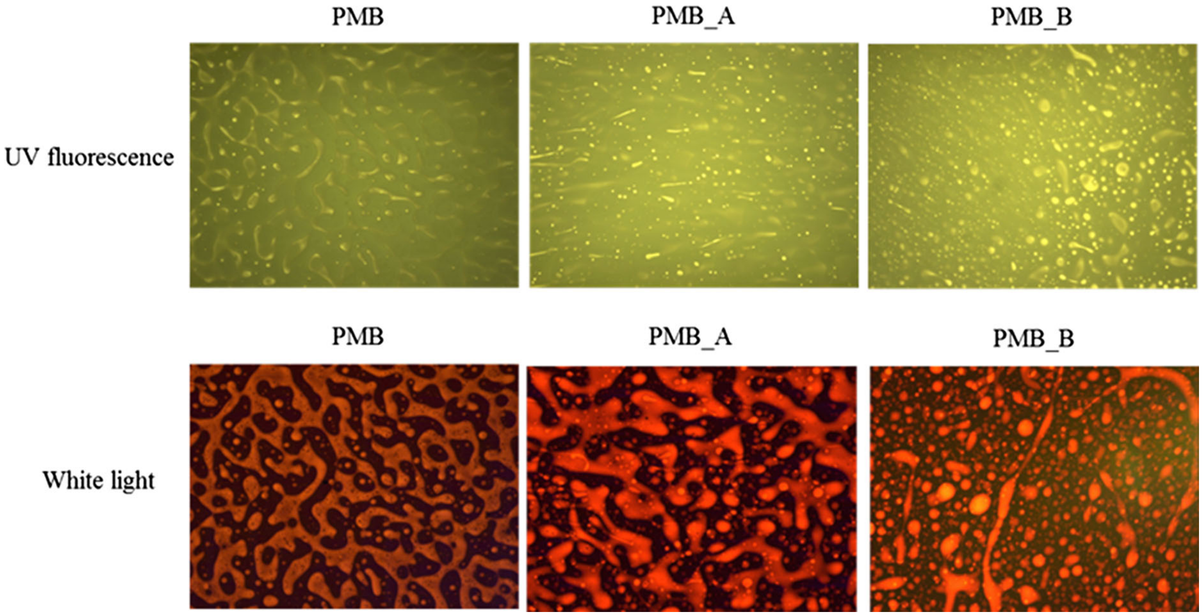


Fig. 8 UV fluorescence and White light for transmitted photographs of drops of PMB with and w/o additives (magnification ×100)

Table 5 FTIR testing results

Binders	Area 1460	Area 1375	C=C 1600	C=O 1700	S=O 1030	$A_{1460}+A_{1375}$	I_{ARO}	I_{CO}	I_{SO}
70/100	5.54	1.57	1.36	0.20	0.19	7.10	0.19	0.029	0.027
70/100_A	5.42	1.53	1.10	0.13	0.15	6.95	0.16	0.018	0.022
70/100_B	5.24	1.47	1.19	0.09	0.15	6.70	0.18	0.013	0.023
PMB	5.71	1.29	2.18	0.00	0.36	7.00	0.31	0.000	0.051
PMB_A	5.70	1.26	2.70	0.00	0.38	6.96	0.39	0.000	0.055
PMB_B	5.39	1.27	2.03	0.00	0.36	6.66	0.30	0.000	0.053

For quantitative analysis, three structural indexes were determined through the ratio of the areas calculated according to Eqs. (2), (3) and (4):

$$I_{\mathrm{ARO}} = \frac{A_{1600}}{\Sigma A} \quad (2)$$

$$I_{\mathrm{CO}} = \frac{A_{1700}}{\Sigma A} \quad (3)$$

$$I_{\mathrm{SO}} = \frac{A_{1030}}{\Sigma A} \quad (4)$$

where A_{1600} is the area of the aromatic band centered on 1600 cm^{-1}, A_{1700} is the area of the carbonyl band centered on 1700 cm^{-1}, A_{1030} is the area of the sulphoxide band centered on 1030 cm^{-1}, and ΣA is the area of the spectra bands between a wavenumber of 1375 and 1460 cm^{-1}.

Table 5 shows that the additive effect on the structure-change indexes (I_{ARO}, I_{CO} and I_{SO}) of binders is negligible, except the case of I_{CO} value of the pen bitumen (70/100). The reduction in this index after adding the WMA additives might suggest that certain chemical reaction has occurred. However, to have a solid answer, further investigation is needed.

This probably means that FTIR analysis is not able to point out significant differences between WMA binders prepared with different chemical additives. On the contrary, it could be useful for highlighting aging effects.

5 Conclusions

This paper focuses on the influence of WMA chemical additives on the mechanical performance of neat and polymer modified bitumens.

Results lead to the following conclusions:

- the chemical additives investigated have no noticeable influence on the basic properties of bitumens (in terms of penetration and softening point), especially for PMBs;
- the 70/100 pen bitumen, both with and w/o additives, behaves as Newtonian fluid at the highest temperatures investigated, whereas the PMB shows a shear thinning behavior, that becomes more evident where chemical additives are added. Therefore, chemical additives do not affect viscosity of neat bitumens but strongly influence viscosity of polymer modified bitumens. Specifically, the addition of chemical additives to the PMB produces microscopic and rheological modifications similar to the addition of a higher amount of polymer, reducing the viscosity temperature susceptibility of PMBs in the temperature range between 80 and 140 °C;
- chemical additives have no significant effects on the rutting behavior of 70/100 pen bitumen whereas for PMB, decreased rutting potential is observed;
- the two chemical additives studied do not change the rheological properties of the 70/100 pen bitumen, whereas they have a remarkable influence on the viscoelastic response of PMB. Specifically, the addition of the chemical additives leads to structural modifications or to bitumen phase transitions;
- the comparison between Black diagrams and morphology images shows that the polymer morphology may significantly influence the viscoelastic response of PMBs;

- the Black diagram and the MSCR results confirm that lower phase angles at low frequencies and/or high temperatures are beneficial when the resistance to permanent deformation is considered;
- FTIR analysis shows that the addition of the chemical additives investigated does not alter, in general, the structure indexes of the binders.

Compliance with ethical standards

Conflicts of interest The authors declare that there is no conflicts of interest regarding the publication of this paper.

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