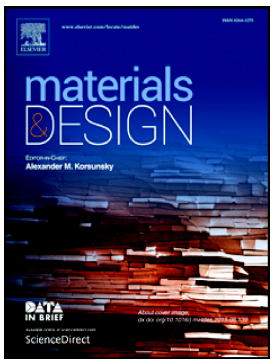


Effect of temperature and chemical additives on the short-term ageing of polymer modified bitumen for WMA

Davide Ragni, Gilda Ferrotti, Xiaohu Lu, Francesco Canestrari

PII: S0264-1275(18)30744-5
DOI: doi:10.1016/j.matdes.2018.09.042
Reference: JMADE 7403

To appear in: *Materials & Design*

Received date: 23 May 2018
Revised date: 20 September 2018
Accepted date: 24 September 2018

Please cite this article as: Davide Ragni, Gilda Ferrotti, Xiaohu Lu, Francesco Canestrari , Effect of temperature and chemical additives on the short-term ageing of polymer modified bitumen for WMA. Jmade (2018), doi:10.1016/j.matdes.2018.09.042

EFFECT OF TEMPERATURE AND CHEMICAL ADDITIVES ON THE SHORT-TERM AGEING OF POLYMER MODIFIED BITUMEN FOR WMA

Davide Ragni[1], Gilda Ferrotti[1]*, Xiaohu Lu[2] and Francesco Canestrari[1]

[1]*Università Politecnica delle Marche, via Brecce Bianche, 60131, Ancona, Italy*

d.ragni@pm.univpm.it; g.ferrotti@univpm.it; f.canestrari@univpm.it

[2] *Nynas AB, SE 149 82, Nynäshamn, Sweden*

Xiaohu.lu@nynas.com

* Corresponding author. Tel. and fax: +39 071 220 4507

E-mail address: g.ferrotti@univpm.it

ABSTRACT

Nowadays warm mix asphalt (WMA) is recognized as a very competitive alternative to hot mix asphalt (HMA). This technology allows to obtain an excellent and environmentally-friendly material for road construction. This paper focuses on the effect of a reduced short-term ageing temperature on the binder behaviour and on the effect of WMA chemical additives on the performance of short-term aged binders. Three asphalt binders (one polymer modified bitumen combined with two WMA chemical additives) were aged through the rolling thin film oven test (RTFOT) at different temperatures (120, 130 and 163 °C). Conventional, rheological and chemical tests were used for characterising the binders. Lower ageing temperatures provided reduced oxidation, implying lower oxidative hardening but also reduced permanent deformation resistance. A general reduction of ageing effects is observed in the WMA binders, with both positive (moderate deceleration of the ageing process) and negative (more noticeable reductions in the permanent deformation resistance) outcomes. The microscopic analysis showed that the chemical additive likely alters the structural interactions of bitumen and polymer. A comparison between WMA binders short-term aged in laboratory and in field, indicates that the RTFOT performed at reduced temperature could properly simulate the field ageing when WMA production temperatures are considered.

Keywords: WMA – RTFOT – Polymer modified bitumen – Chemical additive – FTIR – DSR

1. Introduction

During the production, the laying and the compaction of the asphalt mixture, the workability must be continuously guaranteed. Since bitumen is a viscoelastic material, whose properties highly depend on the service temperature, it is necessary to properly select the binder temperature (usually higher than 150 °C for hot mix asphalts) in order to achieve an optimal material density and a proper aggregate coating. During the last decades, environmental and social concerns have grown in pavement engineering due to energy consumption (e.g. fuel, gas.), asphalt greenhouse gas emissions and workers exposure to emissions. Thus, new solutions that allow to minimize the impact caused by the application of these materials have been investigated. One promising solution is represented by Warm Mix Asphalt (WMA) technologies that allow a reduction of the production temperature from 20 to 40 °C, by simultaneously ensuring mechanical performance comparable with hot mix asphalts (HMAs) [1-5].

In the last years, the use of WMA has been increased due to the numerous benefits offered by these mixtures: higher workability at lower temperatures, comfort and safety of workers, longer haul distances, lower energy consumption and financial costs, lower plant emissions and fumes, higher RAP content in recycled asphalt mixtures and quicker turnover to traffic (due to shorter cooling time). The use of these warm technologies could also result in an extension of the pavement service life thanks to the reduced ageing provided by the lowered production temperatures, even though the resulting mixtures could display lower resistance against rutting, greater moisture susceptibility, coating and bonding drawbacks [6-8].

Different techniques exist to produce warm mix asphalts: foaming processes, use of organic additives and use of chemical additives [9-13]. Foaming process includes several methods that entail the introduction of small amounts of water into a hot asphalt binder, causing its volume expansion and dispersion for the coating of aggregates. After a short period, the foam collapses and the bitumen behaves as a normal binder. Technologies using organic additives are characterized by the addition of synthetic waxes to the mixture or to the bitumen. Waxes are characterized by high molecular hydrocarbon chains with a melting point of 80-120 °C which allows the appreciable modification of the original bitumen properties. Chemical additives include a combination of emulsifying agents, surfactants, polymers and adhesion promoters, able to improve coating, mixture workability and compaction.

It is well known that asphalt mixture production leads to bitumen ageing that strongly influences the bitumen mechanical behaviour. Ageing is a very complex process which involves irreversible and reversible mechanisms [14]. The irreversible process consists in bitumen chemical changes (i.e. oxidation, volatilisation, exudation), whereas the reversible one is called physical hardening and is ascribable to molecule structuring (e.g. reorganisation of bitumen molecules). However, the main mechanism involved is the oxidative ageing that affects physical and mechanical properties of bitumen and it becomes more complicated for polymer modified bitumens (PMBs) as two phenomena, like the polymer degradation and the bitumen oxidation, contemporary occur [15].

Ageing of asphalt binders and mixtures consists of short- and long-term ageing. The short-term ageing happens during the phases of mixture production, transportation, laying and compaction, whereas the long-term ageing is a process that the mixture undergoes in the field during the whole service life and is mainly caused by climatic factors. Short-term ageing of binders for HMA applications is usually simulated in the laboratory with the Rolling Thin Film Oven Test (RTFOT) that is carried out at the standard temperature of 163 ° C, according to EN 12607-1 [16]. Since this temperature is higher than the typical production temperatures of WMA mixtures (100-140 °C), it is fundamental to investigate whether the standard RTFOT procedure is still appropriate for WMA ageing simulation, given that the rate of oxidation usually increases with the temperature.

It has already been shown that unmodified bitumens, with [17] or without [18] the addition of WMA additives, present lower oxidative level with respect to the standard value of 163 °C, when lower short-term ageing temperatures (i.e.123 and/or 143 °C) were considered.

The investigation of PMB binders is more complex as the physical-chemical interactions among polymer and WMA additive should be considered. Ferrotti et al. [19], by studying a PMB with Styrene-

Butadiene-Styrene (SBS) polymer and two different WMA chemical additives, observed that the incorporation of these additives strongly affects both the basic properties (in terms of penetration value and softening point temperature) and the rheological characteristics of the PMB. Dondi et al. [20], investigated the laboratory short-term ageing with neat, warm (with paraffinic wax) and modified (with SBS polymers) binders, by performing the RTFOT at 163 °C and at the equiviscous temperature of the binder (determined with a rotating spindle apparatus). It was found that RTFOT at 163 °C does not reflect the real primary ageing conditions of PMBs, whereas the oxidative process observed during mixing is better simulated by the RTFOT performed at the equiviscous temperature.

Another important aspect that should be further investigated is the use of warm recycled mixtures characterized by the inclusion of reclaimed asphalt pavement (RAP). Since the RAP binder is already aged, it could increase the stiffness of the bituminous blend and alter the short-term ageing of WMAs [6]. In this sense, Frigio et al. [21] demonstrated that, after short-term ageing, the binder extracted from WMA mixtures prepared with different additives (organic, chemical and zeolite) and 15% of RAP, provides a reduced increase in stiffness as compared to the bitumen extracted from a HMA containing the same amount of RAP. Moreover, Stimilli et al [22] indicate that warm recycled mixtures guarantee adequate in situ performance without significant modification of the asphalt plant and production processes. However, the effective long-term durability of WMA has not yet been fully tested [1, 23].

The primary objectives of this experimental study are the investigation of the effect of the temperature on the short-term ageing of a SBS polymer modified bitumen containing different WMA chemical additives and the effect of these additives on the performance of short-term aged binders. Laboratory binder ageing with RTFOT was performed considering the standard temperature of 163 °C and two reduced temperatures (120 and 130 °C) that represent operating temperatures for WMA field production. Moreover, in order to investigate whether the standard RTFOT procedure is still appropriate for WMA ageing simulation, a further comparison was made between RTFOT and field ageing by considering a binder extracted and recovered from a field trial section laid in Italy with a WMA mixture.
All the binders were investigated by performing conventional, rheological and chemical tests.

2. Materials

One base bitumen and two different types of WMA chemical additive were used. The base bitumen (Table 1) is a polymer modified bitumen (coded as PMB) with 3.8% of SBS by bitumen weight. The chemical additives (codes as A and B) are designed and proposed for use in WMA technology and their basic properties are summarized in Table 2. Additive A is mainly composed of reaction products between tetraethylenepentamine and vegetable fatty acids, which acts as surfactants and adhesion enhancers. Additive B consists of fatty amine derivate and, analogously to additive A, acts as adhesion promoter.

With these materials, two WMA binders (coded as PMB+A and PMB+B) were prepared in laboratory according to the producer's specifications, by adding 0.4% (by binder weight) additive to the PMB. Care was taken for the WMA binder preparation. The PMB was pre-heated in a ventilated oven at a fixed temperature of 170 °C for 30 minutes and then placed on a heating plate. The prefixed amount of chemical additive was slowly added to the hot bitumen and, subsequently, the bituminous blend was

mixed for 10 minutes at the fixed temperature (170 °C), by using a portable mixer operating at a stirring rate of 700 rpm.

Table 1. Basic properties of the PMB.

	Standard	Unit	PMB
Penetration [25 °C; 100 g; 5 s]	EN 1426 [24]	0.1 mm	54
Ring and Ball softening point	EN 1427 [25]	°C	71
Elastic recovery [25 °C; 5 cm/min]	EN 13398 [26]	%	89
Dynamic viscosity @ 135 °C	EN 12595 [27]	Pa·s	1.24
RTFOT at 163°C			
Mass loss	EN 12607-1 [16]	%	0.05
Penetration	EN 1426 [24]	0.1 mm	27
Ring and Ball softening point	EN 1427 [25]	°C	77

Table 2. Basic properties of the WMA chemical additives.

	A	B
Physical form at 25 °C	colorless liquid	dark amber liquid
Density at 25 °C (kg/m^3)	1000	970
Viscosity (Pa·s)	0.45 at 15 °C	1.735-3.22 at 10 °C
		0.35-0.645 at 30 °C

Furthermore, in order to compare laboratory and field ageing, two additional WMA binders (coded as PMB_rec and PMB+A+RAP) were studied. Specifically, the PMB_rec was extracted and recovered from a loose WMA mixture produced in an asphalt plant for a field trial section [22]. The WMA mixture was produced by using virgin aggregates, a 25% by aggregate weight of RAP (0/16 mm), the PMB described in Table 1 and the chemical additive A described in Table 2. The RAP was obtained from the milling of bituminous layers containing the same PMB. The recovery of this binder was carried out by means of a rotary evaporator, compliant with EN 12697-3 [28]. Since the RAP directly interacts with the base bitumen, the performance of the PMB_rec was compared with the PMB+A+RAP binder, expressly prepared in laboratory by mixing the base PMB, the additive A and the aged bitumen recovered from RAP (by means of a rotary evaporator) in the same proportions used in the WMA mixture.

3. Experimental program and test procedure

Conventional, rheological and chemical tests were performed in laboratory in order to characterize the un-aged, aged and recovered binders, as described in detail in the experimental program shown in Fig. 1.

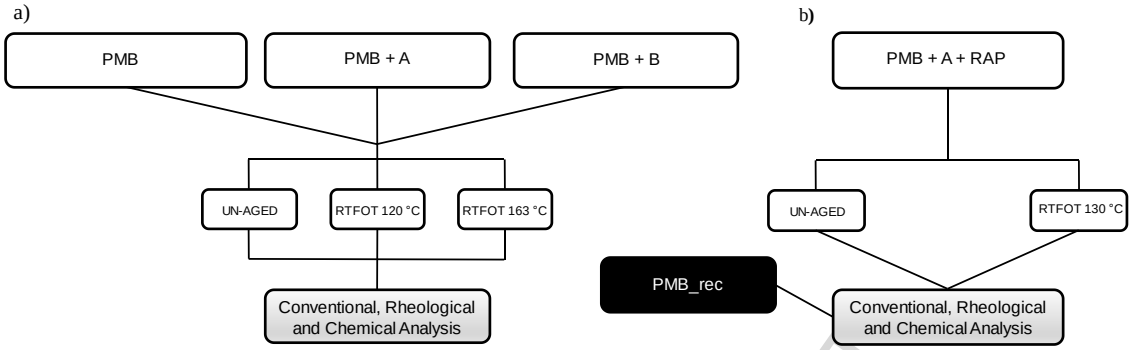


Fig. 1. Experimental program: laboratory (a) and laboratory-field (b) comparison

3.1 Short-term ageing

The RTFOT was performed with an equipment compliant with EN 12607-1 [16].

In this study, different ageing temperatures were adopted depending on the binder investigated. Specifically, 120 °C and 163 °C were considered for binders prepared with and without WMA chemical additives, whereas 130 °C was considered only for PMB+A+RAP (Fig. 1). The ageing temperatures of 120 °C and 130 °C were chosen to represent the operating range of field production of WMA. Specifically, 130 °C was the real temperature adopted to produce the WMA mixture for the field trial section [22].

According to the ageing condition, the code of each binder investigated was combined with the acronym UN for representing the un-aged material or with the numbers 120, 130 or 163 to refer to the ageing temperature.

3.2 Conventional and rheological tests

Penetration and softening point were performed according to EN 1426 [24] and EN 1427 [25], respectively. Viscosity was measured through a Brookfield rotational viscometer compliant with EN 13302 [29], considering five temperatures (105, 120, 135, 150 and 165 °C) and two replicates for each testing condition.

The rheological properties were studied through a dynamic shear rheometer (DSR) by performing Multiple Stress Creep Recovery (MSCR) and frequency sweep tests.

The characterisation of the permanent deformation resistance of all the binders was carried out through the MSCR tests, by using the DSR in the plate–plate geometry with a plate diameter of 25 mm and a gap of 1 mm, in accordance with EN 16659 [30]. Tests were conducted at four temperatures (58, 64, 70 and 76 °C) and two stress levels (0.1 and 3.2 kPa). The test involves 10 creep-recovery cycles with a creep loading time of 1 s, followed by a recovery time (with no loading) of 9 s for each cycle. Specimens were conditioned at the test temperature for 20 minutes before testing. The non-recoverable creep compliance (J_{nr}) was evaluated to assess the resistance to permanent deformations under repeated loading.

The DSR device was also used to perform frequency sweeps in plate-plate configuration. Tests were carried out at temperatures ranging from 0 °C to 80 °C (with a step of 10 °C) and frequencies ranging from 0.1 to 10 Hz. The norm of the complex shear modulus ($|G^*|$) and the phase angle were evaluated

under controlled strain conditions within the linear viscoelastic range of the materials, considering a control strain amplitude of 0.5%. Two replicates were performed for each testing condition, for both MSCR and frequency sweep tests.

3.3 FTIR-ATR and microscopic analysis

The chemical investigation was carried out through microscopic and FTIR-ATR (Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance) analysis.

The morphology of the binders was observed with a fluorescence microscope by using two light sources: ultraviolet (UV) for fluorescence and white light for transmitted structures. Samples were prepared by pouring a drop of hot bitumen on a glass plate and the measurements were performed at room temperature. Since different sample preparation techniques affect the results [31], the procedure adopted has been the same for all the binders investigated.

FTIR-ATR analysis was carried out by placing a very small amount of bitumen directly on an ATR crystal (ZeSe) and measuring the IR reflection from the specimen, with wavenumbers between 400 cm^{-1} and 4000 cm^{-1}. The amounts of aromatic, carbonyl and sulfoxides compounds were assessed by measuring the areas of IR bands at about 1600, 1700 and 1030 cm^{-1}, respectively.

4. Analysis and discussion of the results

In the following sections, the results of conventional, rheological and chemical data are discussed considering the effect of a reduced short-term ageing temperature on the binder behaviour and the effect of WMA chemical additives on the short-term ageing of WMA binders. The latter aspect can be evaluated through a series of ageing indices (AI), defined [32] as follows:

$$AI = \frac{X_{AGED}}{X_{UN-AGED}} \quad (1)$$

where X_{AGED} is the value of the parameter X measured for the aged condition and $X_{UN-AGED}$ is the same parameter measured for the un-aged condition. In this investigation, an ageing index for each parameter (viscosity, permanent deformation, master curve and FTIR-ATR parameters) was introduced.

All the results reported in the following sections are shown as average values of several replicates and are displayed together with the corresponding error bars. It can be observed that, in general, the standard deviations obtained are quite low, except in some isolated cases. Thus, any comment concerning the average values can be considered reliable.

4.1 Conventional tests

For all the binders, the results of the conventional tests were shown in terms of penetration values at 25 °C, softening point temperatures (Fig. 2) and retained penetration (Fig. 3). The retained penetration (RP), which has been introduced for describing the ageing resistance [16], can be calculated by using the following equation:

$$RP\ [\%] = \frac{P_{AGED}}{P_{UN-AGED}} \times 100 \quad (2)$$

where P_{AGED} and $P_{UN\text{-}AGED}$ are the penetration values after and before the RTFOT, respectively. As expressed by Eq. (2), lower retained penetration value implies a higher age-hardening degree.

It is expected that a decrease in the short-term ageing temperature leads to a reduction of the rigidity of the bitumen because of a lower oxidation, with a consistent increase in the penetration value and a decrease in the softening point temperature [18, 33]. This effect is not so evident in Fig. 2.a, where not univocal trends for both penetration and softening point can be observed, especially when additive A is considered. This is probably due to a combined effect of bitumen oxidation and SBS polymer degradation that can soften the aged bitumen and partially compensate the bitumen oxidative hardening [34].

The comparison between laboratory and field ageing (Fig. 2.b) shows that PMB_rec displays a penetration value similar to PMB+A+RAP_130 and a slightly higher softening point temperature.

As far as the effect of additives on binder short-term ageing is concerned, Figure 3 shows that, in parity of RTFOT temperature, the retained penetration of binder with additive is higher than that of the corresponding binder without additive. This result implies that the addition of additive has a significant effect on the characteristics of the selected bitumen, tending to reduce the effect of age-hardening.

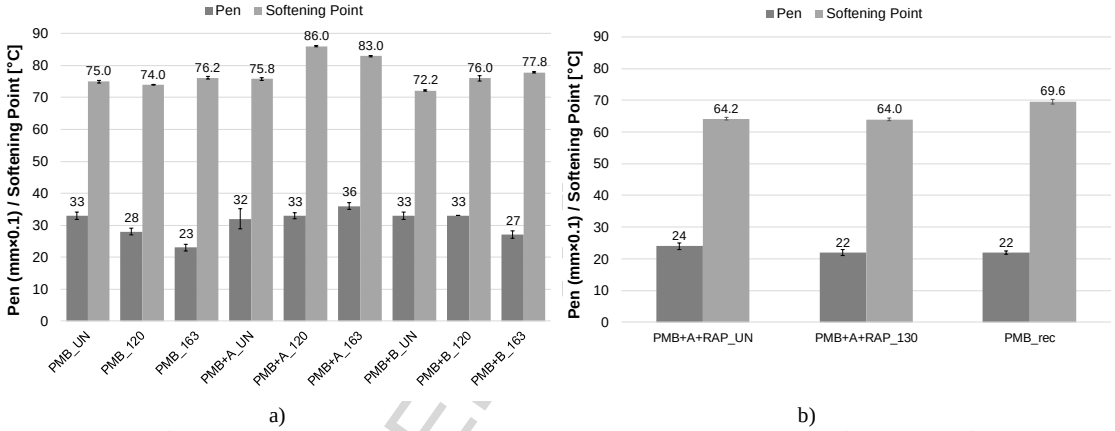


Fig. 2. Results of penetration and Ring & Ball tests: a) PMB with and w/o additives; b) binders for laboratory-field comparison.

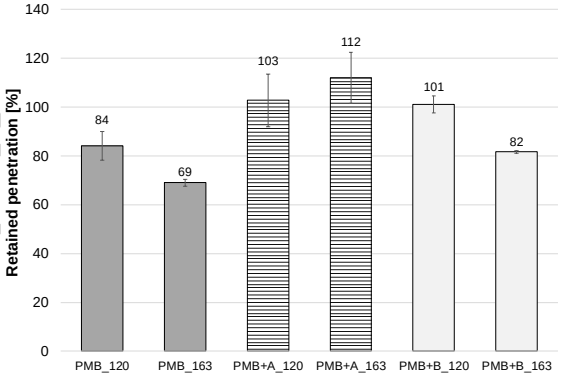


Fig. 3. Retained penetration.

4.2 Viscosity

Fig. 4 presents the dynamic viscosity η of all the binders at the investigated temperatures. As expected, the viscosity decreases with increasing testing temperature and increases with ageing, for all the binders (with and without additives), except for PMB+A that does not show a clear trend (Fig. 4.b). Indeed, the reduction of the RTFOT ageing temperature from 163 °C to 120 °C causes a decrease in viscosity (Fig. 4.a and 4.c).

As far as the comparison between laboratory and field ageing is concerned, Fig. 4.d shows similar viscosity values for both PMB_rec and PMB+A+RAP_130 binders, confirming the reliability of the reduced testing temperature adopted for the laboratory ageing.

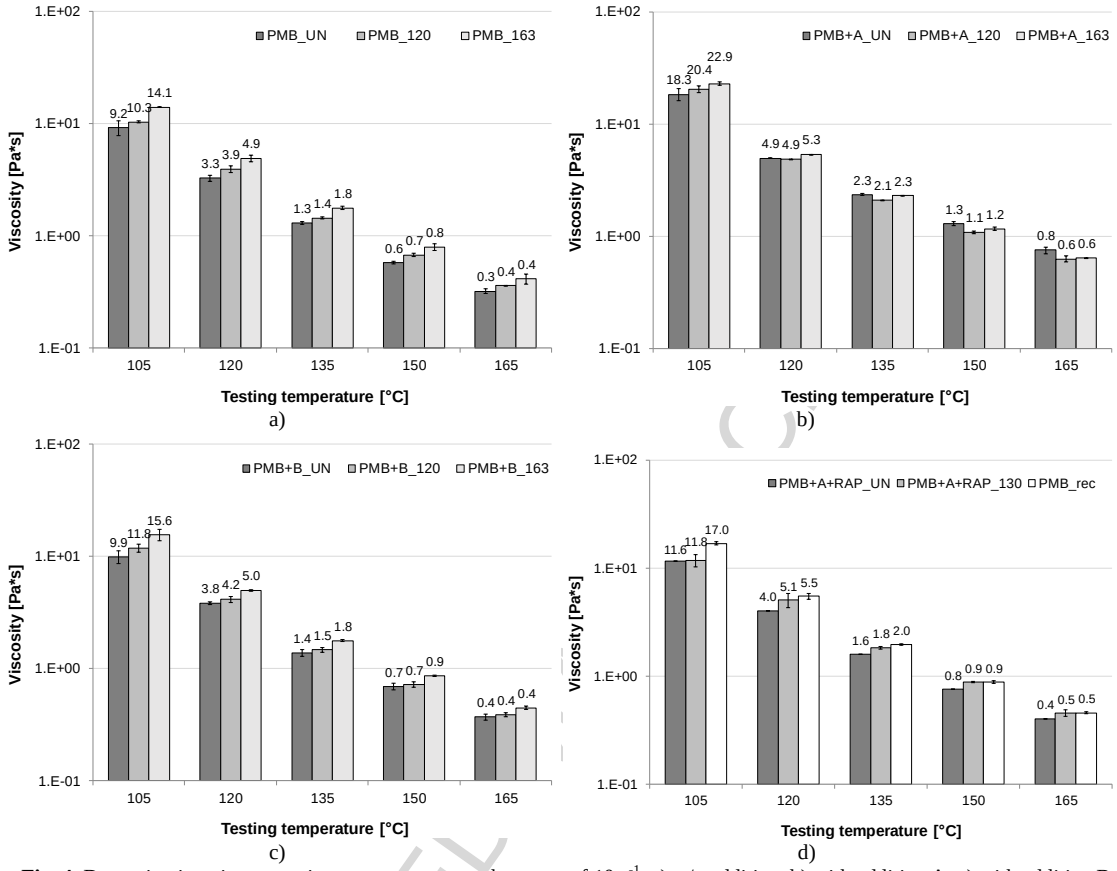


Fig. 4. Dynamic viscosity vs. testing temperature at a shear rate of 10 s^{-1}: a) w/o additive; b) with additive A; c) with additive B; d) laboratory-field comparison.

In order to better understand the effect of the additives on the short-term ageing of the binder, at each test temperature, the ageing index $AI\eta_{ij}$ was calculated as follows:

$$AI\eta_{ij} = \frac{\eta_{ij}}{\eta_{i\_UN}} \quad (3)$$

where η_{ij} is the viscosity of the binder *i* (both with and without additives) after RTFOT performed at the temperature *j* (=120 ºC or 163 ºC) and η_{i_UN} is the viscosity of the same binder before ageing (UN condition), measured at the same test temperature (105, 120, 135, 150 or 165 °C). Higher AIη values imply a higher effect of ageing on viscosity and AIη values less than one represent a reduction of viscosity with ageing.

The AIη_{ij} values are shown in Table 3 for all the binders tested, for each RTFOT ageing temperature and for each testing temperature. The effectiveness of the parameter AIη_{ij} can be preliminary verified comparing RTFOT ageing at 120 and 163 °C in identical conditions (without additive, with additive A and with additive B). As expected, RTFOT ageing at 163 °C always provides higher AIη_{ij} values than RTFOT ageing at 120 °C, confirming that, at higher temperature, a higher ageing effect is induced on the binder.

The effect of the additives on the short-term ageing of the binder can be estimated comparing, at a given RTFOT temperature, the condition without (w/o) and with additive (A or B). Table 3 shows that, in general, the additives tend to reduce the effect of ageing, reducing AIη_{ij} with respect to the condition without additive. When the additive A is considered, this parameter reaches values less than one, suggesting that it could provide a moderate deceleration of the PMB ageing process.

Table 3. AIη_{ij} values for all the binders (with and w/o additives).

Testing	AIη_{ij} for j=120 °C			AIη_{ij} for j=163 °C		
temperature	w/o additive	additive A	additive B	w/o additive	additive A	additive B
105 °C	1.12	1.11	1.19	1.53	1.25	1.57
120 °C	1.21	0.98	1.09	1.51	1.08	1.31
135 °C	1.11	0.90	1.07	1.36	0.98	1.29
150 °C	1.17	0.84	1.04	1.38	0.90	1.24
165 °C	1.13	0.83	1.05	1.29	0.85	1.21

4.3 Multiple Stress Creep Recovery (MSCR)

The MSCR test results were used to calculate the average non-recoverable creep compliance (J_{nr}), in order to assess the resistance of an asphalt binder to permanent deformations under repeated loading. Lower values of J_{nr} indicate higher resistance against permanent deformations. The J_{nr} values at a stress level of 3.2 kPa are shown in Fig. 5 as functions of the testing temperature.

As observed for conventional and viscosity tests, the reduction of the RTFOT ageing temperature from 163 to 120 °C affects MSCR results with an increase in deformation for all the binders investigated but with different behaviours. When additives are not considered (Fig. 5.a), J_{nr} after RTFOT at 120 ºC is very close to the un-aged condition (UN), whereas there is a significant reduction of J_{nr} when the RTFOT ageing temperature reaches 163 ºC. When additives A and B are added (Fig. 5.b and 5.c, respectively), the trend observed for the PMB significantly changes. Indeed, with the additive A, the J_{nr} value of the PMB+A_120 ºC is higher than that of PMB+A_UN (Fig. 5.b) and, when the additive B is considered, this is also obtained at the ageing temperature of 163 °C (Fig. 5.c). This behaviour can be explained considering the effect of WMA additives on ageing, as already done for the viscosity. To this purpose, the parameter AIJ_{ij} can be introduced as follows:

$$AIJ_{ij} = \frac{J_{ij}}{J_{i\_UN}} \quad (4)$$

where J_{ij} is the J_{nr} at a stress level of 3.2 kPa of the binder *i* (both with and without additives) after RTFOT performed at the temperature *j* (=120 ºC or 163 ºC) and J_{i_UN} is the J_{nr} at a stress level of 3.2 kPa of the same binder before ageing (un-aged condition UN), measured at the same test temperature (58, 64, 70 and 76 °C). AI*J* values lower than one means that, after ageing, the binder shows a reduction in the permanent deformations. On the contrary, AI*J* values greater than one means that, after ageing, the binder provides a lower resistance against permanent deformations.

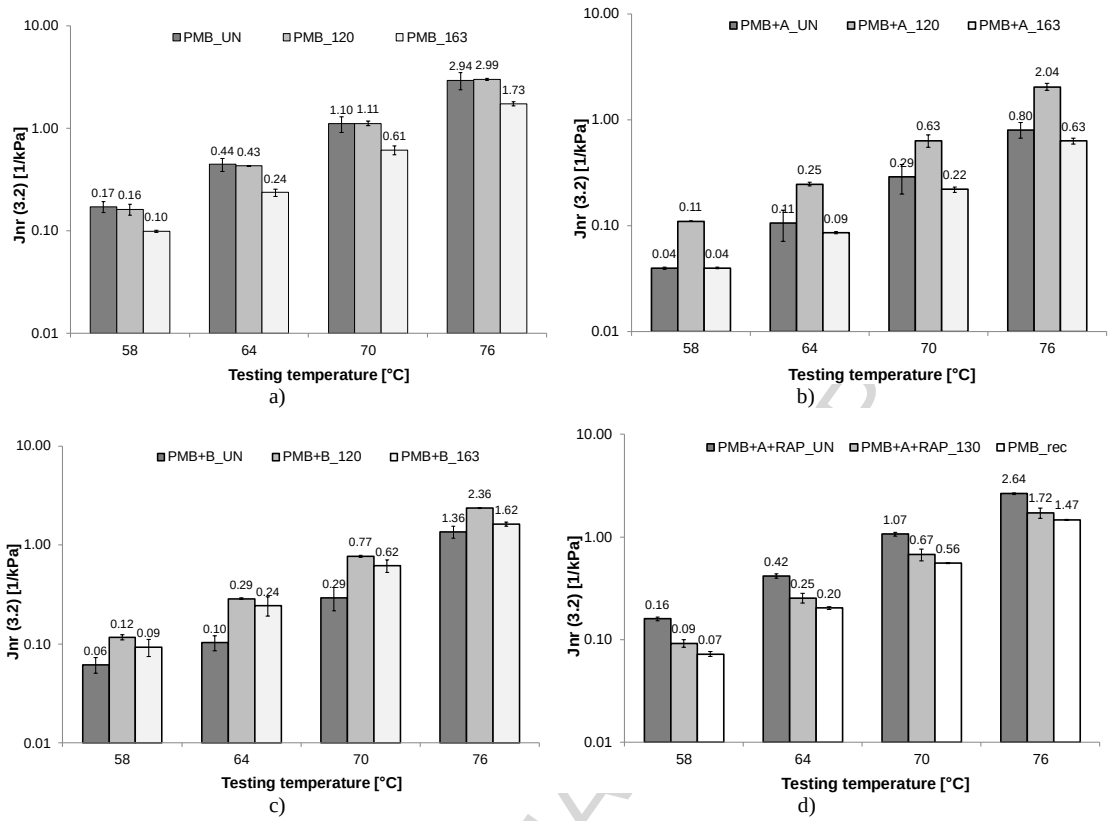


Fig. 5. Non-recoverable creep compliance at a stress level of 3.2 kPa: a) w/o additive; b) with additive A; c) with additive B; d) laboratory-field comparison.

Table 4 shows that both additives, for each short-term ageing temperature, tend to reduce the effect of ageing and thus to reduce the permanent deformation resistance, due to the increase of the AIJ_{ij} values with respect to the condition without additive, contrarily to what happens when the un-aged PMB is considered. In fact, Ferrotti et al. [19] showed that both additive A and additive B provide, with respect to the condition without additive, a higher resistance to permanent deformation when added to the un-aged PMB.

As regards the influence of the RTFOT-ageing temperature, it can be observed that, as expected, the AI*J* values for the PMBs (both with and without additives) decrease when the RTFOT temperature increases as the J_{ij} value decreases (Fig. 5). However, a different trend with short-term ageing temperature can be detected for the two additives. In fact, after ageing (at both 120 and 163 °C), additive B provides an increase in the permanent deformation (AI*J* >1) and thus a reduction in the permanent deformation resistance with respect to the un-aged condition. On the contrary, after ageing at 163 °C, additive A provides increased permanent deformation resistance with respect to the un-aged condition (AI*J* <1), showing that different additives give different contributions.

About laboratory and field comparison (Fig. 5.d), only slight differences can be noticed between PMB_rec and PMB+A+RAP_130 that, in turn, show a lower J_{nr} value with respect to the un-aged condition (PMB+A+RAP_UN). Considering that the last material is the same of Fig. 5.b (PMB+A_UN) with the addition of RAP, the results obtained proves that the presence of the aged binder from RAP

reduces the permanent deformation resistance (as J_{nr} increases) as already shown by Singh et al. [35], even when WMA additives are employed. This is probably due to the damage of the polymer network provided by the addition of RAP.

Table 4. AIJ_{ij} values for all the binders (with and w/o additives).

Test	AIJ_{ij} for j=120 °C			AIJ_{ij} for j=163 °C		
temperature	w/o additive	additive A	additive B	w/o additive	additive A	additive B
58 °C	0.94	2.77	1.89	0.58	1.00	1.51
64 °C	0.97	2.33	2.77	0.53	0.81	2.37
70 °C	1.01	2.20	2.62	0.55	0.76	2.10
76 °C	1.02	2.55	1.73	0.59	0.78	1.20

A further parameter to investigate with the MSCR tests is the percent recovery (*%R*), which provides information on the strain recovery as it considers the reversible strain behaviour of the binders. The *%R* versus the J_{nr} values at a stress level of 3.2 kPa, are plotted in Fig. 6, for all the binders and the ageing conditions studied. Each point represents a different testing condition, taking into account that the symbols denote the ageing (UN, 120 °C, 130 °C), the filling colours denote the MSCR testing temperature (i.e. from a dark colour for 58 °C to a light colour for 76 °C), the dotted lines indicate the regression curves and the continuous line represents the reference MSCR curve [36, 37] that is the borderline between unmodified and elastomeric polymer-modified binders. Specifically, if data points are above the reference MSCR curve, the corresponding binder is characterized by high elasticity (such that exhibited by elastomeric polymers), whereas data points below this curve correspond to materials with poor elasticity.

Fig. 6.a shows that PMB, in all ageing conditions, is characterized by high elasticity (as expected because of the presence of SBS polymers), that becomes more evident when WMA chemical additives are added (Fig. 6.b and 6.c). Specifically, with both additives, the percent recovery increases even at low MSCR testing temperatures and for both the ageing conditions. These results suggest that the recoverable behaviour is influenced by both short-term ageing temperatures and chemical additive type.

The comparison between laboratory and field ageing (Fig. 6.d) shows that PMB_rec displays values similar to PMB+A+RAP_130 and that the ageing process seems to lead to an increase of %R. However, it is interesting to note that the experimental data are below the reference MSCR curve indicating a low recovery, which is an indication of low elasticity. Such a reduction of %R cannot be exclusively due to the contribution of the aged bitumen recovered from RAP but could also be related to traces of solvent used for the extraction of the recovered binder.

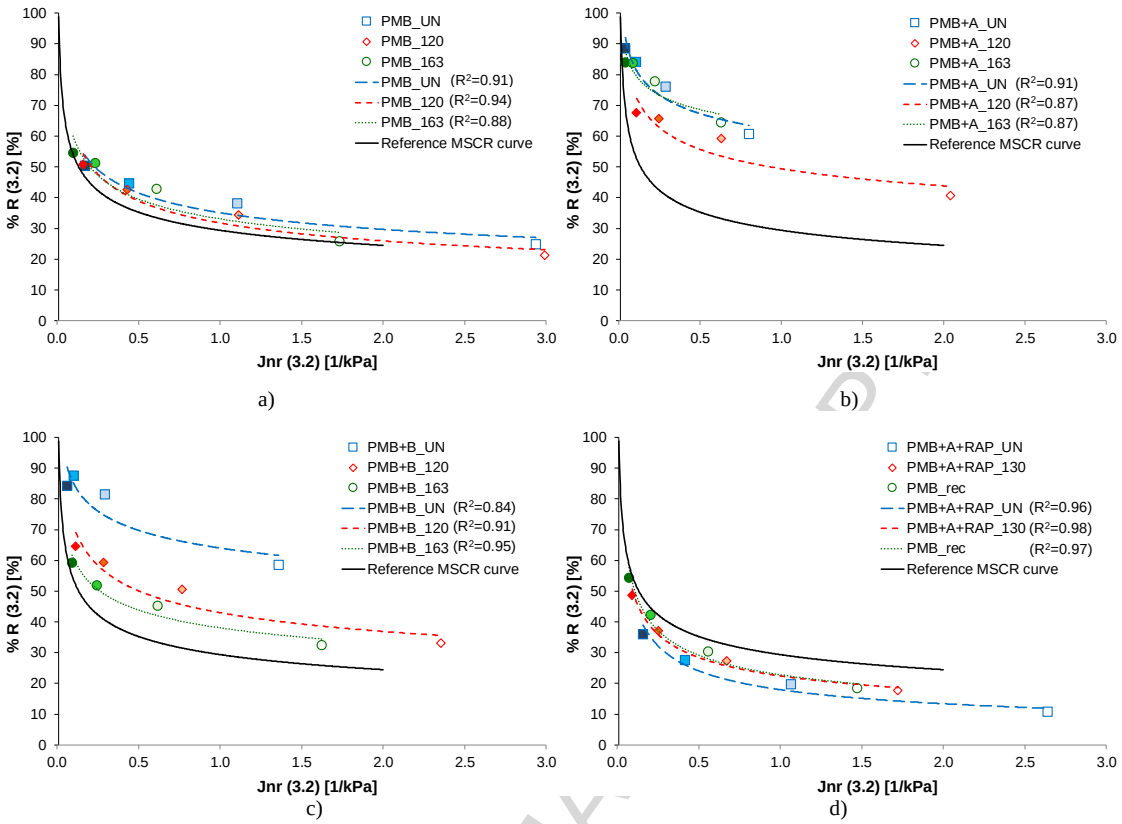


Fig. 6. Percent recovery versus non-recoverable creep compliance at a stress level of 3.2 kPa: a) w/o additive; b) with additive A; c) with additive B; d) laboratory-field comparison.

4.4 Frequency sweep test

The test data of the norm of the complex modulus $|G^*|$ and of the phase angle for all the binders investigated are presented in the Black diagram (Fig. 7 and 8).

Fig. 7 shows that the measured data cannot be fitted with a continuous curve, due to the thermo-rheologically complex behaviour of these materials [38]. This mainly reflects the temperature and the thermal history dependence of PMB morphology which directly affects binder rheology [39, 40]. In the range of temperatures investigated, the effect of ageing on PMB (Fig. 7.a) induces, at low $|G^*|$ values, a slight horizontal translation of the Black diagram curves towards lower phase angles (more elastic response). A similar behaviour is also observed for PMB with both additives (Fig. 7.b and 7.c) at high $|G^*|$ values, whereas they seem to progressively shift towards higher phase angles with an increase in the viscous response, at low complex modulus values. Such an outcome can be attributed to a structural change (rearrangement or degradation) on the polymer networks after RTFOT ageing [41] and/or to a combined effect of SBS polymer degradation and bitumen oxidation [34], as already shown by viscosity tests.

In the case of bituminous blends containing RAP binder, Fig. 8 shows that the Black diagram curves shift towards lower phase angles after ageing when field and laboratory ageing are compared.

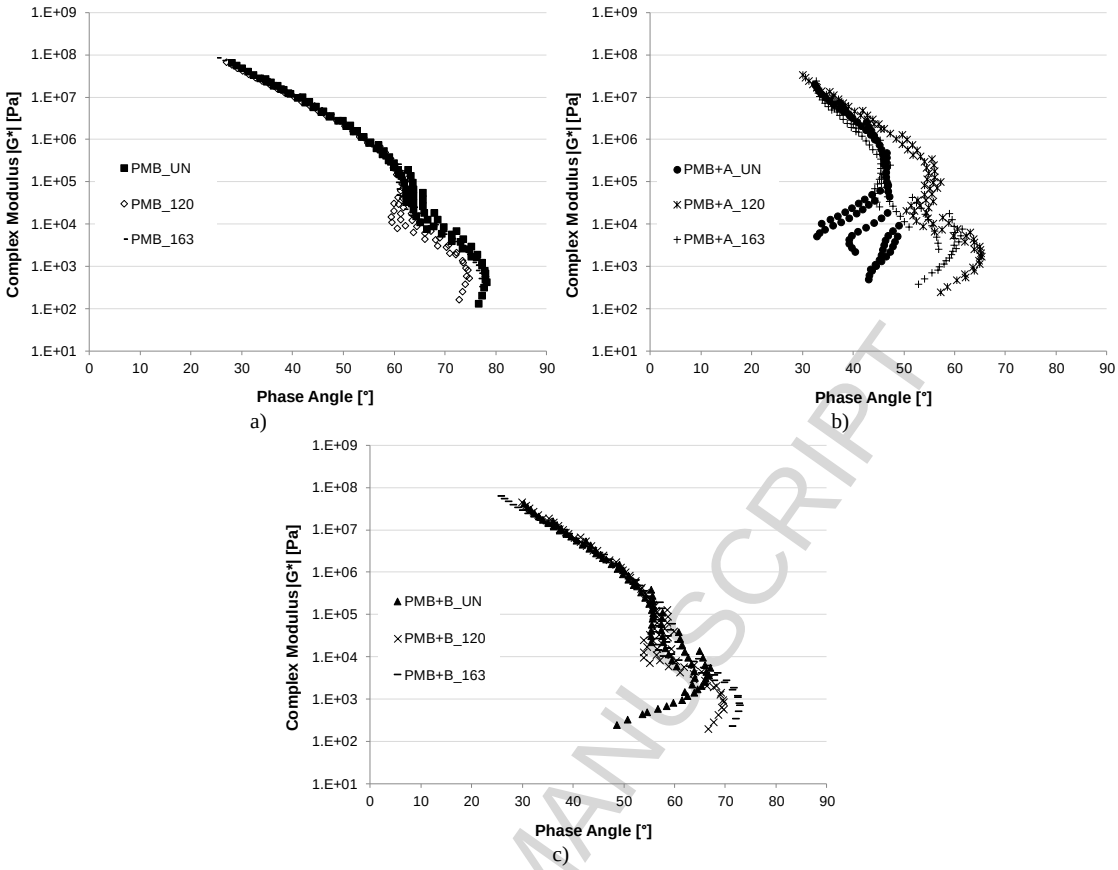


Fig. 7. Black Diagram: a) PMB; b) PMB+A; c) PMB+B.

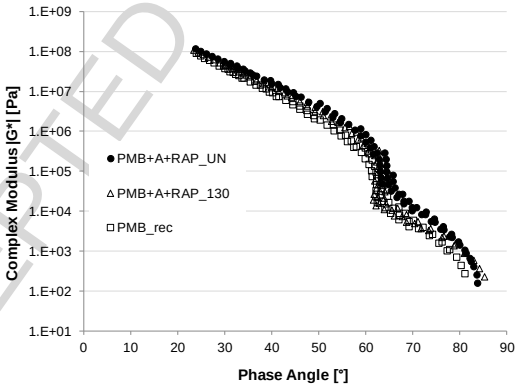


Fig. 8. Black Diagram of the binders for laboratory-field comparison.

According to Olard and Di Benedetto [42], the Partial Time-Temperature Superposition Principle (PTTSP) can be applied to PMB. The master curves were represented through the 1S2P1D (1 Spring, 2 Parabolic elements, 1 Dashpot) model, that is the application of the 2S2P1D model [42] to bitumens. The 2S2P1D is an analogical rheological model resulting from the generalisation of the Huet-Sayegh model [43] and it is now widely used to describe the linear viscoelastic properties of both bituminous binders and mixtures.

According to 2S2P1D model, G^* is expressed, at a given temperature, by the following equation:

$$G^*(\mathrm{i}\omega\tau) = G_0 + \frac{G_g - G_0}{1+\delta(i\omega\tau)^{-k}+(i\omega\tau)^{-h}+(i\omega\beta\tau)^{-1}} \quad (5)$$

where:

- ω is the pulsation, equal to $2\pi f$ with f the load frequency;
- i is the imaginary unit;
- G_0 and G_g are, respectively, the static ($\omega \to 0$) and the glassy ($\omega \to \infty$) modulus;
- k and h are dimensionless parameters defined such that $0<k<h<1$;
- δ is a dimensionless parameter;
- β is a dimensionless parameter related to the Newtonian viscosity η of the dashpot and is defined by Eq. 6:

$$\eta = (G_g - G_0)\beta\tau \quad (6)$$

- τ is the characteristic time (function of temperature), defined by Eq. (7):

$$\tau(T) = a(T)\tau_0 \quad (7)$$

where $a(T)$ are the shift factors at the testing temperature T and τ_0 is the characteristic time at the reference temperature T_{ref}. The shift factors $a(T)$ were determined through the Williams-Landel-Ferry (WLF) law [44], as follows:

$$\log a(T) = \frac{-C_1(T-T_{ref})}{(C_2+T-T_{ref})} \quad (8)$$

where C_1 and C_2 are constants determined empirically.

According to Eq. (5) and Eq. (8), nine parameters (G_g, G_0, k, h, δ, τ, β, C_1 and C_2) are needed to calibrate the model. However, to entirely characterize a bitumen, only seven parameters are required because G_0 can be assumed equal to 0 and G_g equal to 1 GPa, as suggested by Yusoff et al. [45]. The other parameters (k, h, δ, τ, β, C_1 and C_2) are iteratively determined to achieve the best fit between the model and the measured data by minimising the sum of the square of the differences between the experimental values of the complex modulus and the model.

Table 5, where the values of these parameters are depicted for all the binders investigated, shows that k and h are not affected by the ageing process, remaining substantially unaltered before and after ageing, whereas δ, τ and β increase as the ageing temperature increases, according to Perez-Martinez et al. [46] findings. Specifically, the trend of the parameter β, linked to the viscosity of the dashpot of the model through Eq. (6), confirms the results obtained for the binder viscosity (Fig. 4), according to which higher viscosity values imply higher effect of ageing.

The effect of ageing can be also observed by considering the WLF constants C_1 and C_2, which should increase with binder ageing, as proved by several authors [47, 48]. Table 5, where C_1 and C_2 of the aged binders are higher than those of the un-aged ones, confirms this trend.

Moreover, according to Yusoff et al. [45], the parameter δ can be considered as an ageing indicator, such that when δ increases the material becomes harder. Thus, the effect of the WMA additives on the short-term ageing can be estimated through the parameter $AI\delta_{ij}$, introduced as follows:

$$AI\delta_{ij} = \frac{\delta_{ij}}{\delta_{i\_UN}} \quad (9)$$

where δ_{ij} is the δ of the binder i (both with and w/o additives) after RTFOT performed at the temperature j (=120 ºC or 163 ºC) and δ_{i_UN} is the δ of the same binder before ageing (UN condition). Higher AIδ values imply a higher effect of ageing.

Table 6 shows that the addition of both additives causes a reduction of AIδ values, for both the RTFOT temperatures, demonstrating a reduced effect of ageing. These results hint in the same direction as previous findings obtained for viscosity and MSCR tests.

The master curves of PMB at T_{ref} = 10 °C are shown in Fig. 9 and 10. The solid curves correspond to the model and the dots to the experimental measurements. The rheological properties of the binders, as predicted by the 1S2P1D model, correctly fits the experimental data, except at very low frequencies. As expected, the effect of ageing leads to an increase in the stiffness, particularly at low reduced frequencies (high temperatures) for all the binders investigated. However, a different behaviour can be detected for PMB+A and PMB+B when different ageing temperatures are considered. For PMB+A, a negligible difference between the master curves at different stages of ageing (UN, 120 °C and 163 °C) can be detected, suggesting that the effect of ageing can be reduced by the presence of this additive, whereas PMB+B shows a behaviour very similar to PMB.

Nevertheless, the master curves of $|G^*|$ for PMBs aged with RTFOT at 120 °C are quite close to those determined for the corresponding un-aged bitumens at all reduced frequency ranges, confirming that lower RTFOT temperatures (i.e. 120 °C) moderate the ageing process.

Finally, the master curves of the laboratory-filed comparison (Fig. 10) indicate that the ageing procedure followed in laboratory is appropriate to simulate the field ageing condition as the master curves of PMB+A+RAP_130 and PMB_rec almost overlap.

Table 5. Model parameters for all binders investigated and coefficient of determination R^2.

Binder	k	h	δ	τ_0 (10°C)	β	C_1	C_2	R^2
PMB_UN	0.27	0.60	7.59	2.1E-04	440	20	167	0.99
PMB_120	0.27	0.60	8.00	2.6E-04	3162	25	200	0.99
PMB_163	0.27	0.59	9.51	8.5E-04	5012	27	194	0.99
PMB+A_UN	0.27	0.52	7.65	5.0E-06	630957	19	122	0.99
PMB+A_120	0.27	0.52	8.00	2.1E-05	707946	25	190	0.99
PMB+A_163	0.27	0.50	**7.03**	**7.9E-06**	933254	27	203	0.99
PMB+B_UN	0.27	0.60	9.17	7.6E-05	6310	26	208	0.99
PMB+B_120	0.27	0.60	9.30	1.1E-04	7079	26	211	0.99
PMB+B_163	0.27	0.56	9.57	2.9E-04	12589	30	220	0.99
PMB+A+RAP_UN	0.27	0.60	7.70	1.3E-03	370	20	140	0.99
PMB+A+RAP_130	0.27	0.60	8.80	1.7E-03	1260	25	180	0.99
PMB_rec	0.27	0.60	9.00	1.4E-03	1260	27	210	0.99

Table 6. AIδ_{ij} values for all the binders (with and w/o additives).

AIδ_{ij} for j=120 °C			AIδ_{ij} for j=163 °C		
w/o additive	additive A	additive B	w/o additive	additive A	additive B
1.05	1.05	1.01	1.25	0.92	1.04

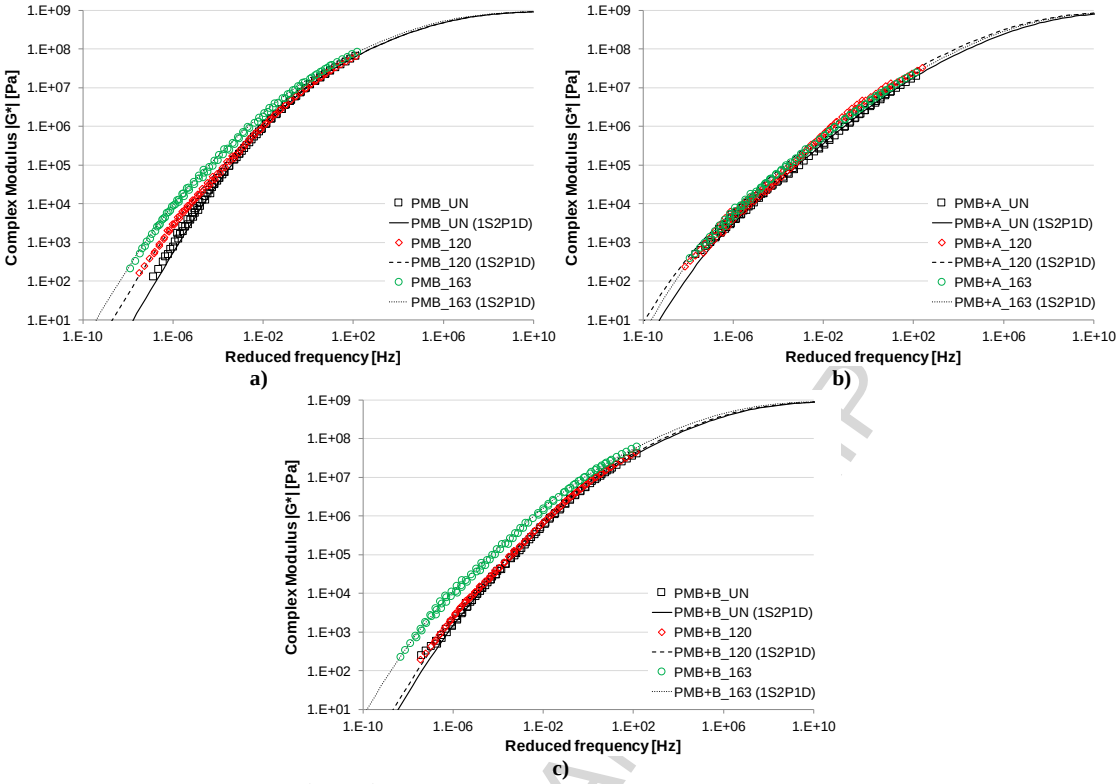


Fig. 9. Master curves of |G*| of PMB (T_{ref} =10 °C): a) w/o additive; b) with additive A; c) with additive B.

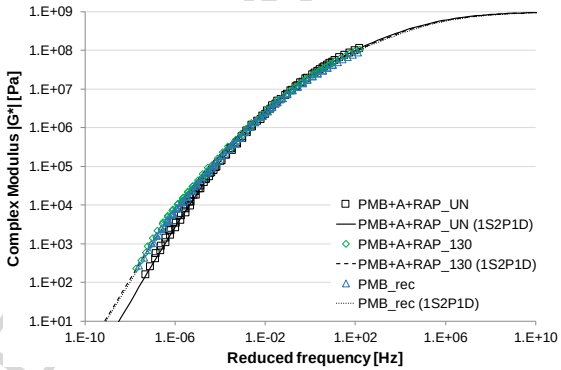


Fig. 10. Master curves of |G*| of laboratory-field comparison (T_{ref} =10 °C).

4.5 Microscopic analysis

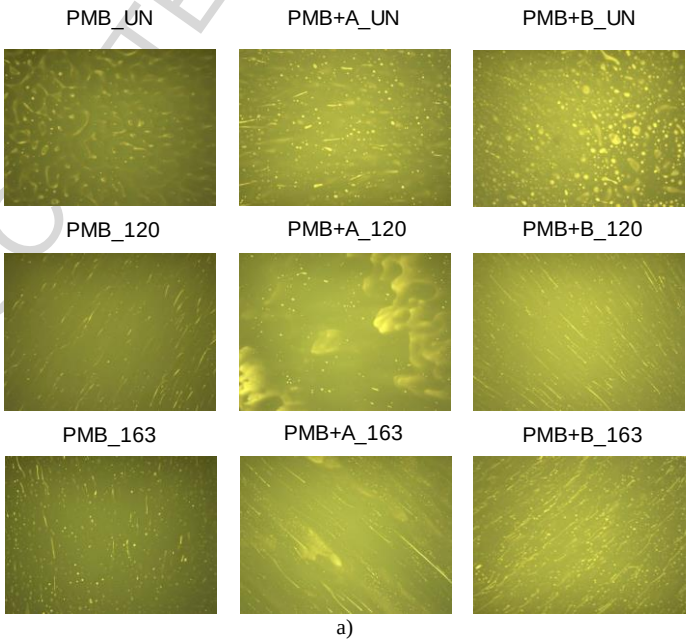
In order to better understand the effect of ageing on the phase structure of the binders, a microscopic analysis was also carried out as structural and rheological properties are strictly related [31]. This is particularly important for PMBs because these binders require the study of the effects of both polymer degradation and bitumen oxidation. Images of the PMBs are depicted in Fig. 11, where two lights sources (i.e. ultraviolet for fluorescence in Fig. 11.a and white light for transmitted structures in Fig. 11.b) and the same magnification are used.

The images display the typical bi-phase heterogeneous system of PMBs [39, 40]. With the UV light source (Fig. 11.a), the polymer-rich phase and the bitumen-rich phases appear light and dark, respectively. With the white light sources (Fig. 11.b), the polymer-rich phase appears red and the bitumen-rich phases appears dark. Before RTFOT (UN condition), polymer and bitumen phases are

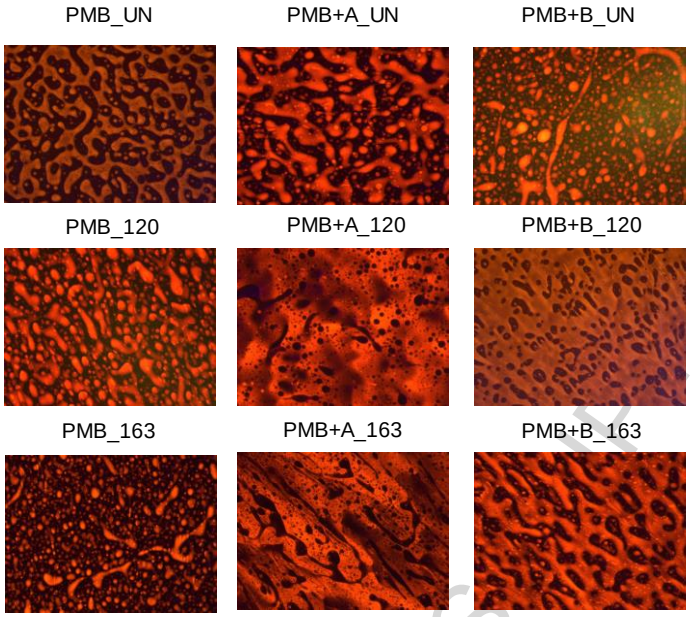
clearly distinguishable in this heterogeneous system whereas, after RTFOT, finer dispersion of the polymers can be seen in the studied binders. Hence, the ageing process seems to lead to a breakdown in the polymer structures, causing the decrease of the effectiveness of the polymer-rich phase network. Since in a PMB both bitumen and polymers are affected by ageing and since the polymer morphology may significantly influence the rheological properties of the binder, the change in rheology of PMBs previously detected may be attributed to the bitumen oxidation and polymer degradation, observed with the microscopic analysis.

It is interesting to notice that the presence of the WMA chemical additive likely alters the structural interactions (or compatibility) of bitumen and polymer. This is more evident for PMB+A, whose images (Fig. 11.b) show a continuous polymer phase with a dispersed bitumen phase, even when aged conditions are considered. The addition of the chemical additive A is probably the explanation of such morphology that inevitably affects the rheological characteristics of these modified binders, as observed in Fig. 7 and already shown by Ferrotti et al. [19]. The apparent contradiction with the results shown in Table 3 (related to the viscosity tests), where the additive B seems to give a larger effect than additive A, can be explained considering that microscopic analysis is performed at room temperature (that is around 20 °C) whereas viscosity tests were carried out at higher temperature (from 105 °C to 165 °C). In fact, it has already been shown [19] that the influence of the chemical additives on the binder performance is strongly related to the testing temperature and to the interaction between bitumen, polymer and additive.

The images depicted in Fig. 12, related to laboratory and field comparison, show slight differences between PMB+A+RAP_130 and PMB_rec, as already remarked in Fig. 10. However, it is important to appreciate that these differences may also be associated to the laboratory ageing procedure as well as to the binder recovery method [49].

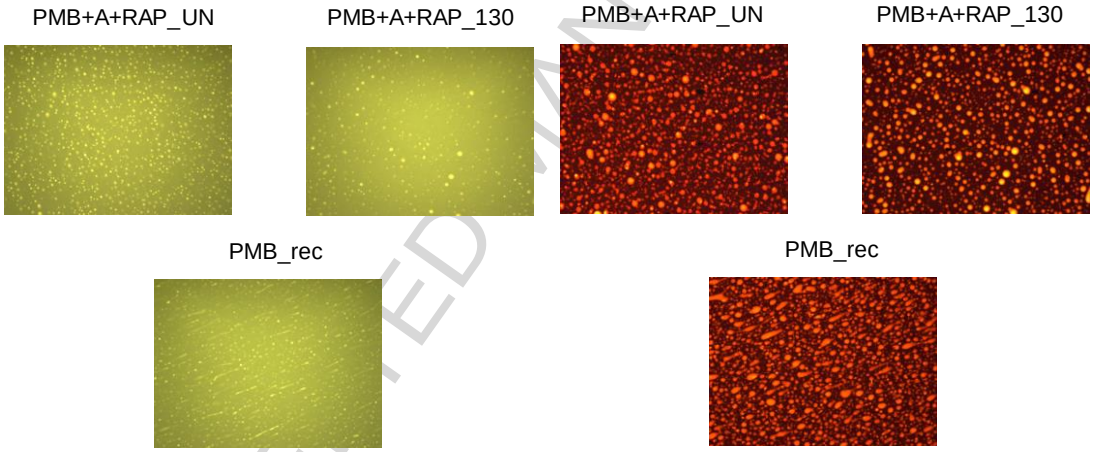


a)



b)

Fig. 11. Photographs of drops of PMB with and w/o additives (magnification 100x): a) UV fluorescence; b) White light for transmitted structures.



a) b)

Fig. 12. Photographs of drops of laboratory-field comparison (magnification 100x): a) UV fluorescence; b) White light for transmitted structures.

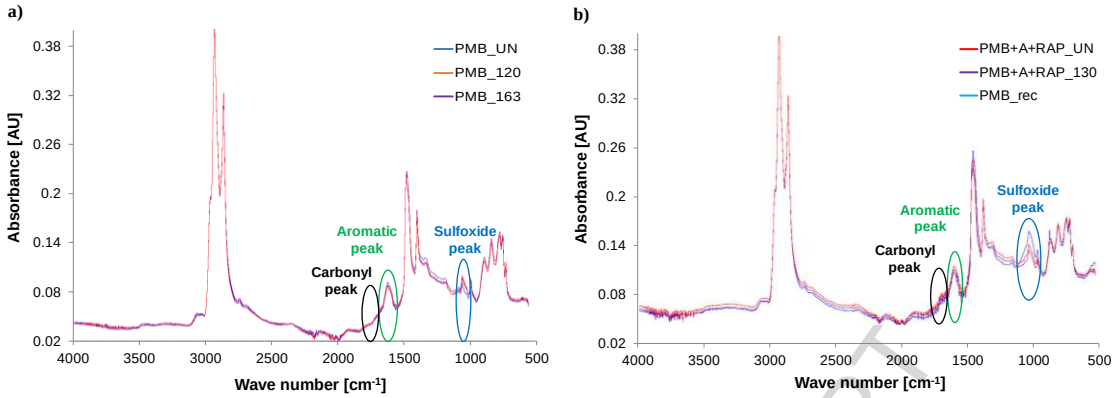
4.6 FTIR-ATR

Examples of infrared spectrograms at different stages of ageing are shown in Fig. 13. By analysing specific functional groups before and after ageing, it is possible to assess the oxidative ageing effect. The changes of aromatic C=C (at 1600 cm^{-1}), carbonyl C=O (at 1700 cm^{-1}) and sulfoxide S=O (at 1030 cm^{-1}) groups were analysed through three structural indices (I_{ARO}, I_{CO}, I_{SO}), determined as follows:

$$I_{ARO} = \frac{Aromatic\ band\ area\ (1600\ cm^{-1})}{\text{Spectra bands area } (\sum 1375\ and\ 1460\ cm^{-1})} \quad (10)$$

$$I_{CO} = \frac{Carbonyl\ band\ area\ (1700\ cm^{-1})}{\text{Spectra bands area } (\sum 1375\ and\ 1460\ cm^{-1})} \quad (11)$$

$$I_{SO} = \frac{Sulfoxide\ band\ area\ (1030\ cm^{-1})}{\text{Spectra bands area } (\sum 1375\ and\ 1460\ cm^{-1})} \quad (12)$$



a) b)

Fig. 13. FTIR-ATR spectrograms at different stages of ageing: a) PMB; b) laboratory-field comparison.

The index I_{ARO} indicates the ageing due to aromatic (C=C) group at 1600 cm^{-1}, I_{CO} the ageing due to carbonyl compounds (C=O) at 1700 cm^{-1} and I_{SO} the ageing due to sulfoxide compounds (S=O) at 1030 cm^{-1}. Normally the parameter I_{ARO} does not provide a clear trend with ageing, so that it cannot be used as ageing indicator. On the contrary, it has been observed that an increase of I_{CO} and I_{SO} values implies more oxidation [50]. It is worth mentioning that these parameters are largely dependent on chemistry of the bitumen. Table 7, where these indices are given for all the binders tested, shows that I_{CO} remains equal to zero, suggesting that short-term ageing simulation does not lead to a visible formation of carbonyl compounds. Meanwhile, as expected, I_{SO} generally increase after RTFOT for all the binders investigated, with an increase in oxidation (higher I_{SO} values) when the RTFOT temperature increases from 120 °C to 163 °C, except for PMB+A_163 (in bold in Table 7). Therefore, the index I_{SO} can be properly used to chemically detect the ageing process of the binders studied.

In order to better observe the effect of ageing, the ageing index AI_{SO} was calculated as follows:

$$AI_{SOij} = \frac{I_{SOij}}{I_{SOi\_UN}} \quad (13)$$

where I_{SOij} is the I_{SO} value of the binder *i* (both with and w/o additives) after RTFOT performed at the temperature *j* (=120 ºC or 163 ºC) and I_{SOi_UN} is the I_{SO} value of the same binder before ageing (UN condition). Lower AI_{SO} values imply a lower effect of ageing. In this sense, Table 7 shows that the binders with the WMA additives display, in general, a lower tendency to ageing compared to the binders without the addition of additives. The observation is in agreement with what was reported by Edwards et al. [32].

Data concerning the laboratory and field comparison show that the carbonyl compounds are, in this case, greater than zero, differently from the binders prepared in laboratory without RAP. This different behaviour, as detectable in other studies [34, 51], could be due to the presence of the aged bitumen recovered from RAP, which contains the carbonyl compounds. The laboratory aged material (PMB+A+RAP_130) provides higher I_{CO} and I_{SO} values than the un-aged one (PMB+A+RAP_UN), whereas the binder recovered from the field trial (PMB_rec) provides lower I_{CO} and higher I_{SO} values than the laboratory aged material (PMB+A+RAP_130), in agreement with Lu et al. [52] findings. Nevertheless, this chemical discrepancy between laboratory (PMB+A+RAP_130) and field aged

(PMB_rec) materials could also be attributed to the binder recovery method used for the extraction of PMB_rec [49], contrarily to what happens to the rheological properties (Fig. 5d, 6d, 8 and 10), which demonstrate that the laboratory procedure simulates the field ageing conditions reasonably well.

Table 7. I_{ARO}, I_{CO}, I_{SO} and Ageing Index (AI_{SO}) of all binders investigated.

Binder	I_{ARO}	I_{CO}	I_{SO}	AI_{SO}
PMB_UN	0.312	0.000	0.051	-
PMB_120	0.332	0.000	0.074	1.44
PMB_163	0.322	0.000	0.081	1.57
PMB+A_UN	0.389	0.000	0.055	-
PMB+A_120	0.368	0.000	0.062	1.13
PMB+A_163	0.403	0.000	**0.049**	0.89
PMB+B_UN	0.304	0.000	0.053	-
PMB+B_120	0.368	0.000	0.057	1.07
PMB+B_163	0.371	0.000	0.061	1.15
PMB+A+RAP_UN	0.267	0.024	0.155	-
PMB+A+RAP_130	0.282	0.040	0.182	1.17
PMB_rec	0.257	0.014	0.275	-

5. Conclusions

This paper focuses on the suitability of the RTFOT method to simulate the binder ageing that takes place during the production and compaction of WMAs. A comprehensive laboratory experimental program, considering one SBS polymer modified bitumen and two chemical additives, is aimed at investigating the effects of temperature and chemical additives on the short-term ageing of asphalt binders.

The chemical additives investigated show the potential to positively affect the short-term ageing as the PMB binder suffers less ageing after being added with the additives, as demonstrated by the ageing indices calculated for both the rheological and the chemical parameters investigated. This finding could result in a potential increase of the resistance to fatigue and thermal cracking of the pavement but could also have a negative impact in terms of resistance to permanent deformation, as shown by the non-recoverable creep compliance (J_{nr}). In fact, after RTFOT, J_{nr} generally increases in the presence of the chemical additives, even if different behaviours are provided by the different chemical additives. The chemical additive type, together with the short-term ageing temperature, also affects the recoverable behaviour of the binders investigated.

The microscopic analysis indicates an apparent change in the binder morphology after RTFOT, especially when additives are added. This is also reflected in a change in the binder rheology.

In general, lower RTFOT temperatures moderate the ageing process of PMBs as compared to the RTFOT at 163 °C. It appears that the standardized RTFOT ageing protocol with a temperature of 163 °C does not truly represent the ageing that takes place during the production and compaction phases of WMAs. Further investigations are needed in order to define a proper RTFOT temperature for the simulation of the short-term ageing of WMA binders. In this paper, a comparison between laboratory

aged and field aged samples seems to indicate that the RTFOT performed at reduced temperature can properly replicate the ageing in the field when the temperature is the same as for WMA production. However, this important finding needs to be further verified by other field comparisons.

Conflict of interest

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

Data availability

The raw and processed data required to reproduce these findings cannot be shared at this time as the data still form part of an ongoing study.

References

[1] Rubio, M. C., Martinez, G., Baena, L., & Moreno, F. (2012). Warm mix asphalt: an overview. Journal of Cleaner Production, 24, 76–84. https://doi.org/10.1016/j.jclepro.2011.11.053

[2] D'Angelo, J., Harm, E., Bartoszek, J., Baumgardner, G., & Corrigan, M., et al. (2008). Warm Mix Asphalt: European Practice. Federal Highway Administration, Report FHWA-PL-08-007, Alexandria, USA.

[3] Capitão, S. D., Picado-Santos, L. G., & Martinho, F. (2012). Pavement engineering materials: Review on the use of warm-mix asphalt. Construction and Building Materials, 36, 1016-1024. https://doi.org/10.1016/j.conbuildmat.2012.06.038

[4] Almeida-Costa, A., & Benta, A. (2016). Economic and environmental impact study of warm mix asphalt compared to hot mix asphalt. Journal of Cleaner Production, 112, 2308-2317. http://dx.doi.org/10.1016/j.jclepro.2015.10.077

[5] European Asphalt Pavement Association (EAPA) (2014). Position Paper on the Use of Warm Mix Asphalt.

[6] Zaumanis, M., Poulikakos, L. D., & Partl, M. N. (2018). Performance-based design of asphalt mixtures and review of key parameters. Materials and Design, 141, 185-201. https://doi.org/10.1016/j.matdes.2017.12.035

[7] Xu, S., Xiao, F., Amirkhanian, S., & Singh, D. (2017). Moisture characteristics of mixtures with warm mix asphalt technologies-A review. Construction and Building Materials, 142,148-161. https://doi.org/10.1016/j.conbuildmat.2017.03.069

[8] Button, J., Estakhri, C., & Wimsatt, A. (2007). A synthesis of warm-mix asphalt. Report FHWA/TX-07/0-5597-1. Texas: Texas Transportation Institute.

[9] Bonaquist, R. (2011). Mix design practices for warm mix asphalt. NCHRP Report 691. Transportation Research Board, Washington D.C.

[10] Kheradmand, B., Muniandy, R., Hua, L. T., Yunus, R. B., & Solouki, A. (2014). An overview of the emerging warm mix asphalt technology. International Journal of Pavement Engineering, 15(1), 79-94. https://doi:10.1080/10298436.2013.839791

[11] Jamshidi, A., Hamzah, M. O., Kurumisawa, K., Nawa, T., & Samali, B. (2016). Evaluation of sustainable technologies that upgrade the binder performance grade in asphalt pavement construction. Materials and Design, 95, 9-20. http://doi.org/10.1016/j.matdes.2016.01.065

[12] Pereira, R., Almeida-Costa, A., Duarte, C., & Benta, A. (2018). Warm mix asphalt: Chemical additives' effects on bitumen properties and limestone aggregates mixture compactibility. International Journal of Pavement Research and Technology, 11, 285-299. https://doi.org/10.1016/j.ijprt.2017.10.005

[13] Morea, F., Marcozzi, R., & Castaño, G. (2012). Rheological properties of asphalt binders with chemical tensoactive additives used in Warm Mix Asphalts (WMAs). Construction and Building Materials, 29, 135-141. https://doi.org/10.1016/j.conbuildmat.2011.10.010

[14] Lu, X., & Isacsson, U. (2002). Effect of ageing on bitumen chemistry and rheology. Construction and Building Materials, 16(1), 15-22. https://doi.org/10.1016/S0950-0618(01)00033-2

[15] Lu, X., & Isacsson, U. (2000). Artificial ageing of polymer modified bitumen. Journal of applied polymer science, 76, 1811-1824. https://doi.org/10.1002/(SICI)1097-4628(20000620)76:12<1811::AID-APP12>3.0.CO;2-1

[16] EN 12607-1 (2014). European Standards for bitumen and bituminous binders - Determination of the resistance to hardening under the influence of heat and air - Part 1: RTFOT method.

[17] Banerjee, A., de Fortier Smit, A., & Prozzi, J. A. (2012). The effect of long-term ageing on the rheology of warm mix asphalt binders. Fuel, 97, 603–611. https://doi.org/10.1016/j.fuel.2012.01.072

[18] Hofko, B., Cannone Falchetto, A., Grenfell, J., Huber, L., Lu, X., Porot, L., Poulikakos L. D., & You, Z, (2017). Effect of short-term ageing temperature on bitumen properties. Road Materials and Pavement Design, 18(sup2), 108-117. https://doi.org/10.1080/14680629.2017.1304268

[19] Ferrotti, G., Ragni, D., Lu, X., & Canestrari, F. (2017). Effect of warm mix asphalt chemical additives on the mechanical performance of asphalt binders. Materials and Structures, 50, 226. https://doi.org/10.1617/s11527-017-1096-5

[20] Dondi, G., Mazzotta, F., Simone, A., Vignali, V., Sangiorgi, C., & Lantieri, C. (2016). Evaluation of different short-term ageing procedures with neat, warm and modified binders. Construction and Building Material 106, 282-289. https://doi.org/10.1016/j.conbuildmat.2015.12.122

[21] Frigio, F., Raschia, S., Steiner, D., Hofko, B., & Canestrari F. (2016). Ageing effects on recycled WMA porous asphalt mixtures. Construction and Building Material, 123, 712-718. https://doi.org/10.1016/j.conbuildmat.2016.07.063

[22] Stimilli, A. Frigio, F., Canestrari, F., & Sciolette, S. (2017). In-plant production of warm recycled mixtures produced with SBS modified bitumen: a case study. Proceedings of the AIIT International Congress on Transport Infrastructure and Systems, Rome, Italy.

[23] Diab, A., Sangiorgi, C., Ghabchi, R., Zaman, M., & Wahaballa, A. M. (2016). Warm Mix Asphalt (WMA) technologies: Benefits and drawbacks-a literature review. Proceedings of the 4th Chinese-European Workshop on Functional Pavement Design (CEW), Delft, Netherland.

[24] EN 1426 (2015). European Standards for bitumen and bituminous binders - Determination of needle penetration.

[25] EN 1427 (2015). European Standards for bitumen and bituminous binders - Determination of the softening point - Ring and Ball method.

[26] EN 13398 (2010). European Standards for bitumen and bituminous binders - Determination of the elastic recovery of modified bitumen.

[27] EN 12595 (2015). European Standards for bitumen and bituminous binders - Determination of kinematic viscosity.

[28] EN 12697-3 (2013). European Standards for bituminous mixtures - Test methods for hot mix asphalt - Part 3: Bitumen recovery: Rotary evaporator.

[29] EN 13302 (2010). European Standards for bitumen and bituminous binders - Determination of dynamic viscosity of bituminous binder using a rotating spindle apparatus.

[30] EN 16659 (2016). European Standards for bitumen and bituminous binders - Multiple Stress Creep and Recovery Test (MSCRT).

[31] Soenen, H., Lu, X., & Redelius, P. (2008). The morphology of bitumen-SBS blends by UV microscopy: an evaluation of preparation methods. Road Materials and Pavement Design, 9(1), 97-110. https://www.tandfonline.com/doi/abs/10.1080/14680629.2008.9690109#metrics-content

[32] Edwards, Y., Tasdemir, Y., & Isacsson, U. (2005). Influence of commercial waxes on bitumen ageing properties. Energy & Fuels, 19 (6), 2519-2525. https://doi.org/10.1021/ef050166r

[33] Miró, R., Martìnez, A. H., Moreno-Navarro, F., & del Carmen Rubio-Gámez, M. (2015). Effect of ageing and temperature on the fatigue behaviour of bitumens. Materials and Design, 86, 129-137. http://dx.doi.org/10.1016/j.matdes.2015.07.076

[34] Stimilli, A., Ferrotti, G., Conti, C., Tosi, G., & Canestrari, F. (2014). Chemical and rheological analysis of modified bitumens blended with ‘‘artificial reclaimed bitumen”. Construction and Building Materials, 63, 1-10. https://doi.org/10.1016/j.conbuildmat.2014.03.047

[35] Singh, D., & Sawant, D. (2016). Understanding effects of RAP on rheological performance and chemical composition of SBS modified binder using series of laboratory tests. International Journal of Pavement Research and Technology, 9, 178-189. http://doi.org/10.1016/j.ijprt.2016.06.002

[36] AASHTO TP 70 (2013). Standard Method of Test for Multiple Stress Creep Recovery (MSCR) Test of Asphalt Binder Using a Dynamic Shear Rheometer (DSR).

[37] Hossain, Z., Ghosh, D., Zaman, M., & Hobson, K. (2016). Use of the multiple stress creep recovery (MSCR) test method to characterize polymer-modified asphalt binders. Journal of Testing and Evaluation, 44, 507-520. http://dx.doi:10.1520/JTE20140061

[38] Airey, G. (2002). Use of black diagrams to identify inconsistencies in rheological data. Road Materials and Pavement Design, 3(4), 403-424. http://doi:10.1080/14680629.2002.9689933

[39] Zhu, J., Lu, X., Balieu, R., & Kringos, N. (2016). Modelling and numerical simulation of phase separation in polymer modified bitumen by phase-field method. Materials and Design, 107, 322-332. http://dx.doi.org/10.1016/j.matdes.2016.06.041

[40] Zhu, J., Balieu, R., Lu, X., & Kringos, N. (2018). Microstructure evaluation of polymer-modified bitumen by image analysis using two-dimensional fast Fourier transform. Materials and Design, 137, 164-175. https://doi.org/10.1016/j.matdes.2017.10.023

[41] Airey, G. (2003). Rheological properties of styrene butadiene styrene polymer modified road bitumen. Fuel, 82, 1709-1719. https://doi.org/10.1016/S0016-2361(03)00146-7

[42] Olard, F., & Di Benedetto, H. (2003). General "2S2P1D" Model and Relation Between the Linear Viscoelastic Behaviours of Bituminous Binders and Mixes. Road Materials and Pavement Design, 4(2), 185-224. https://doi.org/10.1080/14680629.2003.9689946

[43] Sayegh, G. (1967). Viscoelastic Properties of Bituminous Mixtures. Proceedings of the Second International Conference on Structural design of Asphalt Pavement, Held at Rackham Lecture Hall, University of Michigan, Ann Arbor, USA, 743-755.

[44] Williams, M. L., Landel, R. F., & Ferry, J. D. (1955). The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-Forming Liquids. Journal Americans Chemical Society, 77, 3701-3707.

[45] Yusoff, N. I. M., Mounier, D., Marc-Stéphane, G., Hainin, M. R., Airey, G. D., & Di Benedetto, H. (2013). Modelling the Rheological Properties of Bituminous Binders Using the 2S2P1D Model. Construction and Building Materials, 38 (January), 395-406. https://doi.org/10.1016/j.conbuildmat.2012.08.038

[46] Perez-Martinez, M., Marsac, P., Gabet, T., & Chailleux, E. (2016). Prediction of the mechanical properties of aged asphalt mixes from FTIR measurements. Proceedings of the 8th RILEM International Symposium on Testing and Characterization of Sustainable and Innovative Bituminous Materials, RILEM Book series 11.

[47] Chailleux, E., Ramond, G., Such, C., & de La Roche, C. (2006). A mathematical-based master-curve construction method applied to complex modulus of bituminous materials. Road Materials and Pavement Design, 7(sup1), 75-92. https://doi.org/10.1080/14680629.2006.9690059

[48] Delaporte, B., Di Benedetto, H., Chaverot, P., & Gauthier, G. (2007). Linear viscoelastic properties of bituminous material: from binder to mastic. Journal of association of asphalt paving technologies, 76, 455-494.

[49] Nosler, I., Tanghe, T., & Soenen, H. (2008). Evaluation of binder recovery methods and the influence on the properties of polymer modified bitumen. Proceedings of the 4th Eurasphalt and Eurobitume Congress, Copenhagen, Denmark.

[50] Hofko, B., Porot, L., Falchetto Cannone, A., Poulikakos, L., Huber, L., Lu, X., Mollenhauer, K., & Grothe, H. (2018). FTIR spectral analysis of bituminous binders: reproducibility and impact of ageing temperature. Materials and Structures, 51:45. https://doi.org/10.1617/s11527-018-1170-7

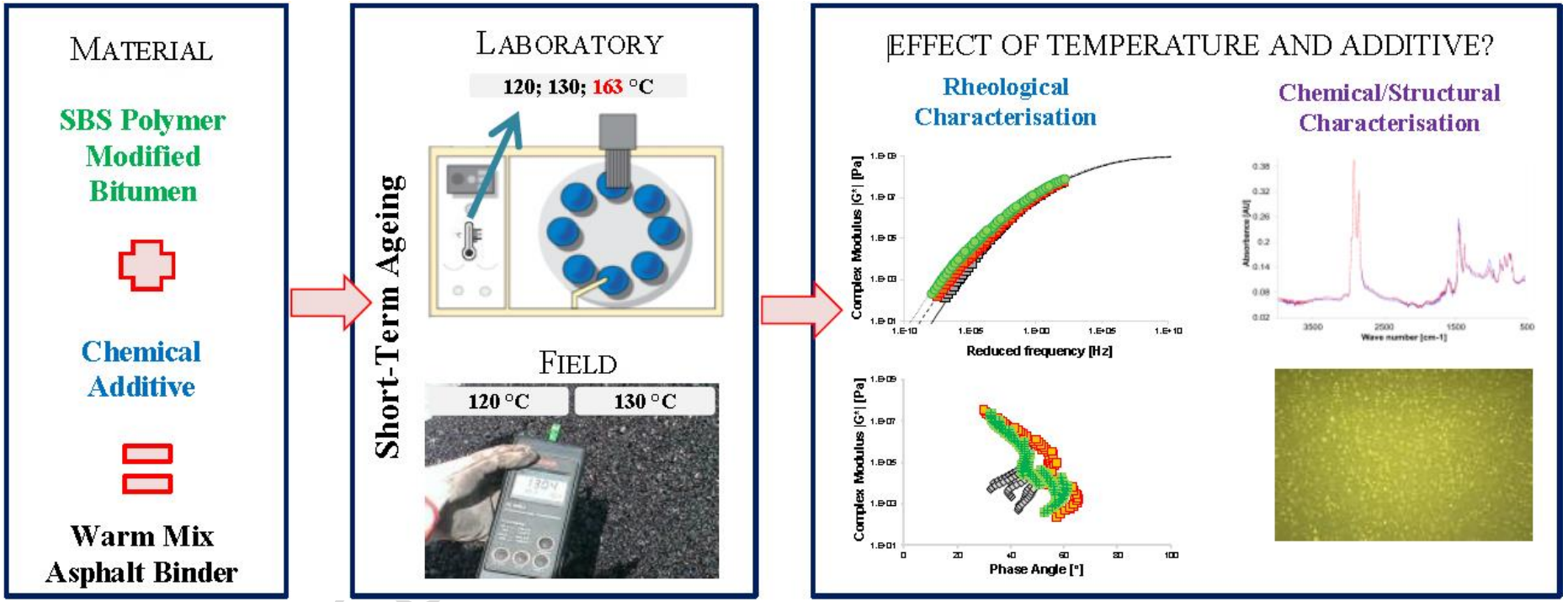
[51] Poulikakos, L., dos Santos, S., Bueno, M., Kuentzel, S., Hugener, M., & Partl, M. (2014). Influence of short and long-term ageing on chemical, microstructural and macro-mechanical properties of recycled asphalt mixtures. Construction and Building Materials, 51, 414-423. http://dx.doi.org/10.1016/j.conbuildmat.2013.11.004

[52] Lu, X., Talon, Y., & Redelius, P. (2008). Ageing of bituminous binders – laboratory tests and field data. Proceedings of the 4th Eurasphalt and Eurobitume Congress, Copenhagen, Denmark.

Author Contributions Section

All the authors equally contributed to the paper, starting from the drawing up of the experimental program to the execution of the investigation and the writing of the paper.

Graphical abstract



Paper title: **Effect of temperature and chemical additives on the short-term ageing of polymer modified bitumen for WMA**

Corresponding author: Gilda Ferrotti

E-mail address: g.ferrotti@univpm.it

Highlights

- Chemical additives tend to reduce the effect of short-term ageing on binder performance.
- Chemical additive type and ageing temperature affect the binder recoverable behaviour.
- The structural interactions of bitumen and polymer are altered by the chemical additives.
- Short-term ageing at reduced temperature properly simulates field ageing of warm mix asphalts.