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Characterization of aged bitumen recovered from in-situ polymer-modified HMA and WMA using advanced technologies

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ABSTRACT

The growing attention of public opinion towards the environment has prompted, in the last decades, to find eco-sustainable and economic alternatives to the traditional productions of hot-mix asphalt (HMA). Under these auspices, the use of warm mix asphalt (WMA) technology applied to mixtures containing reclaimed asphalt (RA) has grown, also due to the well-proven advantages in terms of plant odor emissions and improved working conditions. In addition, it is now known that the mechanical performance of WMAs is completely comparable, even superior in some cases, to that of HMAs. However, to date, there is no comparison in terms of long-term performance of bitumens used in full-scale pavements laid with the two different technologies. Therefore, the aim of this research is to evaluate the oxidative and rheological state of four bitumens recovered from different layers of a full-scale pavement prepared with WMA and HMA technologies and set up a methodology tool set for investigating the physicochemical properties of bitumens. An in-depth laboratory investigation, carried out through physicochemical and rheological tests, has shown that the bitumens used in WMA mixtures are characterized by less oxidation than HMA ones (which are characterized by longer relaxation and glass transition times) and the Styrene-Butadiene-Styrene (SBS) polymers inside them are less degraded and still contribute positively to the rheological response even after five years in service, demonstrating the ability of the chemical additive to act as possible "sacrificial agent", safeguarding the rheological characteristics of polymer modified bitumens (PMBs).

1. Introduction

In recent decades, research efforts in the road material sector have been made by scholars and industry to develop eco-friendly and economic alternatives to the traditional and consolidated production of asphalt concretes. In this regard, an eco-sustainable and potentially cheaper alternative to hot mix asphalt (HMA) can be represented by warm mix asphalt (WMA) [1,2], which is produced at lower temperatures with respect to HMA. WMA technology can reduce pollution and odours emissions at the asphalt plant during mixture production by also improving working conditions during the paving [2,3,4], as well as energy costs due to heating of aggregates and mixture. Furthermore, to reduce the use of raw materials, extensive experimental investigations have been made to increase the use of reclaimed asphalt (RA) within asphalt concretes [5,6], also trying to employ WMA technology [4,7]. Moreover, to increase the performance of asphalt mixtures at high and low temperature [8,9] and the service-life of heavy-duty pavements and to reduce the maintenance costs related to the restoration of the main distresses (rutting, fatigue, and thermal cracking), the use of polymer-modified bitumen (PMB) in the asphalt concrete production is now indispensable. Thus, the use of PMBs combined with RA and WMA technology allows for advantages from a performance, environmental and economic point of view [10,11,12]. In addition, the extreme use of RA allows the production of *High Modulus Asphalt Concrete* (HMAC) which can simultaneously guarantee high stiffness (provided by the aged bitumen present in the RA) and satisfactory fatigue resistance [13]. The scientific community is already comparing the mechanical performance of hot and warm mix asphalts containing PMB and RA [14,15], also with full-scale field trials [16,17]. However, a lack of information regards the aging characteristics of bitumens included in HMAs and WMAs after a significative in-service period. In fact, the bitumen included in asphalt concrete mixtures undergoes a double oxidation effect: first during the mixture production, and then during the in-service life.

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The heating during the mixture production causes a bitumen oxidation that has repercussions on its physicochemical characteristics, such as the increase of polar products that impacts on the rheology of the material (increase in viscosity and stiffness) [18] and is strictly dependent on heating temperatures: higher temperatures cause more oxidation. The greater the oxidation of the bitumen, the greater its brittleness and its propensity to crack. Consequently, a bitumen that has undergone lower heating will be less oxidized and will allow the pavement to better resist cracking [19,20]. In this regard, the use of WMA technology can have beneficial effects not only on the environment but also on the performance of the binder [20,21,22]. Several laboratory studies, conducted on bitumens at different aging levels, have confirmed that the lower production and mixing temperatures experienced with WMA technology cause lower bitumen oxidation levels compared to what observed for HMA [23,24,25]. This result is clearly due to the different temperatures to which the bitumens have been subjected and confirms that the thermal history of the bitumen is fundamental to understand and predict its in-service performance [26,27].

The second oxidation effect is caused by the in-service life on real pavements as the bitumen is exposed to the aggression of atmospheric agents. Contrary to the study of bitumen oxidation during mixture production with WMA and HMA technology, which has been extensively investigated, the analysis of in-service oxidation is still almost unknown. Therefore, this paper aims to deepen the oxidation of polymer-modified bitumens, in service on a full-scale field trial for a relative long time (five years), and how their rheological and physicochemical characteristics can affect the performance of mixtures containing RA.

From a physicochemical point of view, the tools to address these issues are already available to the scientific community that deals with road materials and come from research fields. Specifically, recently, the use of various technologies such as *Nuclear Magnetic Resonance* (NMR), *Differential Scanning Calorimetry* (DSC), *optical microscopy, Atomic Force Microscopy* (AFM) and *Confocal Laser Scanning Microscopy* (CLSM) has taken hold in the experimental investigations concerning asphalt mixtures and bitumens and the interest of researchers has grown in them [28,29,30,31,32]. In detail, NMR has been used in many studies to investigate the relaxation time of asphalt mixtures, bitumen, and its components (asphaltenes and maltenes) and to correlate their oxidative level and performance characteristics with this time [33,34,35]. For the same purpose, various researchers have employed DSC to evaluate the oxidation of asphaltenes, also correlating their melting point to observations made using optical microscopy [36,37,38,39]. On the other hand, techniques such as AFM and CLSM, have recently been adopted to investigate the microstructure and the oxidative state of bitumens, as well as the shape, size and dispersion of polymers [40,41,42,43,44,45,46]. Therefore, this set of investigation techniques can help researchers to evaluate differences between bitumens from a physicochemical point of view and compare results with the advanced rheological tests to fill the gap of information on the performance provided by bitumens in service on full-scale pavements for a relative long term.

This study aims at verifying the physicochemical and rheological characteristics of four polymer-modified bitumens recovered from different asphalt concrete mixtures, in service for at least five years on a full-scale trial section. These mixtures were produced with HMA and WMA technology and contained different percentages of RA. The objective of this research is to investigate the long-term benefits of WMA technology on real pavements and to provide other researchers with a methodology tool set for investigating the physicochemical characteristics of bitumens containing additives employed in different asphalt concrete production technologies.

2. Experimental program

2.1. Materials

In this research, four different styrene–butadiene–styrene (SBS) polymer-modified bitumens were studied. These bitumens were recovered from cores extracted [47], EN 12697–27:2017 – Section 4.7] from a full-scale trial section paved in April 2016 along the A1 Italian motorway (south carriageway) subject to 8.5 million equivalent single axle loads (ESALs) per year (considering a 120 kN reference axle with twin wheels) [48] and to an average annual temperature equal to about 15 °C during the period 2016–2020. This full-scale pavement involved the re-construction of three pavement layers (base, binder and wearing) in four different sections (each 200 m long). The thicknesses of the reconstructed layers are shown in the cross section of the pavement shown in Fig. 1 [17]. In detail, the section characterized by the laying of three HMA mixtures (dense-graded DG asphalt concrete for base course, DG asphalt concrete for binder course and open-graded OG asphalt concrete for porous wearing course) mixed at 170 °C, was selected as reference. The other three sections were constructed with the same layers by using WMAs mixed at 130 °C, with a reduction of 40 °C with respect to HMA, thanks to the chemical additive used, which is based on

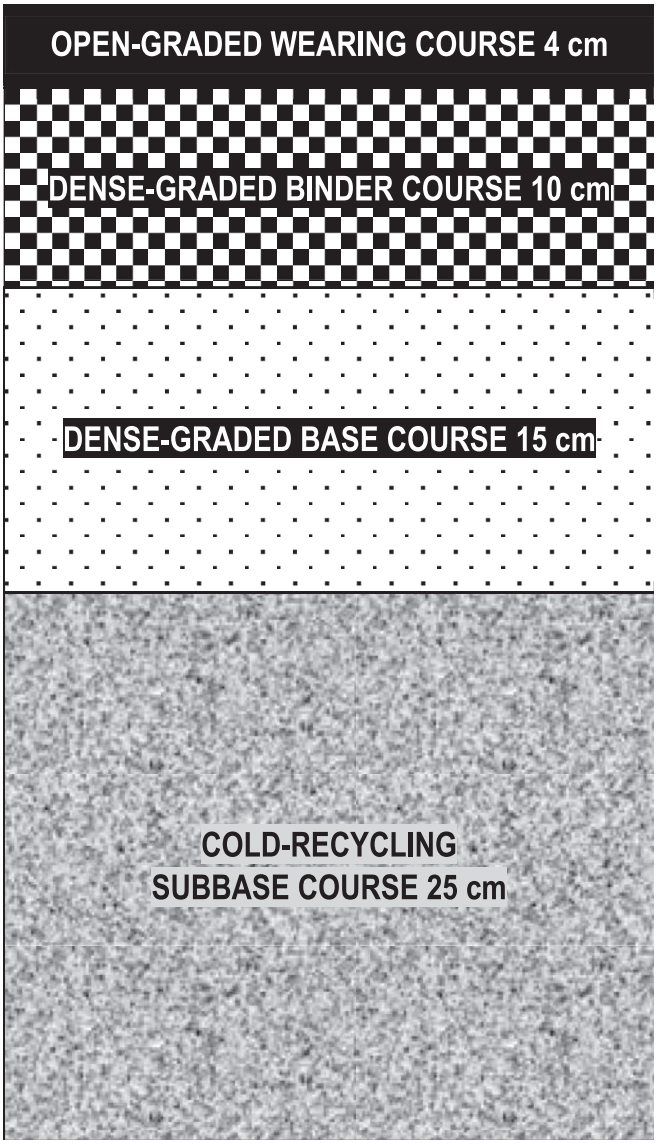

Fig. 1. Typical cross section and nominal thickness for each layer.

amine surfactant that is well known for its warm mix properties. Information about the chemical nature of this surfactant was not provided since the investigation can be considered "blind study" (no information was provided to the test operators in terms of chemical additive used, physical and chemical characteristics of the virgin bitumen used during the pavement construction, origin of the extracted bitumen in terms of HMA or WMA cores) whose goal was to validate the methodology tool set. All the bituminous mixtures contain a certain percentage of reclaimed asphalt (RA), as shown in Table 1 [17].

In November 2021, five years after the construction, two cores were extracted from the reference HMA section and two cores from one of the three WMA sections. Each core extracted was characterized by a diameter of 150 mm and a thickness of about 290-high, which includes wearing, binder and base course, made of asphalt concrete. In each of them, the binder course was sliced at the interface with the porous wearing course and with the base course and the constituent bitumens were recovered [49,50], for a total of four SBS-polymer modified bitumens (two from HMA and two from WMA). Table 1 summarizes the mixture characteristics and the identification codes of the recovered bitumens.

Before starting the laboratory study, the four recovered bitumens were subjected to thermogravimetric analysis (TGA), performed with a Hitachi Nexta ST200 instrument, to check the presence, and eventually the percentage, of residual solvent within them. The TGA tests were performed on specimens of approximately 3 mg and the outcomes obtained for the OGH bitumen are shown, as an example, in Fig. 2, considering that all bitumens provided comparable results. Analyses were performed from 30 °C to 850 °C at a temperature scan rate of 2 °C/min. The TGA tests showed that the percentage of residual solvent is about 2.5 %, making the bitumen specimens suitable for the tests without any further treatment.

2.2 Research plan.

The present research work concerned an in-depth study on the physicochemical and rheological characteristics of the four SBS-polymer modified bitumens recovered from the full-scale trial section, to evaluate their performance, comparing WMA and HMA technologies.

In this sense, the research program aims at evaluating the oxidative state of bitumens and their time and temperature dependence by investigating physicochemical characteristics in terms of relaxation time T_2 (through Nuclear Magnetic Resonance NMR) and rheological properties in terms of frequency sweep tests (through Dynamic Shear Rheometer DSR). Moreover, Atomic Force Microscopy (AFM) and Confocal Laser Scanning Microscopy (CLSM) in fluorescence mode were employed for the observation of the physical structure of the bitumens and for the investigation of the presence of SBS-polymers and their dispersion into the bitumens.

Finally, to investigate the physical characteristics and the oxidative state of the asphaltenes included into the bitumens, the specimens were de-asphaltenized according to the *Modified Conventional Method*, that involves using the chloroform and n-pentane solvents. More details are available in the reference [51]. This allowed the observation of the asphaltene melting points through the optical microscope and the evaluation of their glass transition temperature T_g through the Differential Scanning Calorimetry (DSC).

Finally, the experimental program presented in this research in terms of methods of carrying out physicochemical and rheological tests as well as analysis of the results, can be applied as a valid investigation tool to perform in-depth research on the characteristics of bitumens containing RA and additives, even on in-service real pavements.

3. Methods

3.1. Nuclear magnetic Resonance

The Nuclear Magnetic Resonance, or NMR, is a non-destructive and non-invasive technique for analysing the structure of molecules at the atomic level. The equipment consists of a magnet that generates a magnetic field, a radio frequency transmitter, and a receiver. The specimen is placed in a "probe" which is inserted into the magnetic field generated by the magnet, allowing the specimen nuclei to be aligned with this static magnetic field. Subsequently, the specimen was excited with a secondary oscillating magnetic field which causes the magnetization to rotate 90° in the horizontal xy-plane. The process by which the magnetization in the xy-plane decays to the equilibrium value of zero is called transverse relaxation or spin–spin relaxation and the corresponding time is named relaxation time T_2.

In this work, the spin–spin relaxation time T_2 was measured through an NMR designed at the University of Calabria, operating at a proton frequency of 15 MHz. T_2 measurements required a small amount of bitumen that is heated up to 120 °C and then subjected to the excitation generated with a classic Carr-Purcell pulse sequence [52] (width of $\pi/2$ pulse equal to 5.9 μs; width of π pulse equal to 11.8 μs; τ delay time equal to 0.06 ms). The relaxation time T_2 is a characteristic time of the signal decay and can be obtained, when the Carr-Purcell envelope has a mono-exponential decay, by fitting the experimental echo points with the following equation:

$$A = A_0 e^{\frac{-2\pi\tau}{T_2}} \quad (1)$$

where A is the amplitude of the n^{th} echo in the echo train and A_0 is a constant depending on the sample magnetization, filling factor and other experimental parameters. The shorter the relaxation time T_2, the more the bitumen sample is oxidized. Consequently, the T_2 value can be considered as a fingerprint of the structure of the specimen in terms of rigidity of the system.

NMR tests were performed to compare the relaxation time T_2 at the temperature of 120 °C of different bitumens and correlate the results to their stiffness and oxidation level. In fact, the relaxation time T_2 can be related to the softness of a given bituminous material: the relaxation process of very rigid materials is more evident and corresponds to shorter relaxation times. Since the oxidation of bitumen causes an increase in its stiffness (and so in its brittleness), it is possible to state that the binders characterized by lower T_2 values are more oxidized, viscous, and brittle [30].

3.2. Differential Scanning Calorimetry

Differential Scanning Calorimetry, or DSC, is a thermal analysis technique employed to measure the temperature and the heat flow associated with the thermal transition of a material in comparison to an inert reference material. In this research, a SETERAM micro-DSC 131, which employs an Indium specimen as inert material, was used to investigate the calorimetric behaviour of asphaltene specimens, obtained after the de-asphaltenisation of the studied bitumens.

Table 1
Main characteristics of the mixtures of the investigated bitumens.

Layer	Mixture	%RA	%Total bitumen (by agg. weight)	%SBS	Production technology	Bitumen code
Porous Wearing Course	Open-graded	15	5.25	3.80	HMA	OGH
					WMA	OGW
Binder Course	Dense-graded	30	4.50	3.80	HMA	DGH
					WMA	DGW

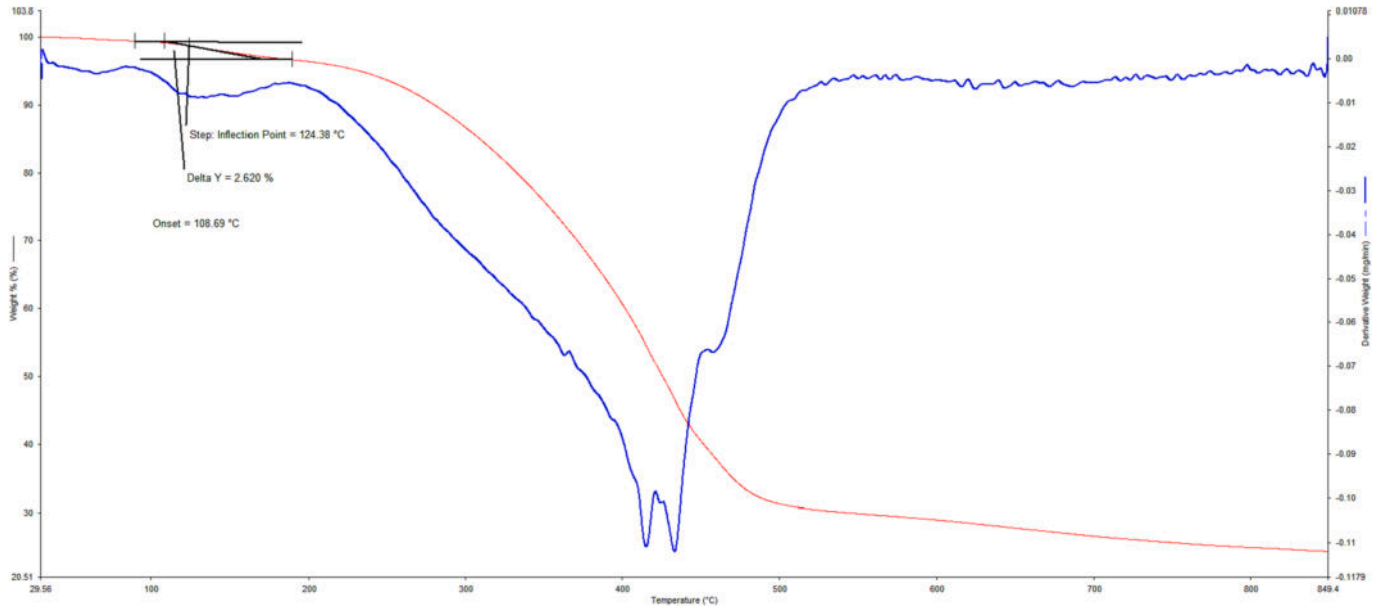

Fig. 2. Result of thermogravimetric analysis on OGH specimen.

Before each test, the instrument must be calibrated through the exact value related to the enthalpy of the inert reference. After that, about 30 mg of asphaltene specimen was weighed in a crucible which was subsequently sealed and subjected to a preliminary thermal treatment (speeded up through nitrogen flow), performed to ensure identical thermal history for all specimens:

- Isotherm phase at 25 °C for 20 min
- Heating phase from 25 °C to 250 °C at 20 °C/min
- Cooling phase from 250 °C to 25 °C at 20 °C/min

The maximum heating temperature was selected because the asphaltenes do not show any thermal degradation phenomena up to 250 °C, as observed with thermogravimetric analysis (TGA) measurements [53]. The cooling scan rate of 20 °C/min was chosen to maximize the probability of freezing the asphaltene specimens in their amorphous state. In fact, we observed that 20 °C/min allows to enhance and to amplify the DSC signal and better to determine T_g value.

After that, a second heating ramp was applied to the specimens:

- Isotherm at 25 °C for 20 min
- Heating from 25 °C to 250 °C at 20 °C/min

by measuring the heat flow as a function of the temperature. The obtained calorimetric curve allows the determination of the glass transition temperature (T_g) that can be easily used to compare different calorimetric behaviour of the investigated bitumens. The higher the T_g values, the higher the oxidation. The oxidation main reactions are dehydrogenation, condensation, and polymerization of unsaturated species, the predominant trend being the formation of more complex material of higher molecular weight and increased polarity and consequently the asphaltenes form aggregated clusters with more compact structure [37].

3.3. Optical microscopy

The melting behaviour of the asphaltene specimens was examined using a Leica Digital Microscope Light Polarized (DMLP), equipped with a Leica DFC280 camera and a CalCTec hot plate.

The asphaltene specimen was inserted in a double-side microscope glass (sandwich model) and a temperature ramp was applied with a starting temperature of 150 °C and a heating rate of 5 °C/min. This specific temperature ramp was selected because it has been shown that it helps to observe the melting point of reactive materials, such as asphaltene [54]. Every 5 °C, the specimen was left at the n^{th} temperature for at least 2 min to ensure uniform and homogeneous heating of the whole specimen, and then several pictures were taken in different areas of the specimen. The optical microscope observation ends when the edges of the asphaltenes are completely rounded and free from roughness which means that the melting point is reached. The higher the melting point of the asphaltenes, the more the bitumen is oxidized.

The optical microscope is a very simple and cheap tool to use for a quick and effective characterization of asphaltenes.

3.4. Confocal laser Scanning microscopy

Confocal Laser Scanning Microscopy (CLSM) in fluorescence was employed to investigate bitumens microstructure and SBS-polymer dispersion.

A small scoop of solid bitumen was smear on a hot glass slide, subsequently covered by another glass slip. To get a bitumen specimen so thin that light can pass through it, the cover slip was gently moved in a circular motion to continuously smear the bitumen, after that all the samples were kept at 25 °C for 15 min before to be analysed. The specimens on microscope slides were observed under Leica inverted TCS SP8 confocal scanning laser microscope equipped with 20 × and 40 × objective lenses. Argon laser excitation wavelength at 488 nm and an emission window of 509 nm were used. Images of the bitumen structure were acquired, allowing the structural comparison among different samples.

3.5. Atomic Force microscopy

The surface structure of the bitumens investigated was studied with an Atomic Force Microscopy (AFM), using a Bruker Nanoscape VIII microscope set to tapping mode. In this mode, the oscillations of a cantilever (with an elastic constant of 5 N/m) were regulated close to its resonance frequency of 150 kHz [55]. Since the cantilever oscillates up and down, the tip is intermittently in contact with the bitumen surface. This interaction between the specimen surface and the cantilever tip brings about the vibration of the cantilever. The morphological features of the bitumen determine the magnitude of the vibrations, which is

influenced by the phase angle shift of the cantilever tip when it vibrates.

For the measurements, a small quantity of each bitumen was placed on a specific support for the observation with AFM, then heated up to 100 °C for 10 min after it was cooled at 10 °C/min. This procedure allows the bitumen to create a smooth surface with comparable structure. Images of surface topography and SBS-polymer dispersion were acquired simultaneously.

3.6. Frequency sweep tests

Frequency sweep tests, according to EN 14770 [56], were carried out to analyse the time and temperature dependence of the investigated bitumens and their rheological behaviour. Tests were conducted in a temperature range between 4 and 88 °C, with a step of 6 °C, applying at each temperature a testing frequency range from 0.159 to 15.9 Hz (from 0.1 to 100 rad/s, respectively). A plate-plate configuration was adopted, employing a plate of 8 mm and a gap equal to 2 mm for relatively low temperatures (from 4 to 34 °C), and a plate with a diameter of 25 mm and gap equal to 1 mm for relatively high temperatures (from 34 to 88 °C). For each testing temperature and frequency, a constant strain amplitude of 0.1 % was maintained. At least two repetitions were carried out for each bitumen sample investigated.

4. Results and discussion

4.1. NMR relaxometry measurements

In this study, the relaxation time T_2 was obtained from the exponential decay represented by the envelope of the recorded signals. Fig. 3 shows the experimental data and the signal envelopes of the bitumens recovered from the binder courses DG (Fig. 3a) and from the porous wearing courses OG (Fig. 3b). Table 2 summarizes the calculated values (according to Eq. (1)) of the relaxation time T_2 for each bitumen investigated.

Fig. 3 and Table 2 show that the bitumen recovered from the warm binder course, DGW, has a much higher T_2 value than the DGH, demonstrating its lower oxidation and, therefore, lower brittleness. In this sense, the contribution of the chemical additive in delaying the oxidation of the material during the production, transport and paving phases seems to be still evident after five years in service.

In terms of bitumens recovered from porous wearing course, OGH has a slightly lower T_2 and thus slightly higher oxidation than OGW, although they have comparable relaxation times. This means that the action of water, de-icing salts, and UV radiation acting on the pavement surface during five years in-service mitigate the initial benefits coming from a lower production temperature. This is also confirmed by the shorter T_2 relaxation times (higher oxidation) of the OG bitumens with respect to the DG ones, which are not subjected to the external agents.

Table 2
Relaxation time T_2 of bitumens investigated and glass transition temperatures T_g, of their asphaltenes.

Layer	Bitumen	T_2 [ms]	T_{g1} [°C]	T_{g2} [°C]
Binder course	DGH	1.87	155.4	244.9
	DGW	2.73	123.4	228.2
Porous wearing course	OGH	0.54	193.5	284.6
	OGW	0.62	198.3	270.0

4.2. Differential Scanning Calorimetry

The calorimetric analysis was conducted to investigate the behaviour of the asphaltene fraction isolated from the maltenic one. The calorimetric analysis allowed to obtain the asphaltene glass transition temperature (T_g), represented by the presence of an inflection point in the heat flow-temperature curve. This parameter can be correlated to the aging state of the bitumens: the higher the T_g values, the higher the oxidation [37,57,58,59].

The calorimetric behaviour of the asphaltenes of bitumens DGH and DGW is shown in Fig. 4a and that of OGH and OGW in Fig. 4b.

All the materials are characterized by the presence of two glass transition temperatures (Fig. 4): the lower temperature can be related to the virgin bitumen added to the mixtures (T_{g1}), whereas the higher temperature can be related to the bitumen coming from the RA (T_{g2}).

Table 2 shows that the glass transition temperature T_{g1} (associated with the virgin bitumen behaviour) of the DGH asphaltenes is significantly higher than that of the DGW asphaltenes, confirming the positive contribution of WMA technology in maintaining over time a lower oxidation level than HMA, according to NMR results obtained for bitumens. Regarding the porous wearing courses, OGH and OGW asphaltenes provided a comparable glass transition temperature T_{g1} (Table 2), demonstrating the severity of external agents (water, de-icing salts, and UV radiations) which can mitigate the benefits of WMA technology in the pavement surface layers. This is also confirmed by the higher T_{g1} value of OG asphaltenes with respect to DG asphaltenes, according to NMR results.

Higher glass transition temperatures for OG asphaltenes than DG ones are also observed for T_{g2}, associated with the bitumen present in the RA. However, in this second case, the differences between OG and DG asphaltenes are less pronounced since it is plausible that the bitumen contained in the RA has reached an oxidation level such as it is less affected by the action of external agents.

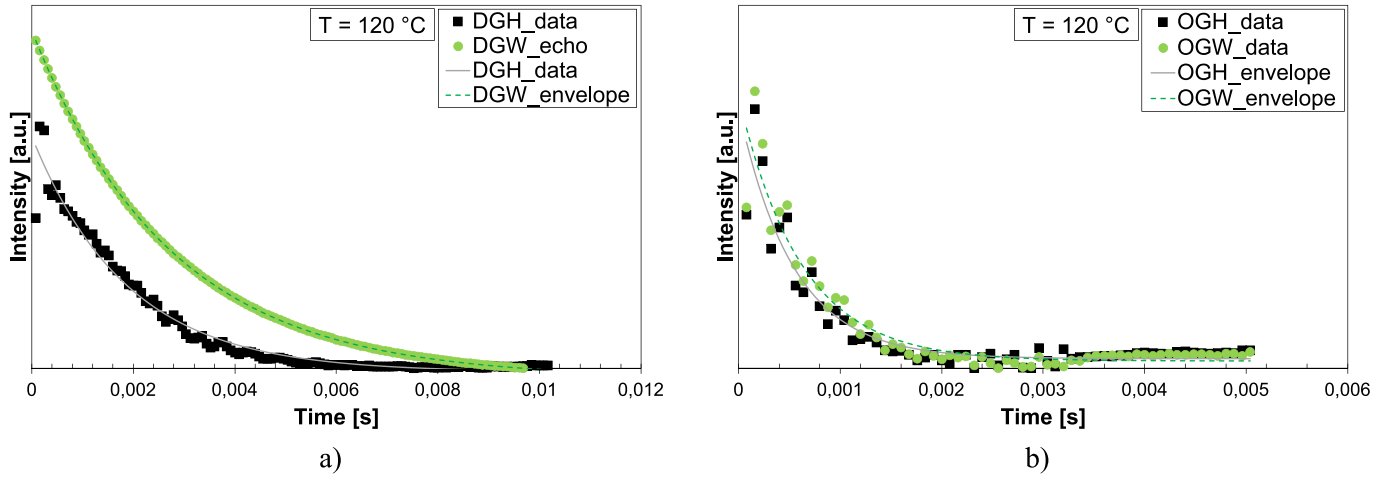

Fig. 3. Experimental data and decay envelopes versus time: a) DGH and DGW, b) OGH and OGW.

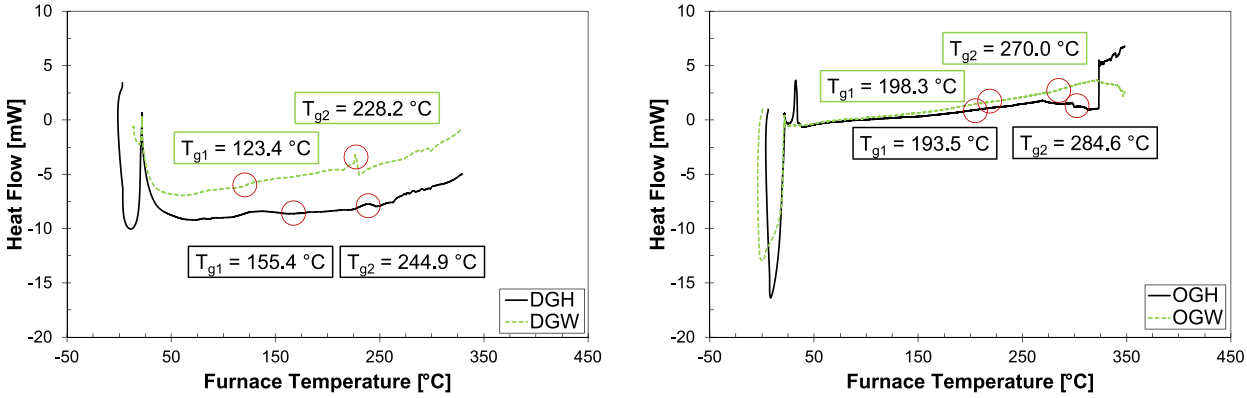

Fig. 4. Differential calorimetric analysis on the asphaltenes of bitumens for a) binder courses; b) porous wearing courses.

4.3. Optical microscopy

To evaluate the melting point of the asphaltenes, images of the asphaltene specimens were captured with a camera during a temperature increase of 5 °C/min. In Fig. 5a (images on the left) it is possible to observe, for all the studied materials, micro-sized agglomerates of asphaltenes at the starting temperature of 150 °C, whereas, in Fig. 5b (images on the right), these agglomerates melt in a temperature range between 200 and 210 °C.

Fig. 5 and Table 3 show that OGH asphaltenes melt around 210 °C and OGW asphaltenes melt around 205 °C, allowing to observe that the two different production technologies (HMA and WMA) provide comparable asphaltene oxidation in the bitumens employed in porous wearing courses after 5 years in-service. Since higher melting points correspond to higher oxidation levels, it can be stated that OGW and OGH have similar aging, confirming the NMR and DSC test results.

As far as the bitumens of the binder courses are concerned, the melting point of DGH asphaltenes is around 210 °C and that of DGW asphaltenes is around 200 °C (Fig. 5 and Table 3). This confirms, also in this case, NMR and DSC results which showed a lower aging of DGW with respect to DGH. The differences observed between the two production technologies (HMA and WMA) confirm that lower mixing and paving temperatures have beneficial effects on the bitumens, even after five years in service.

Finally, Table 3 shows that asphaltenes recovered from mixtures used in porous wearing courses are characterized by a slightly higher oxidation level than those related to the binder courses, according to NMR and DSC results.

4.4. Confocal laser Scanning microscopy

Confocal laser scanning microscopy (CLSM), operating in fluorescence, was used to investigate the physical microstructure of bitumen and the dispersion of SBS-polymers within it. In this regard, Fig. 6 shows the 2D images captured with CLSM, related to the four bitumens investigated.

Observing the microscope images in Fig. 6a and 6c it is easy to see that the DGH and OGH bitumens, respectively, are characterized by a continuous phase of asphaltenes and maltenes, in which it is difficult to distinguish the presence of SBS-polymer that seems to be homogeneously dispersed. This can be due to the oxidation of the material which causes a degradation of the bitumens as well as the polymers.

On the other hand, the presence of a heterogeneous dispersion of SBS-polymers within the continuous phase of asphaltenes and maltenes is clearly visible in OGW (Fig. 6d) and even more in DGW (Fig. 6b) bitumen. This non-homogeneous dispersion inside the bitumen could be due to a lower oxidation, and thus degradation, suffered by the polymers thanks to the presence of the warm chemical additive which could have acted as possible "sacrificial agent". The presence of polymers is more evident in the DGW bitumen (lower polymer dispersion) because the OGW bitumen suffered a higher oxidation and thus polymer degradation due to the direct contact with the external atmospheric agents.

In this regard, it is important to remember that the virgin SBS-polymer modified bitumens used for the production of all four mixtures (DGH, DGW, OGH, OGW) was the same, as the trial section was built in four consecutive days and the mixtures were supplied by the same asphalt plant.

The obtained results allow to observe that the lower production and mixing temperatures of the warm mix asphalts preserved not only the structure of the bitumen from aging, but also the degradation of the polymers, guaranteeing their functionality into the bitumen.

4.5. Atomic Force microscopy

Atomic force microscopy (AFM) was employed to investigate the physical characteristics of the bitumen, making it possible to evaluate the asphaltene conditions and the dispersion of the SBS-polymers into the bitumen. Fig. 7 shows the images acquired for all the recovered bitumens during the experimental study.

The dark areas observed in both DGW and OGW bitumens (Fig. 7b and 7d, respectively) can be attributed to the presence, into the bituminous matrix, of polymers, which are clearly visible and non-homogeneously distributed. On the other hand, the images acquired for the DGH and OGH bitumens (Fig. 7a and 7c, respectively) show the absence of these dark areas, allowing to affirm that the polymers are homogeneously dispersed. These results are in perfect agreement with the CLSM observations, confirming that the reduction of the temperatures during the mixture production and mixing, preserve the structure of the bitumen from aging, also avoiding the degradation of the polymers.

4.6. Frequency sweep tests

Frequency sweep tests permitted the evaluation of the complex modulus (G*) and phase angle (δ) for each bitumen under investigation. The master curves at the reference temperature of 34 °C are shown in Fig. 8 for all the testing conditions. The shift factors were determined through the closed form shifting (CFS) algorithm [60] (able to eliminate subjective uncertainties related to the manual shifting of the experimental data) and compared with those obtained by applying the Williams-Landel-Ferry law [61]. The master curves were constructed by applying the Christensen–Anderson–Marasteanu (CAM) model [62,63] to the shifted data.

By comparing the master curves of the individual layers (Fig. 8a and

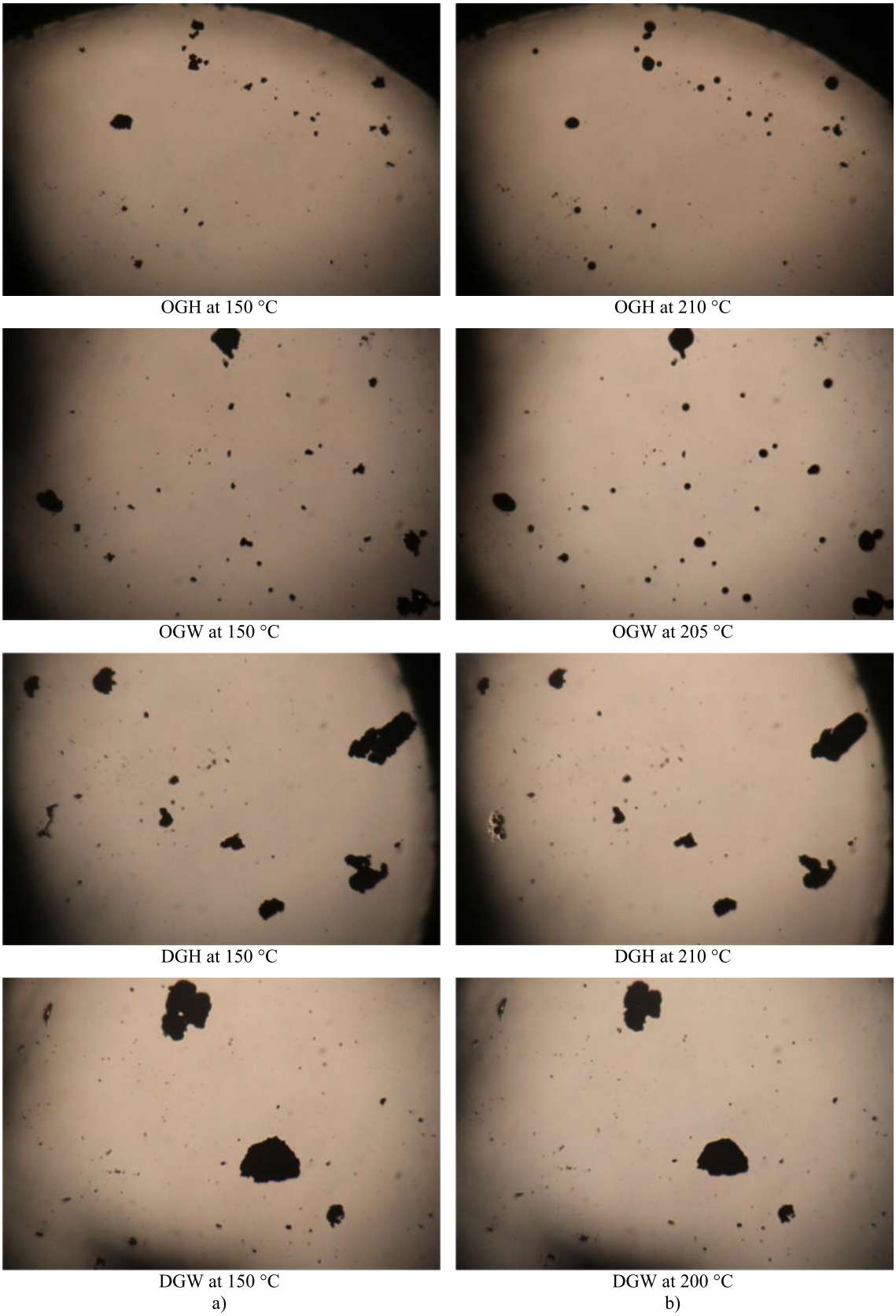

Fig. 5. Images captured under the optical microscope: a) start of heating and b) start of the melting phase.

Table 3
Melting points of the asphaltenes of the bitumens investigated.

Layer	Specimen	Melting point
[-]	[-]	[°C]
Binder Course	DGH	210
	DGW	200
Porous wearing Course	OGH	210
	OGW	205

8b) for different production technologies, it is possible to highlight that the bitumens from HMAs have lower G* values than WMAs, at any frequency but especially at high and intermediate temperatures. This seems to be in apparent contrast with what previously observed with the chemical investigation, which showed higher oxidation for HMA bitumens. However, it should be noted that CLSM and AFM results clearly explain this behaviour. Indeed, since the investigated bitumens are modified with SBS polymers, it is necessary to consider not only the oxidation but also the presence of polymers into the bituminous matrix. CLSM and AFM results showed that higher oxidation (in DGH and OGH bitumens) also results in degradation of the polymers which do not give further contribution to the bitumen stiffness. On the contrary, the presence of the chemical additive seems to guarantee a lower oxidation (in DGW and OGW bitumens) and thus lower degradation of the polymers which are still able to confer higher stiffness to the warm bitumens

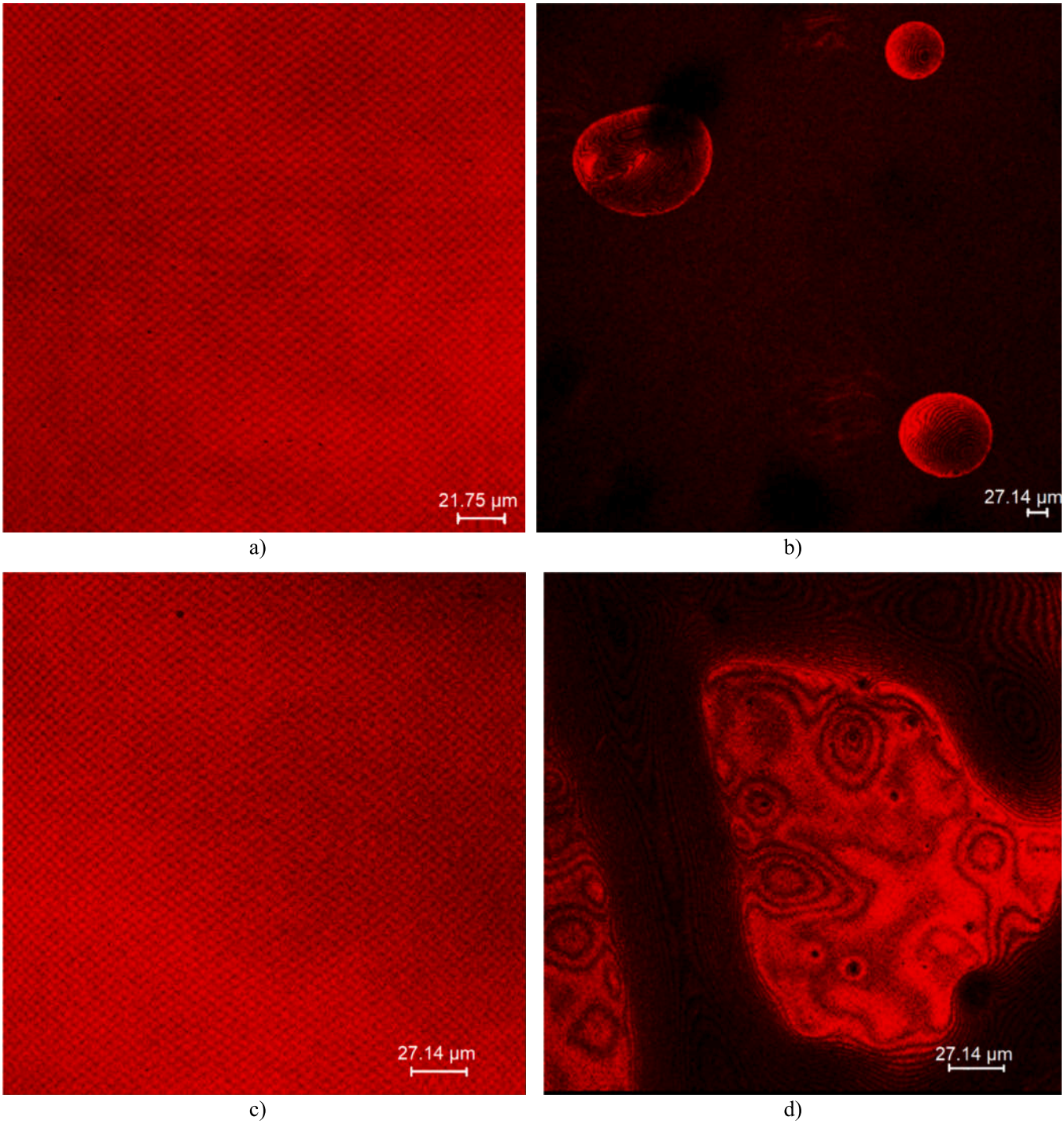

Fig. 6. CLSM fluorescence images: a) DGH, b) DGW, c) OGH and d) OGW specimens.

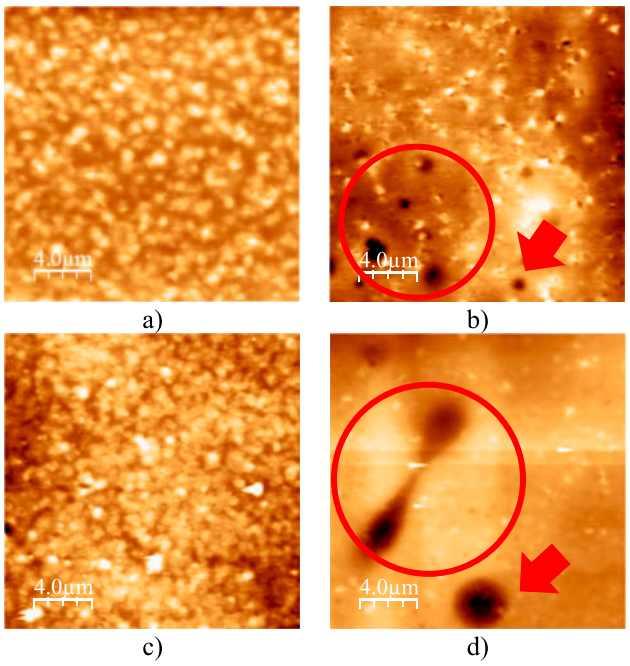

Fig. 7. AFM images: a) DGH, b) DGW, c) OGH and d) OGW specimens. SBS-polymers are indicated by red arrows and circles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with respect to hot ones.

Analogous observations can be made when porous wearing courses (OGH and OGW) are compared with the corresponding binder courses (DGH and DGW), as shown in Fig. 8c and 8d. Indeed, the greater oxidation shown by OG bitumens (due to the external agents) also caused a greater degradation of the polymers (Fig. 6c and 6d) for which the polymers are no longer able to contribute to the bitumen stiffness. For this reason, a higher RA content coupled with a residual functionality of the polymers, cause higher stiffness of the DG bitumens with respect to the corresponding OG ones.

In addition, the data collected in terms of complex modulus (G*) and phase angle (δ) at a frequency of 1.59 Hz and at temperatures between 16 and 34 °C, allowed the calculation of the Glover-Rower parameter (GRP) [64] as follows:

$$GRP = \frac{G^* cos^2 \delta}{sen\delta} \quad (2)$$

The GRP allows the evaluation of the elastic component of a bitumen, which is associated with its brittle behaviour [65]. In fact, the higher the GRP, the greater the propensity of the bitumen to crack [65,66].

In this framework, the results of the GRP calculated on the four bitumens investigated in this research are shown in Fig. 9.

The results of Fig. 9a and 9b show that warm bitumens (OGW and DGW, respectively) are characterized by higher GRP values than their hot counterparts, at any temperature.

This is in perfect agreement with what has been previously observed in the chemical investigation. In fact, in a modified bitumen the presence of the polymer contributes to the increase of G* and to the decrease of δ (that cause an increase in the GRP value). Since the polymers present in the warm bitumens are less degraded than their hot counterparts, this contributes "elastically" to the rheological behaviour of the bitumen, causing an increase of the GRP value.

In Fig. 9c and 9d the GRP values are compared with the same production technology, but for different pavement layers. From the results,

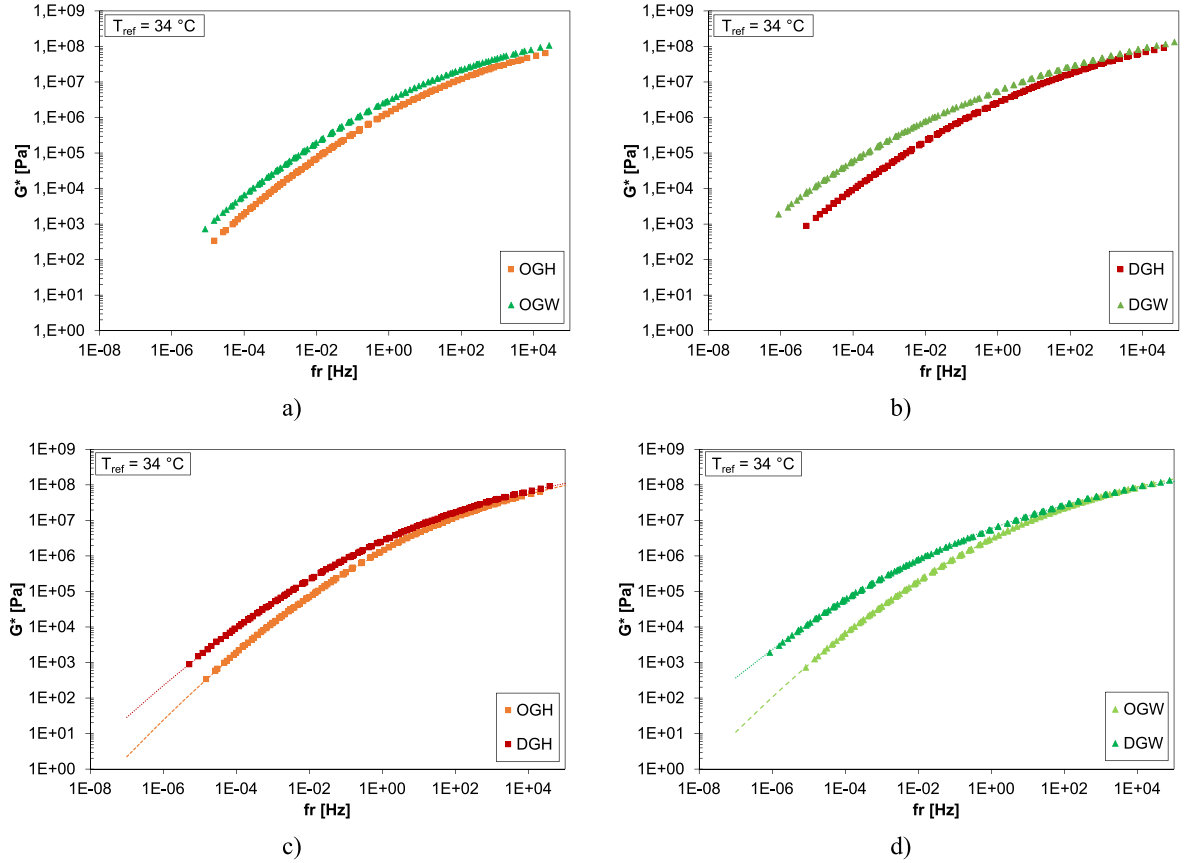

Fig. 8. Comparisons between master curves elaborated from frequency sweep tests: a), OGH vs. OGW b) DGH vs. DGW extension, c) OGH vs. DGH and d) OGW vs. DGW.

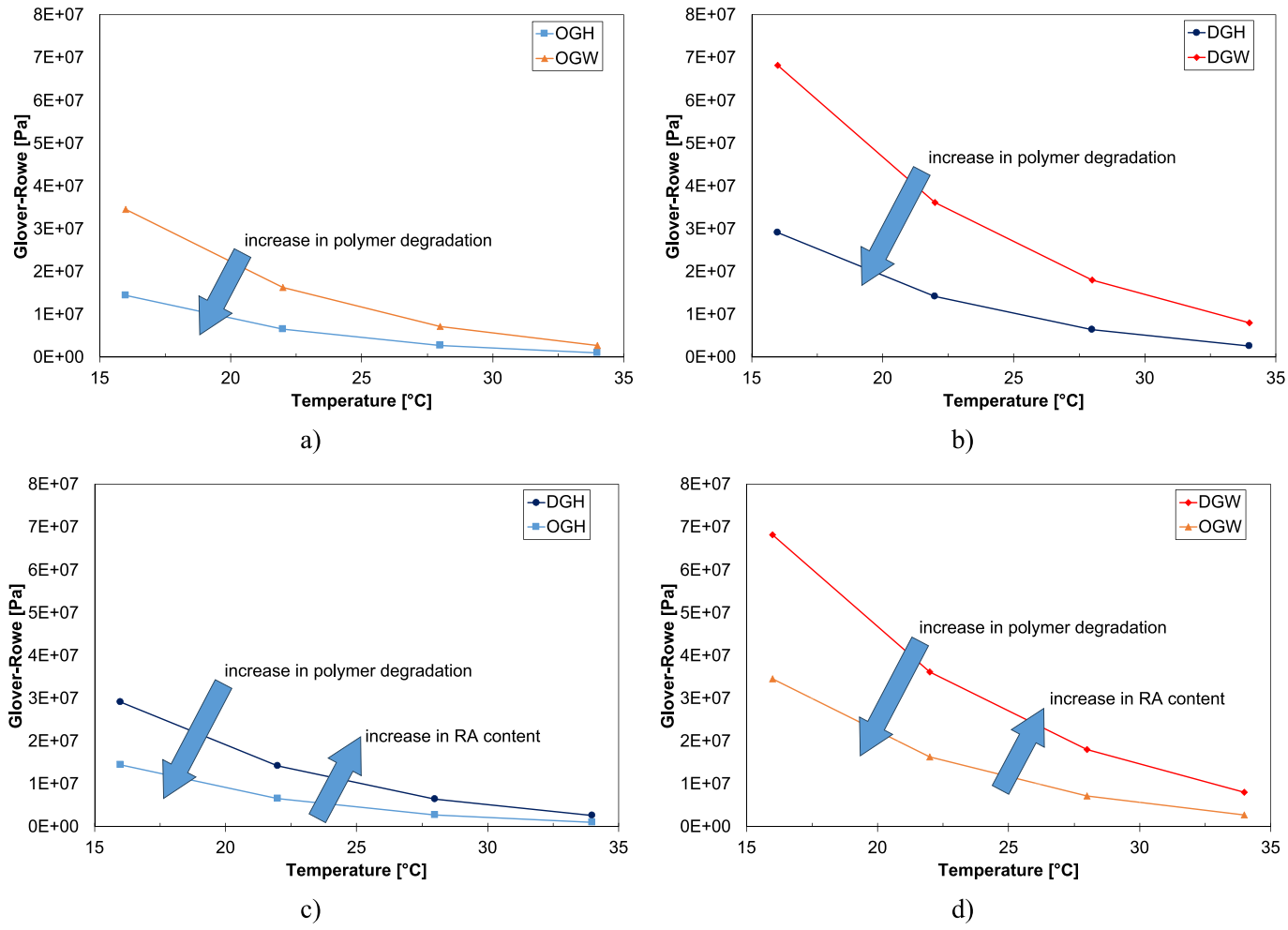

Fig. 9. Comparisons between GRP trends elaborated from frequency sweep tests: a), OGH vs. OGW b) DGH vs. DGW extension, c) OGH vs. DGH and d) OGW vs. DGW.

it is evident that the DG samples have higher GRP values with respect to OG samples. This can be due to the degradation of the polymers (less in DG than in OG) but also to the presence of a greater percentage of binder coming from RA.

5. Conclusions

The goal of this research was to present a physicochemical investigation approach which can distinguish the effect of additive on the oxidation process that involve the asphalt concrete. A scientific guide to analyse the bitumen structure and understand the chemical modification induced by the additive commonly used in the field of road pavement was provided.

To this end, four different SBS-polymer modified bitumens recovered from porous wearing courses and from binder courses of a full-scale trial section, in service for at least five years and paved with the two different production technologies HMA (T_{mixing} = 170 °C, $T_{compaction}$ = 160 °C) and WMA (T_{mixing} = 130 °C, $T_{compaction}$ = 120 °C) also employing RA, have been investigated. The focus of this study was the evaluation of the long-term performance of WMA mixtures compared to the traditional HMAs, laid on real pavements. To this end, an extensive laboratory investigation, consisting of both physicochemical and rheological tests, was performed, including nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), confocal laser scanning microscopy (CLSM), atomic force microscopy (AFM) and frequency sweep tests.

From the experimental results, the following conclusion can be drawn:

(1) The analysis of the T_2 relaxation time, obtained by NMR tests allows to conclude that the bitumens used in the WMA technology are, in general, less oxidized than the HMA ones. This result is more evident among the bitumens recovered from the binder courses (DGH with T_2 = 1.87 ms and DGW with T_2 = 2.73 ms) with respect to the bitumens from porous wearing courses where the difference is reduced (OGH with T_2 = 0.54 ms and OGW with T_2 = 0.62 ms). This is because the wearing course is affected, during its service life, by the action of external agents.

(2) The results of CLSM and AFM allow to state that, in WMA bitumens, the SBS polymers are less degraded, especially in specimens recovered from binder courses. This result could be attributable to the chemical additive used for the WMA technology, which acts as a "sacrificial agent" against oxidation. In detail, the lower production and mixing temperatures of the WMAs preserved not only the bitumen from aging, but also the degradation of the polymers, guaranteeing their functionality into the bitumen.

(3) As regards the asphaltene behaviour, also the DSC and the optical microscope observations confirmed, in terms of glass transition temperature T_g and melting temperature respectively, that the bitumens investigated are more oxidized in the case of HMA mixtures (DGH with T_{g2} = 244.9 °C and OGH with T_{g2} = 284.6 °C), compared to WMA mixtures (DGW with T_{g2} = 228.2 °C and OGW with T_{g2} = 270.0 °C). These results are fully in line with the previous ones and further demonstrate the benefits of WMA technology.

(4) Regarding the frequency sweep tests, WMA bitumens are generally stiffer, especially at low and medium frequencies, than HMA ones. This conclusion may appear to be in contrast with those of the

physicochemical tests; however, this result can be attributed to the positive presence of the less degraded polymers in the WMA bitumens with respect to degraded SBS into the HMA ones. These conclusions allow to confirm the advantages and potential of WMA technology also from a rheological point of view.

(5) As regards the methodology tool set exposed in this research, it is possible to state that frequency sweep rheological tests, conducted with DSR, appear to be a necessary but not sufficient condition for the characterization of bitumen recovered from cores extracted in situ. Therefore, to investigate more in depth the physicochemical characteristics of in service bitumens, it is necessary to implement the results of the rheological tests with the chemical ones, concerning the structure (NMR) and microscopy (CLSM and AFM) of the bitumens and the calorimetric analysis (DSC) of the respective asphaltenes. This set of tests allows to have complete information on the characteristics of an in service bitumen.

In summary it is possible to conclude that five years after the paving of a full-scale trial section, the bitumens used in the WMA mixtures show lower levels of oxidation than the HMA ones and the SBS polymers inside them are less degraded and contributes positively to the rheological response. In this framework, future research activities may include using the presented methodology tool set to investigate the bitumens recovered from the same full-scale trial section after a further 5 years for checking possible changes at a chemical and rheological level. In addition, the important results obtained from this experimental research encourage and support the combined use of WMA technology and RA as a valid alternative for future eco-friendly and high-performance applications on the Italian motorway network.

CRediT authorship contribution statement

S. D'Angelo: . **G. Ferrotti:** . **C. Oliviero Rossi:** . **P. Caputo:** Writing – review & editing, Methodology, Formal analysis. **F. Canestrari:** Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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