Master curves of crumb rubber modified binders containing Montan waxes as warm mix asphalt additives

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ABSTRACT

Energy consumption and the corresponding greenhouse gas (GHG) emissions can be reduced with technology recently developed in the field of road pavement materials: warm mix asphalt (WMA). This technology is being incorporated to improve workability and, consequently, production and compaction temperatures of asphalt mixtures can be lowered without significantly affecting their mechanical properties. However, since this technology is relatively new, the influence of WMA additives on the properties of crumb rubber modified (CRM) binders has not yet been investigated in depth and clearly identified.

The main objective of this study is to investigate the effect of different types and quantities of WMA additives on the high and intermediate temperature properties of a 20%CRM binder. For this purpose, binder´s properties are determined using a dynamic shear rheometer (DSR) which allows elastic, viscoelastic and viscous properties of bitumen to be defined over a wide range of temperatures and frequencies.

The results of this study indicate that there are significant improvements produced by the additives concerning the mechanical behaviour and the elasticity for the whole temperature range; the complex modulus (stiffness) is increased at the high temperatures avoiding permanent deformation and the phase angle curve is shifted on lower values over a wide range of frequencies. However, the increased content of additives slightly shifted the complex modulus master curves in high frequency regions, increasing the stiffness at low temperatures.

Keywords: Additives, Complex Modulus, Rheology, Rubber, Warm Asphalt Mixture

1. INTRODUCTION

Pavements containing crumb-rubber modified (CRM) binders offer an improved resistance to rutting, fatigue and thermal cracking; reduce traffic noise, maintenance costs and prolong pavement life [1-4]. These mixtures, however, present one major drawback: the manufacturing temperature is higher compared to conventional asphalt mixtures as the rubber lends greater viscosity to the binder and, therefore, larger amounts of greenhouse gas (GHG) emissions are produced.

Warm mix asphalt (WMA) technology offers promising solutions to the CRM drawbacks thanks to the use of fluidifying additives which are able to guarantee lower viscosity of bitumen at mix production temperatures without affecting bitumen performance at pavement service temperatures. If asphalt mixtures manufacturing and compaction temperatures are lowered, the energy consumption, the greenhouse gas (GHG) emissions could be reduced and the working conditions at paving sites could therefore be improved [5]. These benefits, combined with the effective reuse of a solid waste product would make asphalt rubber (AR) mixtures with WMA additives an excellent, environmentally-friendly material for road construction.

Although some studies have been carried out regarding organic additives in bitumen focused on the determination of the wax content [6, 7], the crystallization properties [8, 9], chemical structure [10, 11], as well as their influence on bitumen and asphalt performance [12-16], the influence of organic additives on CRM binders have not been identified in great detail [17, 18].

It is important to understand the rheological properties of bitumen as they give information in terms of pavement performance. Asphalt mixtures with binders that deform and flow easily are more prone to rutting while mixtures with stiff bitumen may be more susceptible to fatigue and cracking. Conventional characterization to predict the high temperature and permanent deformation properties (softening point) and cohesive properties (ductility) cannot completely describe the viscoelastic properties needed to relate fundamental physical binder properties, especially for modified binders like CRM binders with WMA additives. In fact, it is considered that the best techniques for representing bitumen´s behaviour are the cyclic (oscillatory) and creep test.

Therefore, in order to evaluate the high and intermediate temperature properties of different CRM binders with WMA additives, a dynamic shear rheometer (DSR) was used to determine the elastic, viscoelastic and viscous properties of the binders over a wide range of temperatures and frequencies.

2. MATERIALS AND TEST PROGRAM

The following sections describe the materials used throughout the whole investigation.

2.1 Virgin binder

The virgin binder used in this study is a bitumen 50/70 (50/70 10^{-1} mm of penetration), which is widely used to produce asphalt mixtures at conventional temperatures. Table 1 summarizes the basic specifications of the virgin binder. The penetration grade was assessed according to UNE-EN 1426 standard (Determination of needle penetration) while the Softening Point was measured according to UNE-EN 1427:2007 (Determination of the softening point – Ring and ball method). The asphalt bitumen was also subjected to a fractionation analysis as specified in the NLT 373/94 standard.

Table 1: Characteristics of the 50/70 virgin binder

Properties	**Unit**	**Test results**
Penetration (25ºC)	0.1 mm	55.4
Softening point	ºC	51.1
Composition	**Unit**	**Test results**
Asphaltenes	(%)	13.8
Saturates	(%)	9.7
Naphthene-aromatic	(%)	48.5
Aromatic-polar	(%)	28.0

2.2 Crumb rubber modifier

The crumb rubber modifier was manufactured by mechanical grinding at ambient temperature (50% from truck tyres and 50% from car tyres) and to ensure consistency, only one batch of crumb rubber was used in this study. The gradation of the crumb rubber is provided in Table 2 and the thermo-gravimetic analysis in Table 3, both provided by the supplier.

Table 2: Gradation of crumb rubber

Sieve (mm) (UNE 933-2)	Accumulated (%)
2.0	100.0
1.5	100.0
1.0	100.0
0.50	94.1
0.250	23.7
0.125	3.7
0.063	0.4

Table 3: Thermogravimetic analysis of crumb rubber

TGA	Rubber
Plasticizer + additives (%)	4.67
Polymer (rubber) (%) Carbon black (%)	57.41 32.22
Ash (%)	6.02

2.3 WMA additives

The WMA technologies can be classified in three groups: organic additives, chemical additives and foaming processes. For this study, only one of these technologies- the organic additives- was chosen.

The WMA additives selected for this study were two different Montan waxes. The additive AA is a Montan wax which is produced by solvent extraction of lignite or brown coal. The additive AB is a refined Montan wax blended with a fatty acid amide.

The study of the binders includes a rheological characterization at high and intermediate temperatures of 6 different binders. 20 % by weight of rubber was added to the 50/70 net bitumen in order to obtain the CRM binders of this study while the dosage rate of the WMA additives referred to the bitumen weight were 2% and 4%.

All the binders and the names that will be referred to hereafter are listed in Table 4. The binders named as B and B20 will be referred to as control binders as they do not contain WMA additives.

Table 4: Binders name and their composition

Binder name	Bitumen / Rubber (%)	Additive (%)	Additive
B	100/0	0	-
B20	80/20	0	-
B20+2AA	80/20	2	AA
B20+4AA	80/20	4	AA
B20+2AB	80/20	2	AB
B20+4AB	80/20	4	AB

2.4. Preparation of CRM binders containing WMA additives

An oil bath with a maximum temperature of 225ºC, a mixer with a maximum velocity of 15,000 rpm, fitted with a propeller agitator and a one-litre metal container for mixing was used for the preparation of the binders. The oil bath has a temperature probe which can be introduced into the mixing receptacle, allowing the temperature of the binder to be controlled with a precision of ± 1 °C. A bitumen sample of 750 g was heated at 140 °C and then placed in the oil bath. WMA additives were carefully added to the bitumen and the blends were subsequently mixed for 15 minutes at 4,000 rpm, ensuring that the additive was properly incorporated into the binder. The blend was then heated to 185ºC and the crumb rubber was added. The mixture was blended for 30 minutes at 2,000 rpm then for another 30 minutes at 900 rpm at a constant temperature of 185ºC. Reheating and homogenization were carefully carried out at a controlled temperature in order to obtain reproducible results [21]. Special attention was then paid to the thermal history and storage conditions of the test samples before testing (1 h at 25 °C ± 0.5 °C), because of their influence on rheological measurements [22].

2.5 Rheological tests

Frequency sweeps performed at different temperatures provide information about the trend of the complex modulus and the phase angle in function of frequency: they are dynamic tests which consist in the application of a fixed shear stress at a constant temperature while the angular frequency changes between 1 and 100 rad/s.

The shear stress applied depends on the test temperature and must belong to the linear region for the analysed binder: in order to obtain significant results, shear stress defined in literature for similar tests were assumed. The chosen couple test temperature – shear stress are listed in Table 5, and they were kept the same for all the binders.

Table 5: Temperature shear stress couple

Test T^a (ºC)	Shear Stress (Pa)
-10	40,000
0	20,000
10	10,000
20	5,000
30	2,000
40	1,000
50	500
60	200
70	100
80	50

The stress sweeps consist in the application of an increasing shear stress on the specimen at a fixed frequency and temperature: at 10°C the shear stress changes between 10^3–10^6 Pa while at 40°C the range becomes 40 – 40000 Pa. The frequency sweeps were done from 1 to 10 Hz in the temperature range between 10 and 80ºC at 10ºC intervals. The plate–plate configuration, 25 mm diameter and 1 mm gap sample geometry was used.

The frequency sweeps were carried out inside the linear viscoelastic region of the studied asphalts. The change of the plate's geometry, from 8 mm diameter to 25 mm diameter, was done between 20°C and 30°C, as recommended in the literature, in order to obtain results which best fit the real trend.

The time-temperature superposition principle (TTSP) gives equivalence between temperature and frequency and allows the construction of a representative curve designated master curve for the material for a wider frequency range. The TTSP implies that the rheological data obtained at higher and lower temperatures can be equated simply and graphically with lower and higher frequency respectively, meaning that data obtained by frequency sweeps can be used to plot a single curve at a reference temperature for an extended frequency range through shift factors. Materials which verify the TTSP principle are called “thermo-rheologically simple” [23].

According to TTSP, master curves are generated by selecting a reference temperature and using shift factors to fit an overall continuous curve at a reduced frequency or time scaled: the shift factors are applied to the frequency values and they assume different values for each temperature data series until the curves converge into a single smooth function.

The amount of the shifting required at each temperature to form the master curve is of particular importance and it is performed by defining the shift factors. It is important to notice that almost all the materials under study have been demonstrated to be non-thermo-rheologically simple, nevertheless, it was decided to continue with this analysis and with the construction of the master curves for the materials. As usually required, master curves are realized for both phase angle and complex modulus versus the reduced frequency.

3. RESULTS AND DISCUSSION

3.1 Frequency dependence comparative for control binders

The binders were tested with Dynamic Shear Rheometer (DSR). The standard used for this test is EN 14770:2012 (Determination of complex shear modulus and phase angle - Dynamic Shear Rheometer (DSR)). Figure 1 shows that the addition of rubber to the net bitumen increases complex modulus G*, consequently, the stiffness of the binders is increased. The phase angle values decrease as the addition of rubber increases the elasticity of the binders. The reference temperature is 60°C.

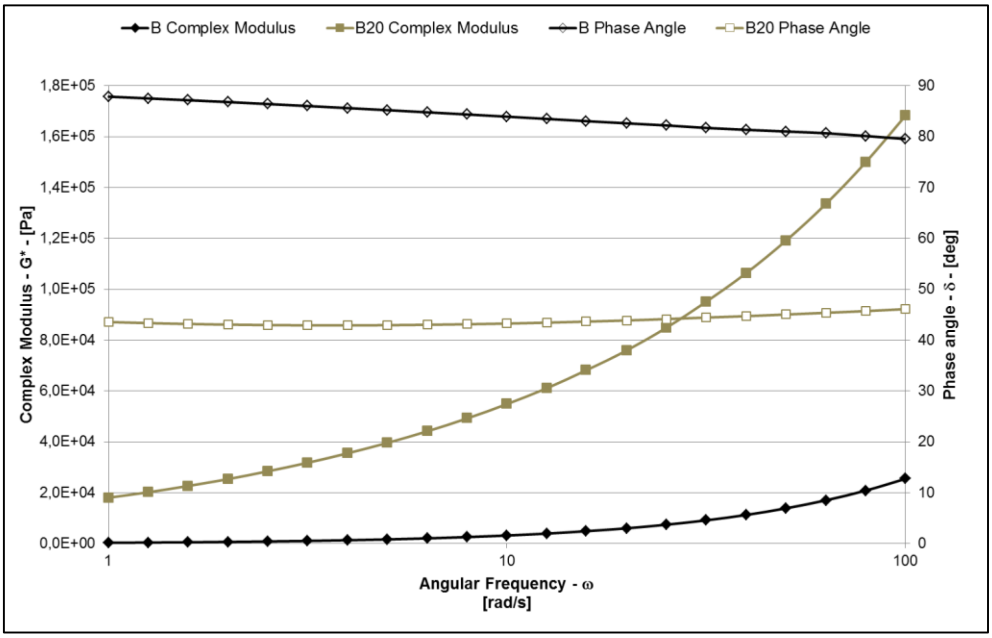

Figure 1. Frequency dependence comparative for control binders

3.2 Frequency dependence for 20% CRM binders with WMA additives

The frequency dependence for 20% CRM binders can be observed in Figure 2 and Figure 3. The reference temperature is 30°C.

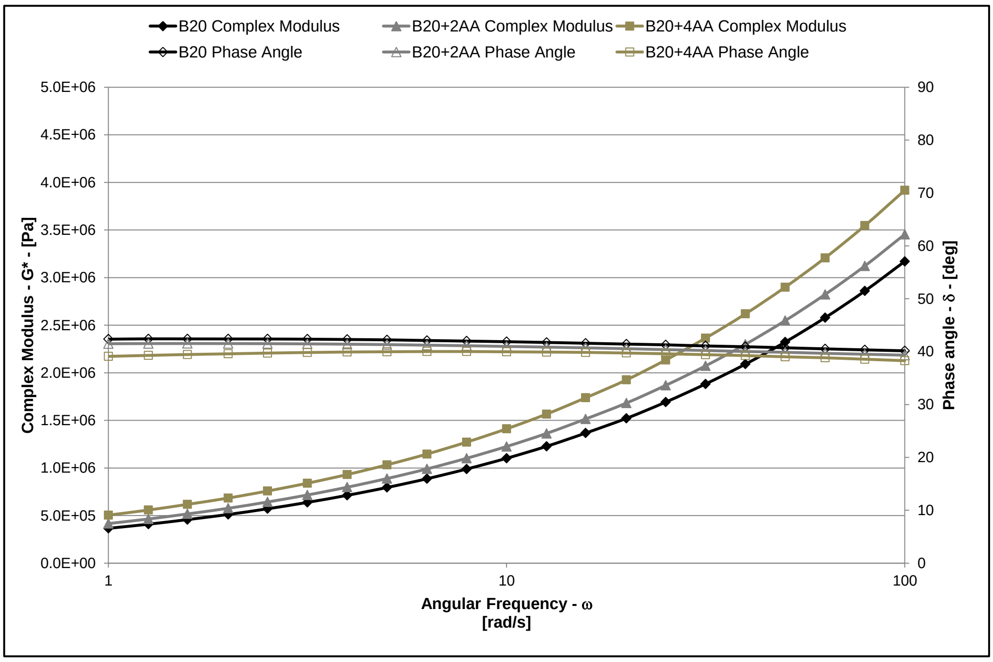

Figure 2. Influence of additive AA on frequency dependence of B20

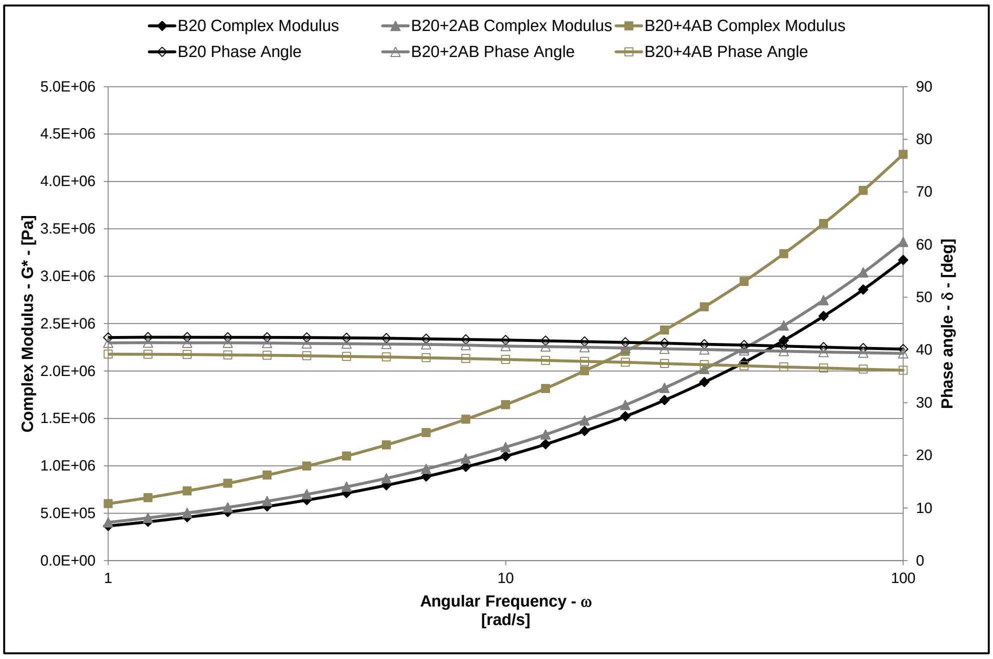

Figure 3. Influence of additive AB on frequency dependence of B20

The effect of the WMA additives on all the binders studied was the same: they increased the complex modulus G* and decreased the phase angle of the respective control binder. This means that the mixtures containing the additives will have superior stiffness and elasticity.

In Figure 4 the complex modulus and the phase angle of the binders containing 20% of rubber and 4% of the waxes studied are plotted together so they can be compared. The wax that increased the stiffness and the elasticity the most was the additive AB.

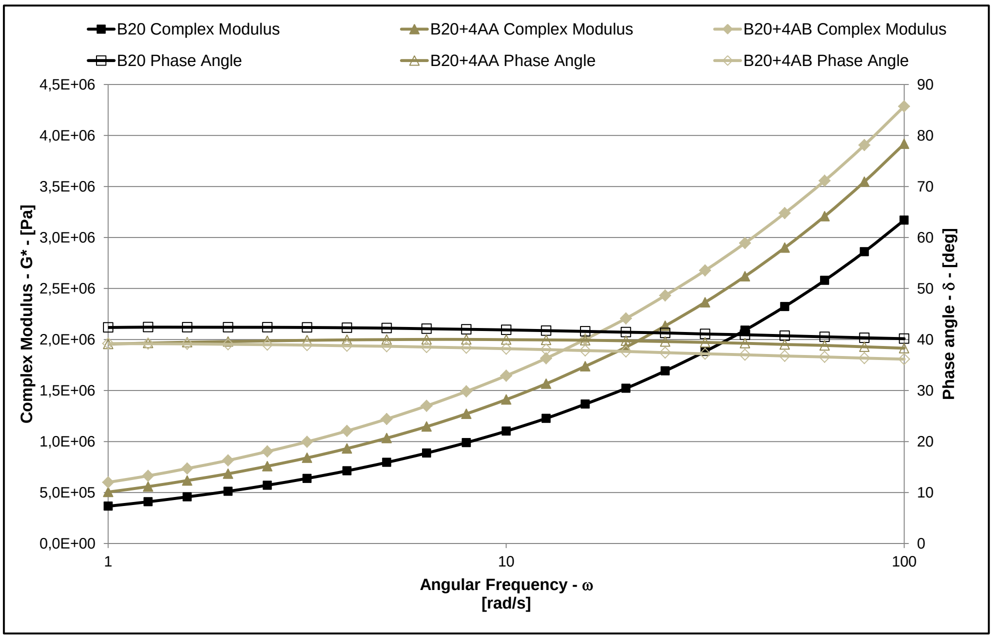

Figure 4. Frequency dependence comparative for 20% CRM binders

3.3 Master curves comparative for control binders

Figure 5 illustrates a comparative study between the control binders of this study. Considering the complex modulus master curves, it can be observed that the addition of rubber shifts the curves on higher values in the low-frequency region (high temperatures) and on lower values in the high-frequency region (low temperatures).

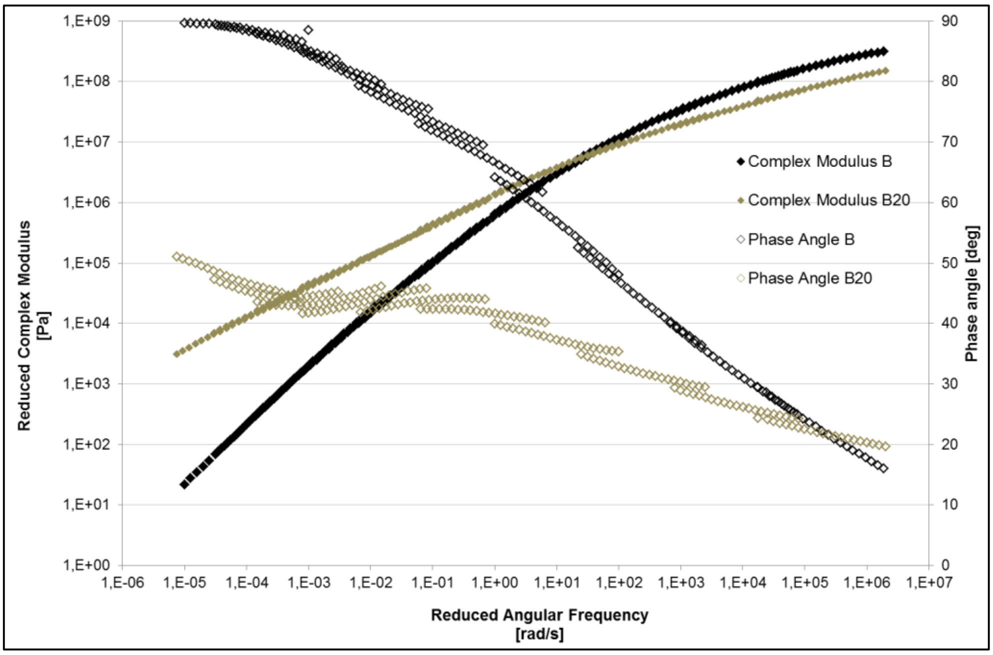

Figure 5. Master curves comparative for control binders B and B20

Compared to the base bitumen, this implies a double effect on the resistance of the pavement regarding both permanent deformation resistance at high temperatures and thermal cracking at low temperatures. At high frequencies (rapid load conditions), B20 has a lower value compared to B. This means that the addition of rubber improves the binder behaviour at low temperatures. On the other hand, at low frequencies (slow load conditions), the addition of rubber shows a relevant increase in the binder stiffness and thus, the resistance to permanent deformation is improved.

The phase angle curves also show evident differences; a marked inflection closely due to the presence of rubber may be observed. The data series recorded at different temperatures appear quite disjointed. It can also be seen that the addition of rubber to the base bitumen causes the phase angle to decrease over a wide range of frequencies. This demonstrates that the addition of rubber makes the binder more elastic, especially at lower frequencies, improving the binder behaviour.

3.4 Master curves for 20% CRM binders with WMA additives

In Figure 6 and Figure 7 the effects of the WMA additives on a 20% CRM binder are illustrated.

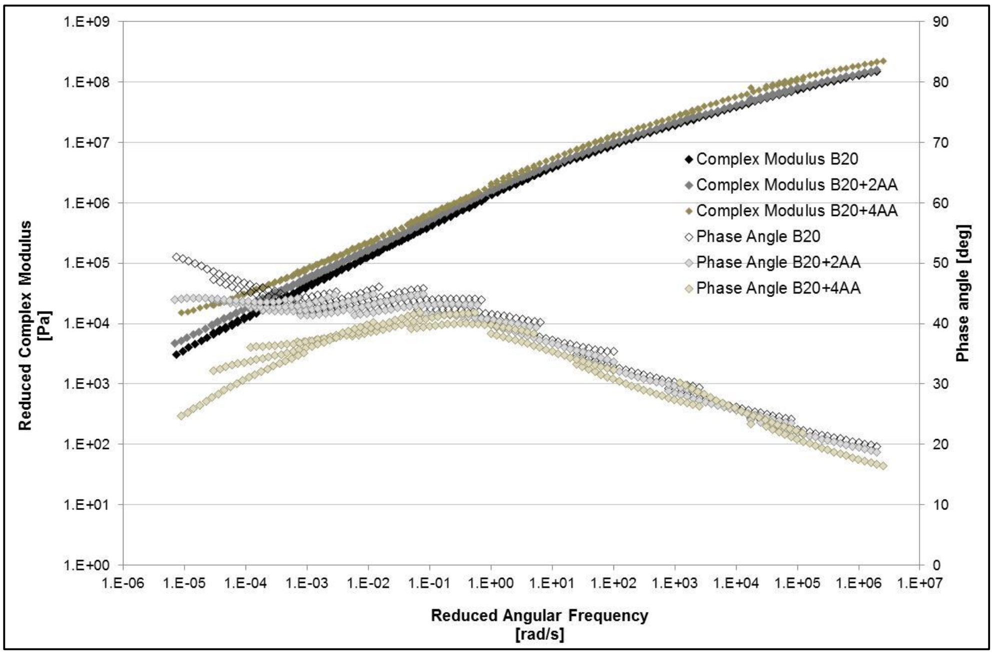

Figure 6. Master curves for B20 with additive AA

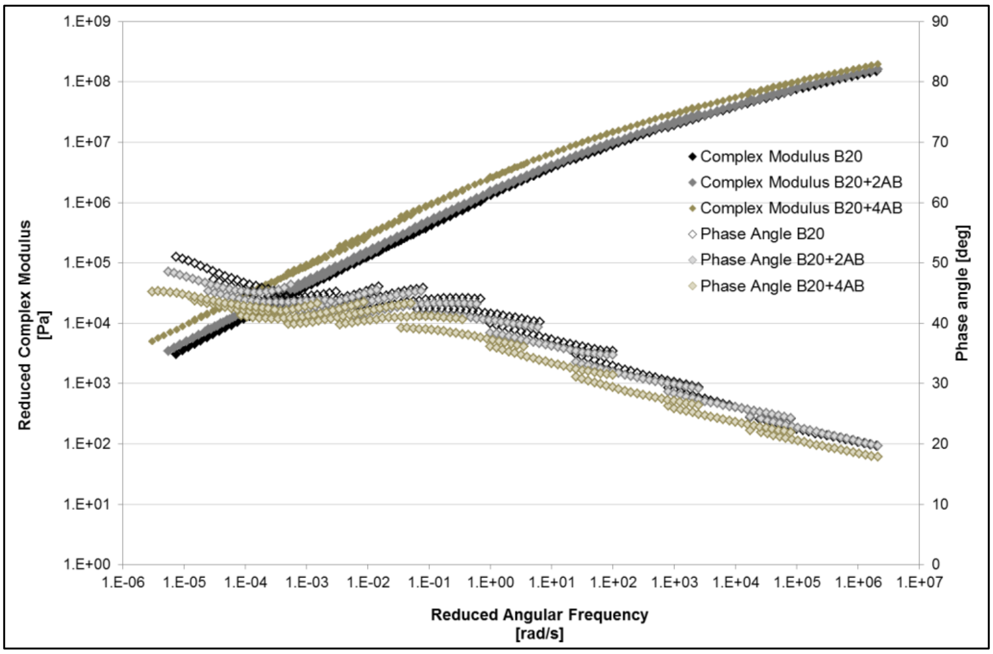

Figure 7. Master curves for B20 with additive AB

The increasing content of additive shifts the complex modulus master curves on higher values in both low and high frequency regions. Hence, the stiffness of the control binder B20 is increased both at low and

high temperatures. In consequence, the binder behaviour will be significantly better at high temperatures avoiding permanent deformation and will be slightly worse at low temperatures.
It is also noteworthy that over the wide range of frequencies, the phase angle decreases as the amount of additive increases, thus, all the waxes studied improve their elasticity by 20% CRM. Apart from this, the addition of wax and rubber to base bitumen leads to an inflection in the curves, shifts them on lower values and the curves becomes more disjointed.

In Figure 8 a comparison between both additives studied for B20 is presented.

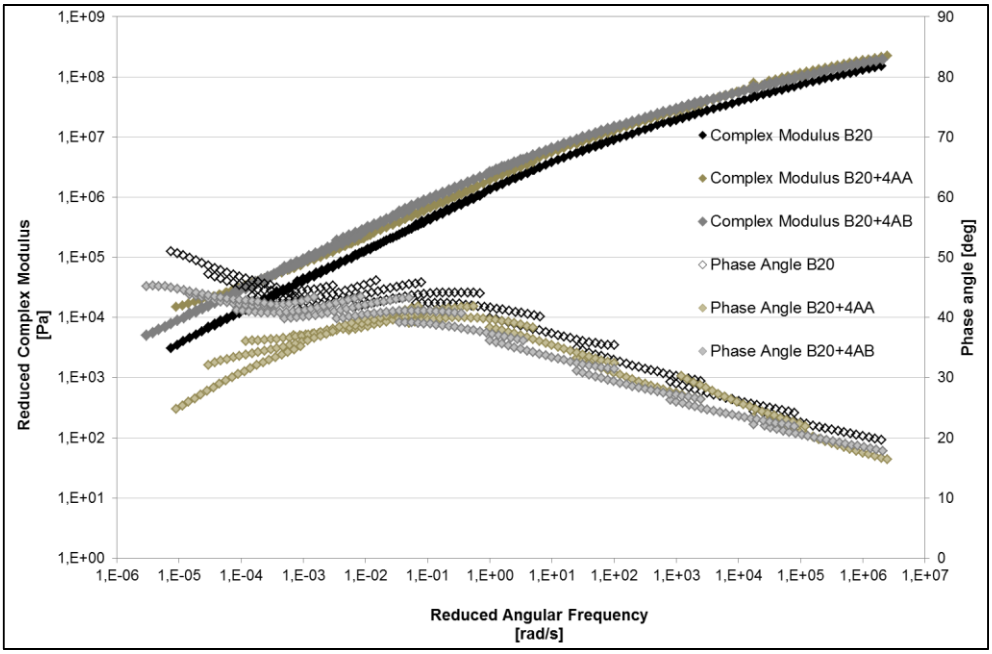

Figure 8. Master curves comparative for 20% CRM binders

As can be observed in the complex modulus master curves, at higher and lower frequencies both additives have a similar effect. The additive AA present a lowest value in the phase angle in the higher and lower frequencies, thus, this is the additive which increases the elasticity the most. In the medium-frequency region the binder with the lowest phase angle is the one containing the additive AB. It appears that the additive which increases the stiffness the most is AB although both waxes show similar values.

4. CONCLUSIONS

In this study, in order to evaluate the high and intermediate temperature properties of rubberized binders with warm asphalt additives, binders were manufactured using a single crumb-rubber modified (CRM) source (ambient), a 20%CRM binder (20% by modified binder weight) and two Montan waxes as WMA additives at 2% and 4% content.
Each binder was tested using a dynamic shear rheometer (DSR) which allows defining elastic, viscoelastic and viscous properties of bitumen over a wide range of temperatures and frequencies.
From these test results, the following conclusions were drawn for the binders created for this study:
For all of the binders studied, the effect of the WMA additives was the same: they increased the complex modulus G* and decreased the phase angle of the control binder. This indicates that the mixtures containing the additives will offer improved stiffness and elasticity.
On the other hand, with the addition of rubber, the stiffness and the elasticity of the net bitumen increased. Therefore, the pavements containing the binders with rubber and any of the additives studied will increase notably their stiffness and elasticity, hence, their resistance to permanent deformation.
The complex modulus master curves showed that the addition of rubber shifted the curves on higher values in the low-frequency region and on lower values in the high-frequency region. This implies an improvement on the resistance of the pavement regarding both permanent deformation resistance at high temperatures and thermal cracking at low temperatures.
The master curves of the CRM binders with the WMA additives have highlighted the significant improvements produced by the additives regarding the mechanical behaviour and the elasticity for the whole temperature range; the complex modulus (stiffness) is increased at the high temperatures avoiding

permanent deformation and the phase angle curve is shifted on lower values over a wide range of frequencies.
The increased content of additives slightly shifted the complex modulus master curves on high frequency regions, increasing the stiffness at low temperatures.

To summarize, the master curves of the CRM binders have highlighted the significant improvement given by rubber and the additives. On one hand, the addition of rubber shifted the curves on higher values in the low-frequency region (high temperatures) and on lower values in the high-frequency region (low temperatures). This shows that compared to a conventional mixture which contains the neat bitumen, the mixtures containing rubber in the binder will improve the resistance of the pavement to rutting at high temperatures and to thermal cracking at low temperatures.
On the other hand, a higher content of any of the Montan waxes studied increased notably the elasticity of the control binder as the phase angle decreased over a wide range of frequencies. Nonetheless, they also shifted the complex modulus master curves slightly in the high frequencies region, which implies an increased stiffness at low temperatures.

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