LABORATORY STUDIES ABOUT PHYSICOCHEMICAL CHANGES IN BITUMEN WHEN WORKING AT LOW TEMPERATURES

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ABSTRACT

RTFOT has considered to be a good method to simulate in laboratory the ageing of the binder when mixed with aggregates in the asphaltic plant. In this paper, the RTFOT is used as a conditioning test that could simulate the physicochemical changes produced in the binder when mixed in the laboratory with the aggregates at temperatures corresponding not only to the Hot mix asphalt (HMA), but also to Warm mix asphalt (WMA) and Half warm mix asphalt (HWMA) techniques.

After the RTFOT, the residues obtained, are tested in the PAV in order to simulate, according with SUPERPAVE, the behavior in the service life of these binders and determine the influence of the temperature of mixing in the long term ageing.

In all cases the binders have been analyzed in terms of chemical composition (ASTM 4124 fractionation, elemental composition, Infrared spectroscopy), physical properties (viscosity, penetration, ring & ball, Fraas) and rheological behavior, in order to evaluate the physicochemical changes produced during the ageing at different mixing temperatures in Laboratory and how these changes affect the long term ageing of the binders in accordance with SUPERPAVE methods.

Keywords: RTFOT, PAV, WMA, HWMA, ageing

1. INTRODUCTION

In the last years a number of technologies have been developed to lower the production, paving and compaction temperature of asphalt mixes. These techniques (WMA and HWMA) have proved to be successful, and provide economic and environmental benefits.

Nevertheless, as a consequence of the bitumen lower process temperature, the physicochemical changes that take place in its structure, can influence of form different from the usual one, the behavior of the road at both, short and long term. Bitumen, as a carbon based product, suffers from oxidation when heated in oxygen presence, and the physicochemical changes that take place in the bitumen structure depend on the temperature at which it has been processed in the asphaltic plant. If the temperature is lower than usual, presumably these changes could be produced in lower extension, which determines the behavior at least, in the first stages after placement of the mixture on the road.

In addition, the evolution of the WMA and HWMA after long term aging remains unknown. In the state of the technology, is very important to determine if the properties after short term aging are masked after the long term aging. And establish if this masked phenomenon is produced in such a manner that after enough time the properties becomes the same, independently of the conditions used for short term aging.

In order to study these physicochemical changes in laboratory, RTFOT has been used to simulate the oxidation process at different temperatures, which correspond to those used in the HMA, WMA and HWMA techniques. After that, the PAV test has been applied to these residues in order to know the effects of the long term aging.

All the products obtained in the different oxidation conditions have been characterized using conventional physical tests and chemical analysis used as aging indicators like infrared spectroscopy, elemental composition and ASTM 4124 fractionation.

2. ROLLING THIN FILM OVEN TEST (RTFOT)

This test is used in laboratory as a conditioning method according to EN 12607-1, and it is carried out at a temperature similar to the production temperature of the HMA (163ºC). But with the continuous development of techniques aimed to reduce the temperature of the asphaltic mixes (like WMA and HWMA techniques), a modification of the RTFOT has been suggested in this paper, to take into account the lower temperature used in the manufacture of the asphalt mix.

Consequently, the parameter that has been changed in the RTFOT is the temperature, while the duration time, sample weight and air flow used in the original test remain the same. Nevertheless, in order to obtain a binder film in the wall glass test vessel similar to that reached in the high temperature test, a previous stage has been introduced, consisting in heating up the bitumen to 160ºC for ten minutes in nitrogen atmosphere, into the RTFOT glass vessel while rotating inside the oven. In this way, one can be sure that the film formed has a thickness similar to the standard test. And the surface exposed to the air is the same for all the temperatures, although the film is not refreshing in the same way because of differences in binder viscosity.

The temperatures chosen for the RTFOT have been those corresponding to the HWMA (85ºC), WMA (125ºC) and HMA (163ºC).

3. PRESSURE AGING VESSEL TEST (PAV)

This method is designed, according to SUPERPAVE procedures, to simulate in laboratory the oxidative aging that takes place during the service time of the binder in the road, also called long term aging. In the present paper, the RTFOT aged residues obtained at different temperatures have been used for PAV aging simulations. The test conditions for the PAV method have been the standard one (100ºC, 20 hours and 2.1 MPa).

Both, the PAV and RTFOT products obtained, have been characterized with the same tests, in order to show the evolution of the binder properties, during the different aging processes.

4. PHYSICOCHEMICAL CHARACTERIZATION

4.1 Physical properties

The results obtained in the conventional tests of physical properties of RTFOT and PAV residues are shown in table 1.

Table 1 : Physical properties

Test	Standard	Units	Original Bitumen A	RTFOT 85ºC B	RTFOT 125ºC C	RTFOT 163ºC D
Penetration	EN 1426	0,1 mm	58	50	43	37
Ring & Ball	EN 1427	ºC	50,0	52,2	53,4	57,6
IP	EN 12591 A annexe		-0,83	-0,64	-0,71	-0,13
Fraas	EN 12593	ºC	-13	-12	-12	-10
Viscosity 135ºC	EN 13302	mPa.s	493	553	578	813
Mass variation	EN 12607-1	%	---	0,01	0,016	0,024
			PAV A	**PAV B**	**PAV C**	**PAV D**
Penetration	EN 1426	0,1 mm	23	23	23	21
Increase in Penetration		0,1mm	35	27	20	16
Ring & Ball	EN 1427	ºC	65,6	66,2	66,2	69,6
Increase in Ring & Ball		ºC	15,6	14	12,8	12
IP	EN 12591 A annexe		0,37	0,47	0,47	0,85
Fraas	EN 12593	ºC	-12	-11	-8	-6
Viscosity 135ºC	EN 13302	mPa.s	1312	1385	1405	1840
Viscosity increase		mPa.s	819	832	827	1027

As expected, there is a gradual hardening of the binder as the temperature increases in the RTFOT. This can be clearly observed in the Penetration, Softening point and Viscosity values of all the residues obtained in this test.

After the PAV test, the decrease in Penetration is lower as harder is the RTFOT residue tested, also the increase in the Ring and Ball is lower. With respect to the Viscosity, except for the RTFOT residue obtained at 163ºC, the increase is the same, independently of the temperature at which they have been obtained. Consequently, the results of Penetration and Ring and Ball tests after PAV could be seen very similar for the same sample independently of the RTFOT temperature used. And the differences between them are inside the interval of precision of the method.

The important differences in the Penetration and Ring and Ball values in the RTFOT residues, could suggest that the asphaltic mix behavior when placed in the road is different depending on the production temperature of the asphaltic plant. However such differences are near zero after PAV, which could suggest that after enough service time this behavior tends to be similar.

With respect to viscosity, the increase observed after PAV aging is similar for all residues, and it follows the same tendency obtained for the RTFOT residues.

It is noticeable that A,B and C PAV residues seem to have similar temperature susceptibility, but different fragility.

4.2 Elemental composition

Original bitumen, RTFOT residues and PAV aged products, have been analyzed by means of a Carlo Erba instrument, in order to determine the elemental composition (C,H,N,S and O). The information provided by this test, show the oxygen gaining as a consequence of the oxidation process and the variation of the ratio C/H as possibly condensation reactions. The results obtained are presented in Table 2.

Table 2 : RTFOT and PAV elemental composition

	Units	Original Bitumen A	RTFOT 85ºC B	RTFOT 125ºC C	RTFOT 163ºC D
C	%	84,00	84,00	83,94	83,90
H	%	9,71	9,70	9,67	9,59
N	%	0,79	0,80	0,79	0,78
O	%	0,95	1,00	1,04	1,17
S	%	4,55	4,56	4,56	4,56

C/H		8,65	8,66	8,68	8,75
		PAV A	**PAV B**	**PAV C**	**PAV D**
C	%	83,88	83,69	83,70	83,67
H	%	9,68	9,70	9,70	9,65
N	%	0,81	0,81	0,80	0,79
O	%	1,13	1,32	1,36	1,40
ΔO	%	0,18	0,32	0,32	0,23
S	%	4,50	4,48	4,50	4,49
C/H		8,66	8,62	8,63	8,67

The oxidation of bitumen increases with temperature in the RTFOT. As higher is the temperature, higher is the Oxygen content. With respect to the composition after PAV, the Oxygen content is also higher, depending on the content of the RTFOT residue. No changes were observed in the sulfur and nitrogen content.

4.3 ASTM 4124 composition

The chemical composition of the bitumen has been determined according to the standard procedure ASTM 4124 (Corbett Method). This method is aimed to separate bitumen into four fractions (asphaltenes, saturates, naphtene aromatics and polar aromatics). The asphaltene fraction is obtained by precipitation in n-heptane, and the rest of fractions contained in the maltenes are separated by adsorption on alumina and desorption with solvents of increasing polarity.

Fractional composition can provide valuable information about the evolution of the binder chemical components, with the processing temperature and service time. The Gaestel index (Ic), defined as the ratio of the sum of asphaltenes and saturates to the sum of polar aromatics and naphtene aromatics, is also an interesting parameter, so that it can show the colloidal changes of the binder from a sol state to a gel state as a consequence of the aging.

Table 3 : ASTM 4124 fractions

	Units	**Original Bitumen A**	**RTFOT 85ºC B**	**RTFOT 125ºC C**	**RTFOT 163ºC D**
Asphaltenes	%	17,7	17,2	17,2	18,4
Saturates	%	8,0	8,5	9,7	9,7
Polar aromatics	%	31,5	31,3	28,6	27,8
Naphtene aromatics	%	42,8	43,0	44,5	44,1
Ic		0,34	0,34	0,36	0,39
		PAV A	**PAV B**	**PAV C**	**PAV D**
Asphaltenes	%	22,7	23,7	24,3	23,3
Saturates	%	9,0	8,5	7,7	8,1
Polar aromatics	%	34,7	35,1	35,1	34,7
Naphtene aromatics	%	33,6	32,7	32,9	33,9
Ic		0,46	0,47	0,47	0,46

In the case of the RTFOT, a tendency was observed, the increase of the Saturates fraction and the decrease of the Polar aromatics content. The Asphaltenes and Naphtene Aromatics contents remain constant. As a result, the Gaestel Index increases slightly with the test temperature.

The PAV test has provided an increase in the Asphaltene content of all the RTFOT residues, and a decrease of the Naphtene aromatic fraction, which is turned into Polar aromatic, as many studies have shown previously [1]. The content of Saturates changes slightly, showing the inert nature of this fraction to the aging process. This changes have been produced in such a manner that final composition of the four PAV residues is similar, independently of the RTFOT temperature. Consequently, the Gaestel Index is the same for all the residues.

Again, for this sample, a masked phenomenon has been observed, the composition of all the PAV residues, measured according to ASTM 4124, are similar, independently of the RTFOT temperature used. This phenomenon suggest that after enough time, the aging level of the bitumen in service could be similar, independently of the temperature at which the asphalt mix has been manufactured.

4.4 Fourier Transform Infrared spectroscopy

This spectroscopy technique, is used to identify functional groups in organic compounds. In the case of the bitumen, carbonyl (C=O) and sulfoxide (S=O) groups are of interest for the aging process study, because these functional groups increase in number with the degree of oxidation of the bitumen, and therefore the absorption peak in the infrared spectrogram is also increased.

The carbonyl area is calculated between 1653-1752 cm^{-1} , this region of the infrared spectrogram covers the absorption peaks for carboxylic acids, ketones and anhydrides, while the sulfoxide area is calculated in the 1030 cm^{-1}peak.

Based on the areas of these two peaks, two structural indices have been defined [2].

Carbonyl index= $A_{1700}/\sum A$

Sulfoxide index= $A_{1030}/\sum A$

Where $\sum A$ represents the sum of areas of the Infrared spectrum bands centered between 2000 and 600 cm^{-1}

Table 4 : FTIR spectrogram results

Peak	Group	Original Bitumen A	RTFOT 85ºC B	RTFOT 125ºC C	RTFOT 163ºC D
A_{1700} cm^{-1}	C=O	0,382	0,588	0,980	0,164
A_{1030} cm^{-1}	S=O	0,304	0,414	0,429	0,472
$\sum A$		179,294	243,339	165,326	142,081
Carbonyl index		0,21	0,24	0,26	0,33
Sulfoxide index		0,17	0,17	0,18	0,19
Carbonyl index gaining[1], %		0	14	24	57
Sulfoxide index gaining[1], %		0	0	6	12
		PAV A	**PAV B**	**PAV C**	**PAV D**
A_{1700} cm^{-1}	C=O	0,768	0,539	0,721	1,062
A_{1030} cm^{-1}	S=O	0,588	0,392	0,510	0,709
$\sum A$		162,187	87,384	121,655	161,161
Carbonyl index		0,47	0,61	0,60	0,66
Sulfoxide index		0,36	0,38	0,42	0,44
Carbonyl index gaining[1], %		124	190	186	214
Sulfoxide index gaining[1], %		112	123	147	159

[1] Referred to the carbonyl and sulfoxide index of the original bitumen

In the RTFOT, carbonyl and sulfoxide indices increase with the test temperature, which is consistent with the increase in the percent weight of oxygen calculated in 2.1. Carbonyl index seems to be more sensitive to changes in the RTFOT temperature than sulfoxide.

The PAV test has provide a higher increase in both indices with respect to RTFOT, indicating that this test provides a much more severe oxidation [3].

Nevertheless, according to the oxygen content, PAV A residue and RTFOT D residue have similar percentage in this element, but PAV A has both indices (carbonyl and sulfoxide) much higher than RTFOT D residue, this may be due to a transformation of the C-O bonds of the original bitumen into C=O in the PAV test, but not in the RTFOT .

In that the sulfoxide index, the sulphur content not vary after the PAV test according to Table 2, and it is oxidised to S=O, while RTFOT does not provide that change in the sulphur.

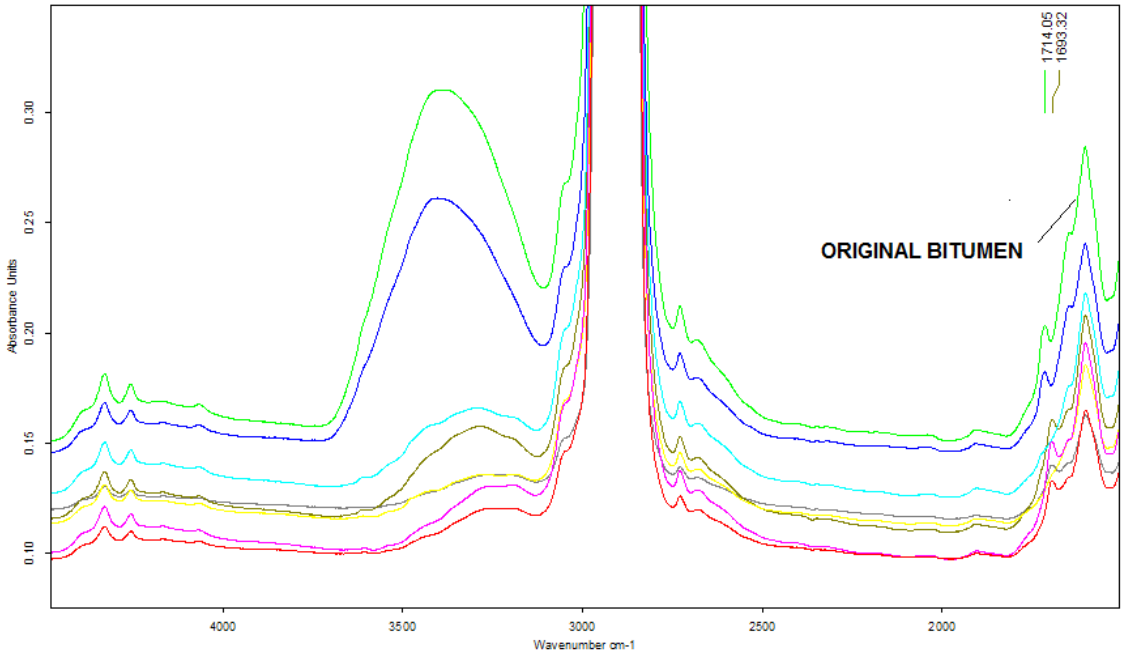

Figure 1: FTIR spectrogram, carbonyl region

4.5 Rheological characterization

The viscoelastic properties may be also used to suggest the evolution of the bitumen with the process temperature in both, the asphaltic plant and the service life. Some parameters like complex modulus (G*) and phase angle (δ) may vary with the aging degree of the bitumen. A Dynamic Shear Rheometer has been used to quantify the viscoelastic characteristics of the original bitumen, RTFOT and PAV residues, over the range of temperatures studied. The results obtained could be observed in Table 5. Black Diagram after RTFOT and PAV are shown in figures 2 and 3, respectively.

Table 5 : SHRP characterization

SHRP test	Units	Original Bitumen A	RTFOT 85ºC B	RTFOT 125ºC C	RTFOT 163ºC D
Dynamic Shear (G*/sinδ) min 1,0 KPa	KPa	1,0	1,0	1,0	1,0
Temperature	ºC	69	71	71	77
Dynamic Shear (G*/sinδ) min 2,2 KPa	KPa	2,2	2,2	2,2	2,2
Temperature	ºC	65	65	65,5	70
		PAV A	PAV B	PAV C	PAV D
Dynamic Shear (G*(sinδ)) max 5000 KPa	KPa	5000	5000	5000	5000
Temperature	ºC	21,9	21,5	21,9	22,9

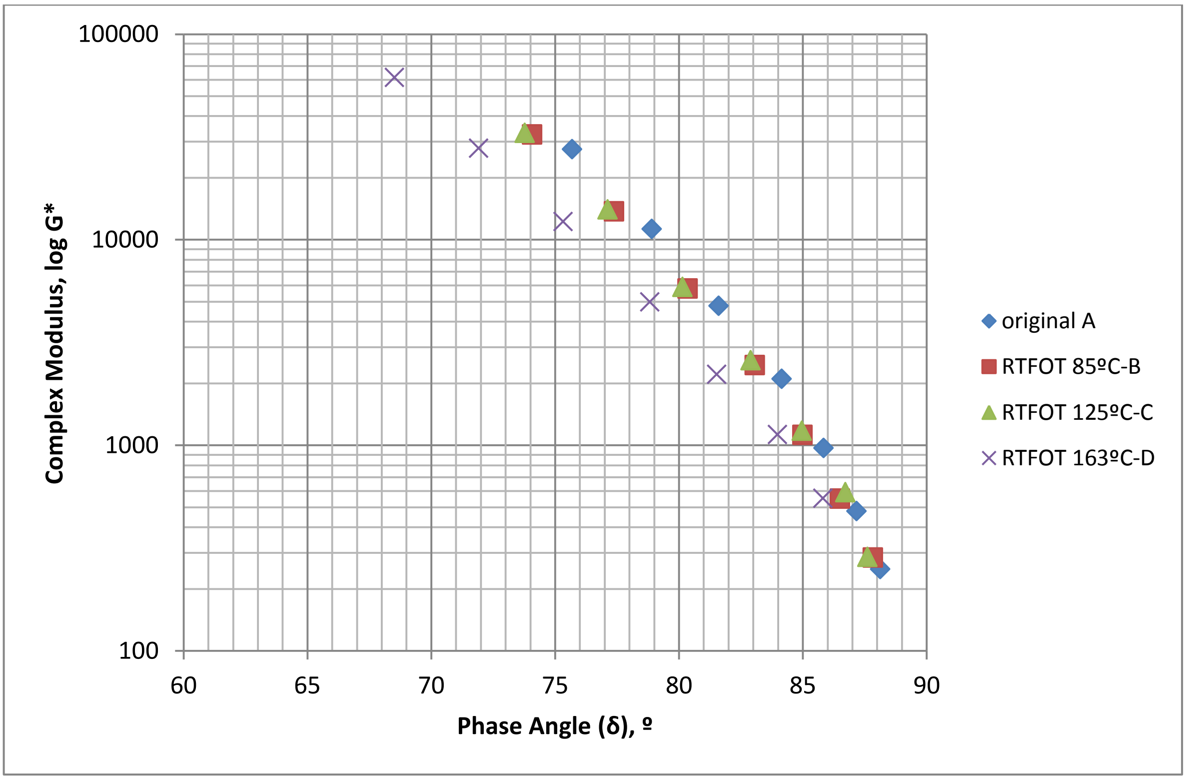

Figure 2: Black Diagram of RTFOT residues

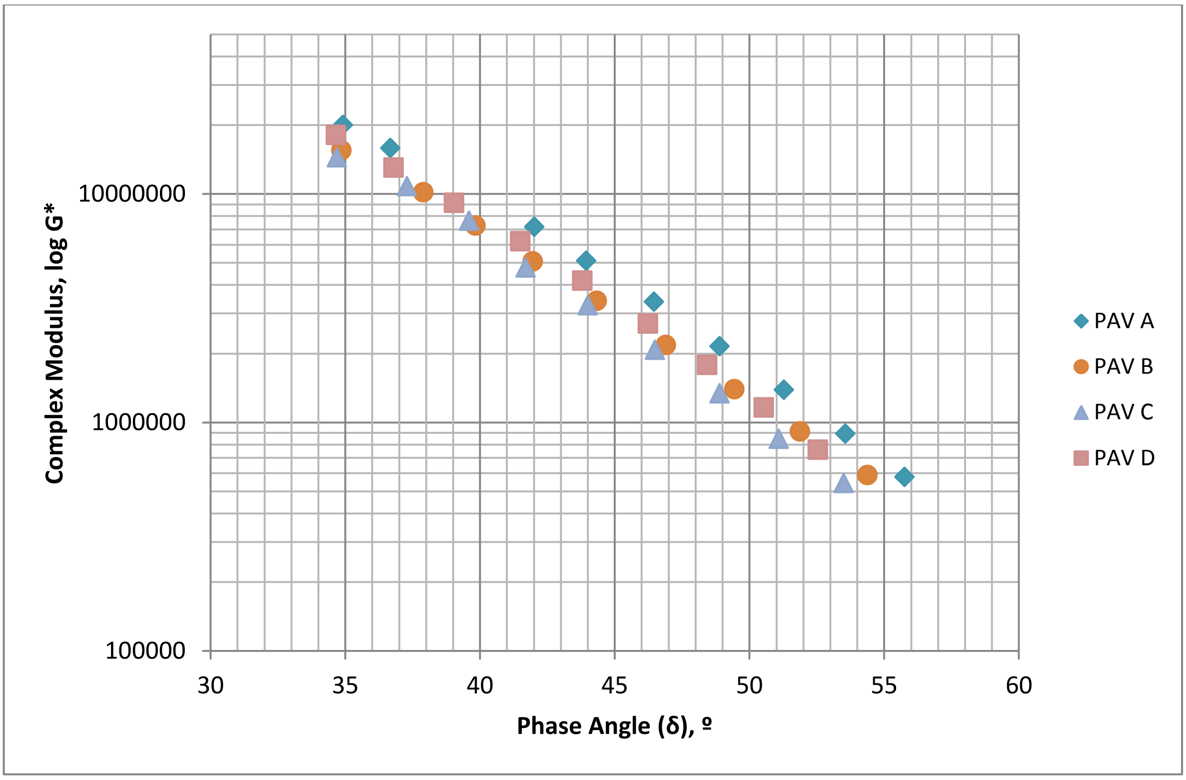

Figure 3: Black Diagram of PAV residues

As can be seen, there is a difference between the Black Diagram of the RTFOT residues obtained at 163ºC (figure 2) and the other. In terms of classical interpretation of the rheological data, the RTFOT residue obtained at 163ºC shows a more elastic behavior, and higher temperature in the rutting factor.

However, for the PAV residues, there are not differences between the four curves (figure 3 and 5). Again, the conclusions are the same. While differences on RTFOT can be appreciated depending on the temperature, in the PAV, the curves tend to be the same. From a performance point of view, the results suggest that after enough time the behavior of the binder tends to be the same, independently of the temperature of mixing and laying.

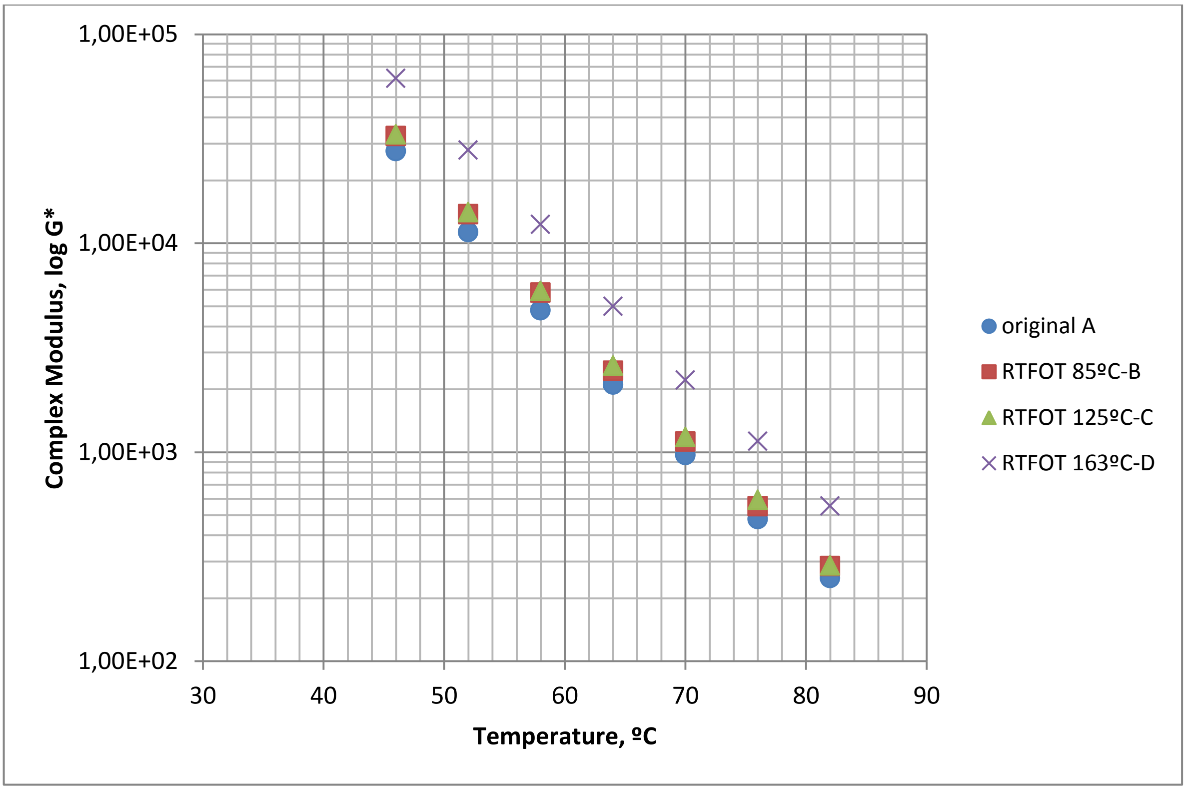

Figure 4: RTFOT residues, G* vs temperature

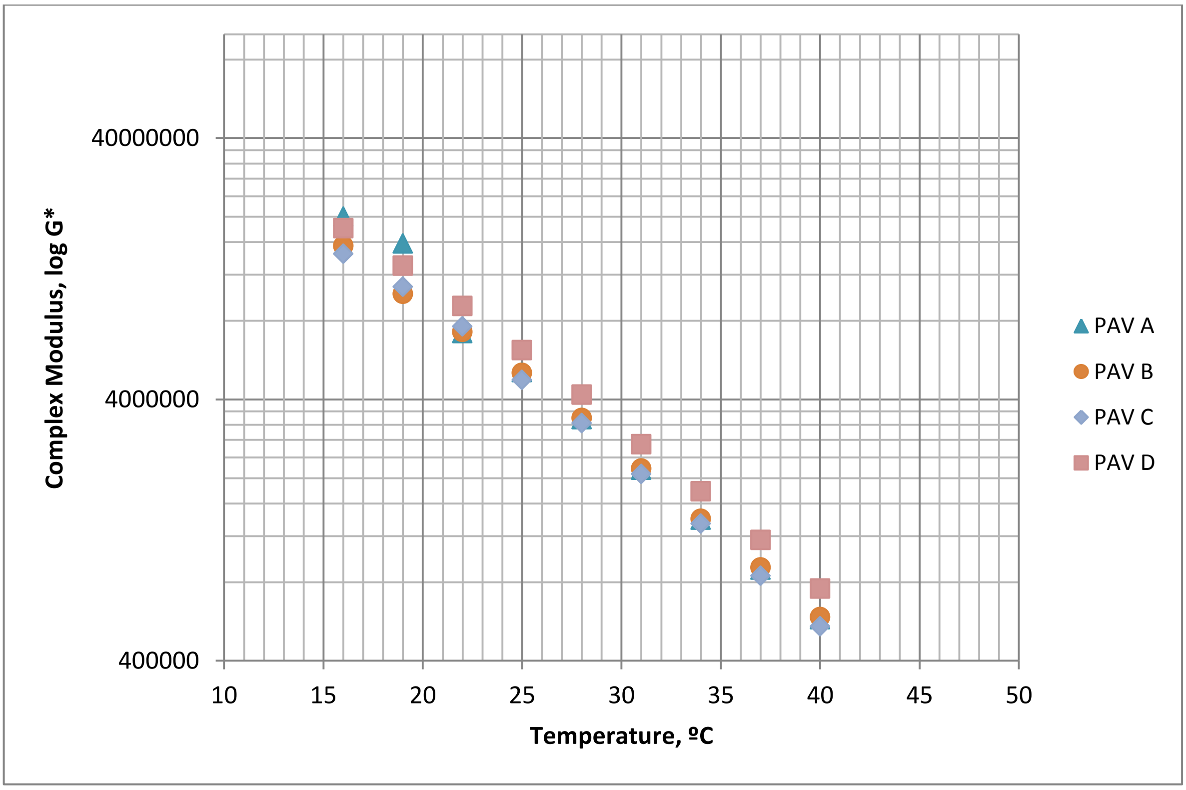

Figure 5: PAV residues, G* vs temperature

5. CONCLUSIONS

Short term aging, measured by means of the RTFOT of bitumen, depends on the temperature used. Physical properties such as Ring and Ball, Fraass Temperatures and Penetration vary as a function of the temperature used in the Test. The elemental composition and carbonyl and sulfoxide indices also show differences, according to the temperature used in RTFOT. These phenomenons suggest that there will be differences in the binder properties, according to the temperature used in the manufacture of the asphalt mix.

However, in the Long term aging, measured after PAV Test, the results of the conventional tests, elemental composition and Performance Related tests measured, tends to be the same, independently of the temperature used in the RTFOT. These phenomenons could indicate that after enough time, the behavior of the binder, tends to be the same, independently of the temperature of mixing and laying.

From a point of view of Specifications, the results obtained in this work could be relevant, because the long term aging results could mask the conditioning results.

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