Long term properties assessment of HMA and WMA with RAP through the apparent molecular weight distribution variation of the bitumen

Miguel Perez-Martinez[1, a], Paul Marsac[1, b], Andrea Themeli[1, c], Emmanuel Chailleux[1, d], Manuela Lopes[2, e], Thomas Gabet[1, f], Ferhat Hammoum[1, g]

[1] *Department of Transport Infrastructure Materials, IFSTTAR, Bouguenais, France*
[2] *Polytechnic School University of São Paulo, University of São Paulo, São Paulo, Brazil*

[a] miguel.perez-martinez@ifsttar.fr
[b] paul.marsac@ifsttar.fr
[c] andrea.themeli@ifsttar.fr
[d] emmanuel.chailleux@ifsttar.fr
[e] mmlengenharia@gmail.com
[f] thomas.gabet@ifsttar.fr
[g] ferhat.hammoum@ifsttar.fr

Digital Object Identifier (DOI): dx.doi.org/10.14311/EE.2016.190

ABSTRACT

The δ-method previously developed in IFSTTAR, is employed to determine the long term properties of asphalt mixes with reclaimed asphalt. This δ-method allows the calculation of apparent molecular weight distribution from rheological measurements. Its potential benefits as a tool for better understanding the key points of bituminous mixes recycling process is assessed. The study is carried out on twelve mixtures including two different types of warm mix asphalt techniques (surfactant and foamed bitumen) combined with the addition of high rates of reclaimed asphalt pavement. Samples are submitted to an oxidative aging process based on the protocol proposed by the RILEM Technical Committee-ATB TG5 consisting in two separate aging phases, a short term stage (corresponding to transport and spreading) and a long term aging equivalent to service life. The changes observed on the apparent molecular weight distribution with ageing and/or when reclaimed asphalt is added show that the δ-method could help to characterize structural ageing according to the different mixtures processes and its evolution. This may allow a better assessment for the long term performances of bituminous mixes depending on the manufacturing process.

Keywords: Ageing, Durability, Reclaimed asphalt pavement (RAP) Recycling, Rheology, Warm Asphalt Mixture

1. INTRODUCTION

Throughout their service period in pavement structures and independently of the traffic supported, asphalt mixtures used in road construction are exposed to various environmental solicitations, affecting significantly their mechanical properties. This ageing effect should be taken into account for a proper assessment of the durability of the structure. The current knowledge on ageing was essentially gained from practical experience on traditional asphalts mixes and typically on Hot Mix Asphalts (HMA). However, the road industry has embraced recycling and developed new techniques, in particular related to Warm Mix Asphalt (WMA) in order to limit environmental impacts. Therefore, more research is needed on bitumen ageing when recycling and WMA procedures are used, separately or combined.

In this framework, the approach followed on this study is to monitor the ageing effect through its impact on the Apparent Molecular Weight Distribution (AMWD) of 12 bitumens. They come from different asphalt mixes, including 2 types of WMA (surfactant and foamed bitumen) combined with the addition of high rates of Reclaimed Asphalt Pavements (RAP). This comparison is achieved by the application of the δ-method, a new method recently developed at IFSTTAR [1], which allows the calculation of an AMWD from rheological measurements on the extracted bitumens. Additionally, the potential of the δ-method as a tool for recycling studies is assessed.

2. MATERIALS

2.1 Bitumen

A 35/50 conventional bitumen with penetration grade of 37 (1/10 mm) and softening point of 52.8°C was selected as reference and base for further modifications. For the production of the surfactant WMA (WMA), the base bitumen was modified in laboratory with 0.5% of surfactant product, which was added and homogenized with the bitumen before mixing with the aggregates. For the foaming WMA process (FWMA), the foaming effect was obtained by injecting 1.5% of water under pressure into the hot bitumen pipe during its introduction into the mixer.

2.2 Reclaimed Asphalt Pavement

The reclaimed asphalt pavement employed on the mixtures came from the milling operation of an asphalt concrete AC10, originally located on the fatigue carousel track at IFSTTAR Nantes, France [2]. The original AC10 bitumen had the same properties as the current 35/50, but from another production date. The RAP characteristics were studied in order to ensure good homogeneity. The procedure consisted in splitting the RAP in granular fractions (0/2, 2/4, 4/8 and 8/12 mm) through sieving for the correct design of the new mixtures [3]. The penetration grade (EN 1426) and softening point (EN 1427) measured on the bitumen extracted from the RAP are respectively 18 (1/10mm) and 63°C.

2.3 Aggregates

The aggregates used in all cases were gneiss for both coarse and fine fractions (0/2, 2/6 and 6/10 mm), in order to keep the continuity on the working formulas, as it was the aggregates nature of the recycled mixture.

2.4 Mixture

An asphalt concrete AC10 mixture design, as close as possible to the initial AC10 design, was chosen to carry out the study. Table 1 and Figure 1 summarize the design and the grading curves. The bitumen content is 5.39% [3] for all the mixtures. The mixer employed is a MLPC BBMAX 80. The sequence of works lasted 75 seconds, with 15 seconds for the aggregates and fines mixing (and RAP when used) plus 60 seconds when the bitumen was added. RAP aggregates were preheated at 110°C during 2h before manufacture and virgin aggregates at different temperatures depending on the type of mixture, as Table 2 shows.

Table 1: Aggregate and RAP combination for the mixtures with and without RAP

		0%RAP	50%RAP
Aggregates	6/10	44.0	20.0
	2/6	22.5	16.0
	0/2	33.0	14.0
	Filler	0.5	-
RAP	8/12	-	25.0
	4/8	-	10.0
	2/4	-	8.0
	0/2	-	7.0
Total		100.0	100.0

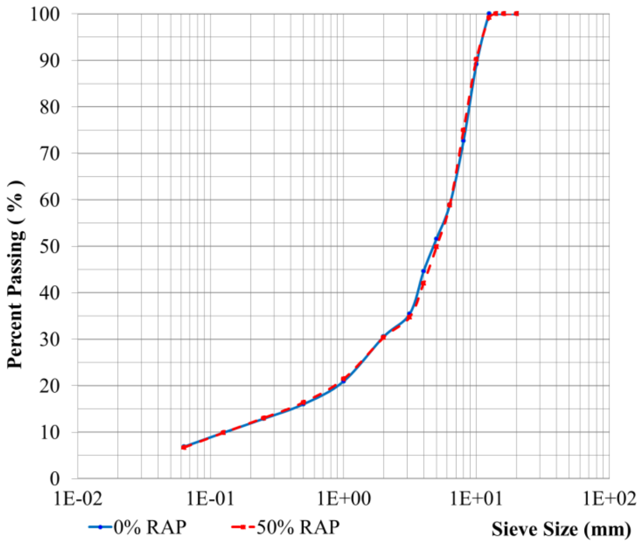


Figure 1: Mixtures gradations with and without RAP

Table 2: Bitumens studied and temperature of mixture manufacture

Mixture	Bitumen Denomination	%RAP	Ageing	Aggregates (°C)	RAP (°C)	Manufacture (°C)
Hot Mix Asphalt	HMA0	0		160	-	160
	HMA0a	0	✓			
	HMA50	50		210	110	160
	HMA50a	50	✓			
Warm Mix asphalt with surfactant	WMA0	0		130	-	130
	WMA0a	0	✓			
	WMA50	50		150	110	130
	WMA50a	50	✓			
Foamed Warm Mix Asphalt	FWMA0	0		130	-	130
	FWMA0a	0	✓			
	FWMA50	50		150	110	130
	FWMA50a	50	✓			
Bitumen always at 160°C						

3. AGEING PROCEDURE

An ageing procedure was applied on 6 of the 12 mixtures. The purpose of this step was to characterise in laboratory what happens during roads construction and service life. The ageing protocol employed is based on the ageing procedure proposed by the RILEM Technical Committee ATB TG5 [4] similar to the project of norm (PR EN 12697-52: Conditioning to address oxidative ageing). It consisted in two phases of oxidative thermal ageing of asphalt mixtures, a short term and a long term ageing.
The short term ageing was developed on the loose mix just after manufacturing, and involved its heating during 4h at 135°C before compaction. In contrast, the long term ageing was adapted due to laboratory constraints to compacted samples, keeping the mixtures during 9 days at 85°C in a ventilated oven. Figure 2 shows the procedure followed.

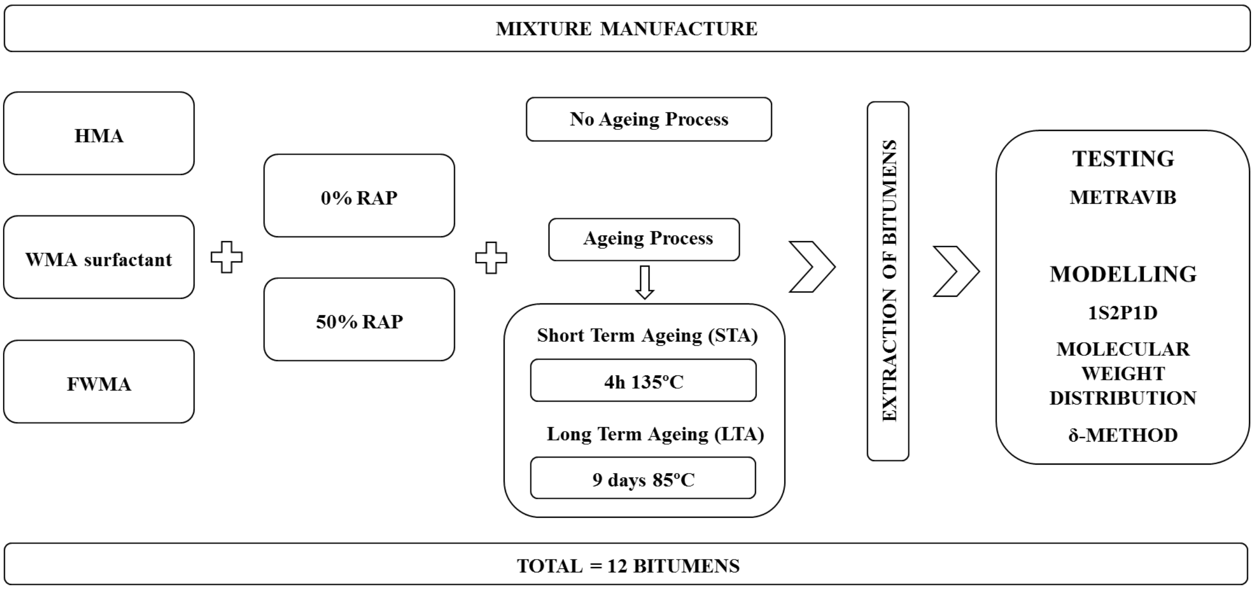


Figure 2: Mixtures manufacture procedure for bitumen extraction and testing

4. RHEOLOGICAL MEASUREMENTS

Once all mixtures were manufactured and the ageing protocols applied. The bitumen of the 12 samples was extracted and recovered using the rotary evaporator for bitumen recovery (EN 12697-3). At that point, complex modulus tests were performed using Metravib® device to assess the rheological properties of the bitumens. The complex modulus (E*) was obtained in traction-compression from -10 to 20°C and 1 to 80 Hz, on the other hand, the complex shear modulus (G*) was obtained with annular shearing geometry from 20 to 60°C and 1 to 80 Hz. The conversion from G* to E* was made assuming a Poisson's ratio of 0.5.
In Figure 3 are represented the raw data obtained from the test (a), the translation coefficients adjusted to the WLF law fitting to calculated aT(b) by the LCPC method [4], and the modulus norm and phase angle master curves at T=0°C.

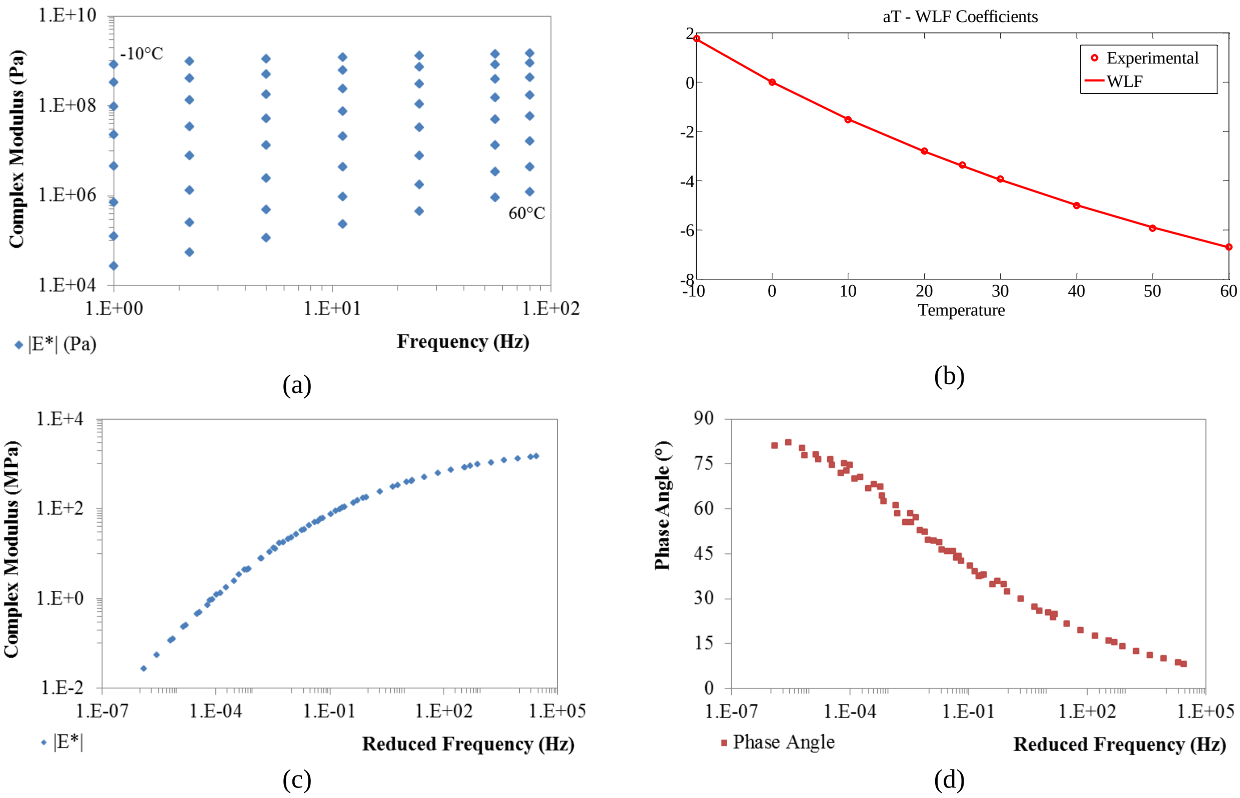


Figure 3: Rheological data from FWMA0 sample, translation coefficients and master curve at T=0°C

5. APPLICATION OF THE δ-METHOD

5.1 General principles of the δ-method

A relationship between the rheological properties and the MWD of bitumen is generally assumed in the literature [5]–[9]. The basic assumption of the δ-method [1] is that the phase angle (δ) of the complex modulus for a given frequency is proportional to the fraction of relaxed molecules at this frequency, considering the material as a combination of monodisperse MW species, therefore, a relationship between the oscillation frequency and the molecular weight can be established. Also, Zanzotto established a relationship between the crossover frequencies at T=0°C and the MW found by vapour pressure osmometry[9] defined by the formula

$$\log (MW)=2.880-0.06768\cdot\log(\omega)$$

If this equation is applied to the ω axis of the phase angle master curve, the phase angle master curve can be plotted as a function of the molecular weight. Then, according to Zanzotto's observations, δ is very sensitive to the MW of regular asphalts [9], so considering the hypothesis that the cumulative molecular weight distribution, cumf, is proportional to the phase angle master curve the formula can be obtained.

$$cumf(MW)=A+B\cdot\delta(MW)$$

Where *f* is differential distribution, *A* and *B* are the proportionality constants which are calculated from the conditions:

$$\text{for } MW\rightarrow 0;\ \delta(MW)=0, cumf(MW)=0$$
$$\text{for } MW\rightarrow\infty;\ \delta(MW)=90°, cumf(MW)=1$$
$$\text{Getting } A=0 \text{ and } B=1/(90°)$$

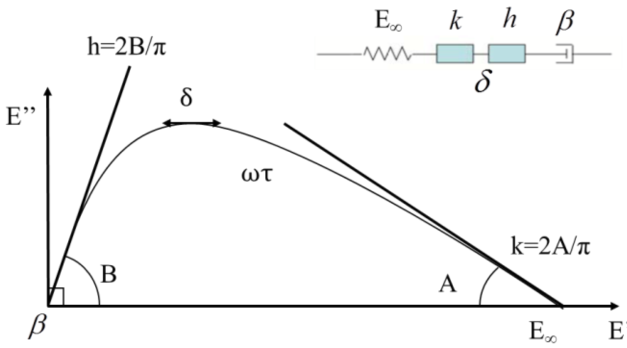
Now, differentiating the last formula, the differential molecular weight distribution (DMWD) can be calculated. The differentiation can be obtained numerically according to the equation:

$$f(MW)=\frac{dcumf(MW)}{dlogMW}\cong\frac{\Delta cumf(MW)}{\Delta logMW}$$

The numerical differentiation is carried out by applying a numerical differential step of 1/3,000 to the *log (MW)*, in order to achieve the convergence. The MWD is termed "apparent" because the proportionality to the phase angle, proved for polymers is assumed for bitumen in this study, but this assumption is to be confirmed. The word "apparent" is also used because the delta method appears to capture effect of group of molecules (like cluster of asphaltenes) and not only of individual molecule.
This differentiation requires a continuous curve, so the data should be fitted with a continuous model. The Huet-Such model [10]–[12] was chosen for this purpose as the best suited.

5.2 Huet-Such model fitting parameters

The Huet-Such model is a combination of one spring, two parabolic creep elements and one dashpot all placed in series with a coefficient that regulates the balance between the two dashpots (Figure 4). Its parameters are fitted from the experimental tests performed on the Metravib® device. The measures of phase angle and the norm of the complex modulus (E*) in function of the different temperatures and frequencies chosen are obtained by the Metravib® test. Then, the master curve at T_{ref}=0°C was calculated, and the experimental data were ready to be fitted by the rheological Huet-Such model.



$$E^*(i\omega\tau)=\frac{E_\infty}{1+\delta(i\omega\tau)^{-k}+(i\omega\tau)^{-h}+(i\omega\beta\tau)^{-1}}$$

Figure 4: Huet-Such model, equation and Cole-Cole representation

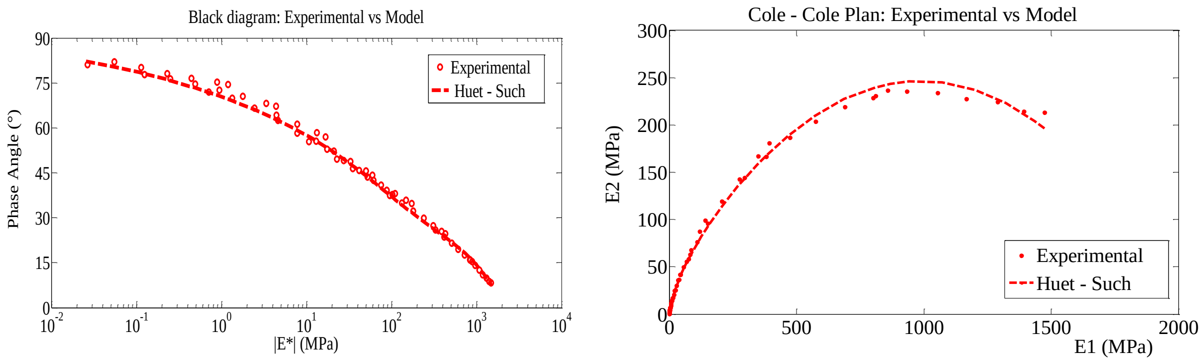


Figure 5: Experimental and Modelling results on FWMA0 bitumen sample

The fitting is carried out by an error minimisation procedure applied at the same time on the norm and the phase angle results. The adjusted parameters (E_∞, δ, k, h, β and τ) of the 12 bitumens are shown in Table 3 and one example is given in Figure 5.

Table 3: Huet-Such rheological model parameters and WLF for all bitumens at T=0°C

Mixture / Parameter	E_∞ (MPa)	δ	k	h	β	τ (s)	C1	C2
HMA0	2,178	5.91	0.28	0.65	87.3	9.38E-01	21.32	124.56
HMA0a	1,979	6.01	0.27	0.63	117.8	1.57E+00	23.51	137.95
HMA50	2,146	5.45	0.26	0.62	98.9	1.09E+00	22.09	126.59
HMA50a	2,021	6.08	0.26	0.62	132.7	1.90E+00	23.40	131.41
WMA0	2,152	5.28	0.27	0.64	88.7	5.92E-01	21.41	123.94
WMA0a	2,735	5.34	0.24	0.58	317.1	7.12E-02	18.86	121.93
WMA50	2,179	5.55	0.25	0.63	82.7	1.30E+00	18.07	91.38
WMA50a	2,171	6.30	0.27	0.64	133.4	1.41E+00	21.54	124.80
FWMA0	2,035	5.92	0.30	0.68	39.6	3.31E-01	21.69	133.85
FWMA0a	2,173	5.89	0.28	0.59	193.4	7.44E-01	25.39	147.88
FWMA50	2,128	5.89	0.29	0.68	60.0	5.38E-01	20.32	119.60
FWMA50a	2,045	6.47	0.27	0.64	141.0	8.89E-01	21.85	130.01

Just to be noted, regardless the type of bitumen and the manufacturing technique employed the value of glassy modulus (E_∞) remained constant around 2.1 GPa. Also, the first parabolic element (k), proportional to the slope of the model in the Cole-Cole plan at low temperature and/or high frequency, remained almost constant at the average value of 0.28. For the h parameter (proportional to the slope of the model in the Cole-Cole plan at high temperature and/or low frequency) its value decreases. On the other hand the value of β (viscosity of the model at very high temperatures or very low frequencies) increases either when ageing occurs or RAP is added, as it happens with the frequency multiplier τ (s).

5.3 Apparent Molecular Weight Distributions

In this section, the AMWD is plotted and described for all bitumens. The molecular weight distributions are represented with the apparent molecular weight (AMW) on the abscise axis and the corresponding probability density f(AMW) on the ordinate. Furthermore, the differences Δf(AMW) between distributions, induced by ageing or RAP addition, are also plotted with the trend line for Δf(AMW) according to the AMW in the range between 200 and 5,000 g/mol. This trend line is used as a first approach to quantify the evolutions of the distributions.

5.3.1 Ageing effect on mixtures without RAP

The change induced by ageing in the AMW distribution, Figure 6, shows a typical pattern for the 3 procedures, with decreasing low molecular weight fractions (~200 to ~1,000 g/mol) and increasing high molecular weight fractions (~1,000 to ~4,000 g/mol). It is supposed that the heaviest fraction observed are the asphaltenes(500-1000 g/mol), but recent works [13] have shown that when the concentration is sufficient, clusters from nanoaggregates of asphaltenes molecules may possibly appear. The slopes of the trend line for Δf(MW) according to the AMW in the range between 200 and 5,000 g/mol are given in Table 4. These slopes are used to quantify the degree of transfer from low to high molecular weight.

Table 4: Slope of MWD differences induced by ageing for HMA0, WMA0 and FWMA0 bitumen.

Bitumen	Slope (10E-3)
HMA0a - HMA0	3.10
WMA0a - WMA0	-2.00
FWMA0a - FWMA0	9.20

According to the slopes values, the FWMA undergoes the most important transfers with ageing, followed by the WMA and the HMA. However, a more complex pattern is detected for the WMA0a, with multiple transfers within the distribution suggesting a more complex structural rearrangement (Figure 6). Part of the oily fraction (mainly resins) seems to be absorbed by the asphaltenes and dispersed in the light matrix [7], [13] organized together into a colloidal system of molecules and clusters as seen on the literature.

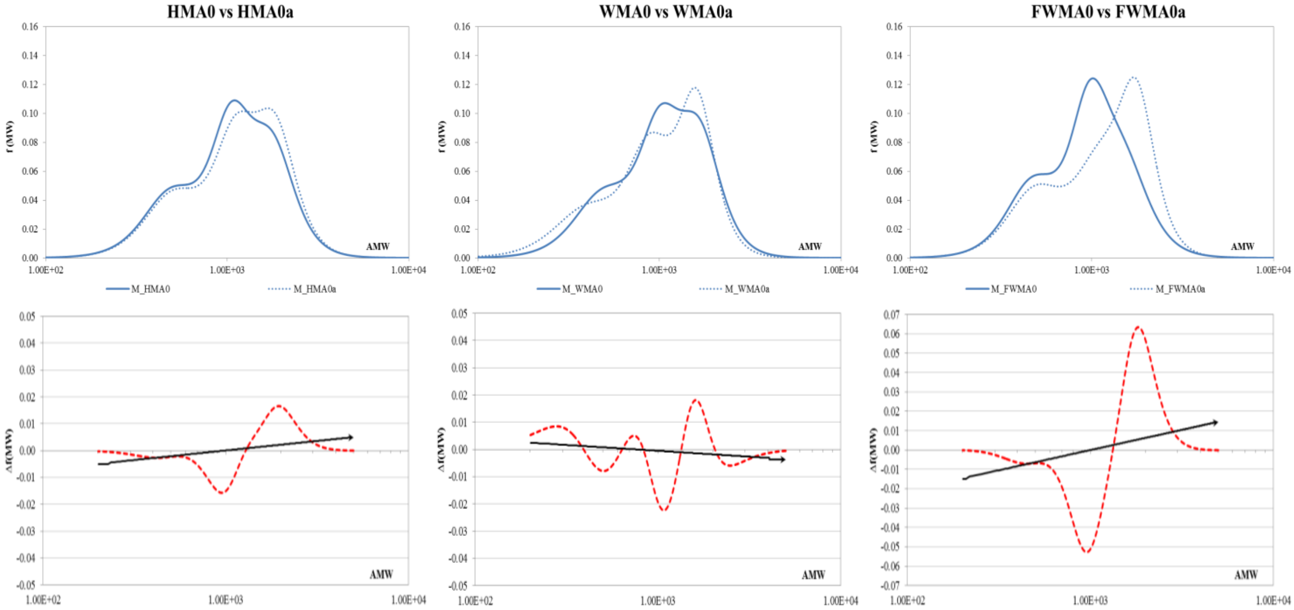


Figure 6: Effect of ageing on the MWD for HMA0, WMA0 and FWMA0

5.3.2 Ageing effect on mixtures with RAP

The same typical transfers from low to high molecular weight are observed in Figure 7. This results in a growth of the breadth of the distribution with increased fractions of higher molecular weights. In relation to the slopes values shown in Table 5, the extent of the transfers from low to high molecular weights is less marked compared to the mixtures without RAP. Being more important for the FWMA50 compared to the HMA50.

In this case, the trend towards higher AMW is softer in comparison to the bitumens without reclaimed asphalt on it. The absorption of oily resins parts from already aged bitumen to conform new clusters is less severe than what was observed for the mixtures without RAP.

Table 5: Slope of MWD differences induced by ageing for mixture with RAP

Bitumen	Slope (10E-3)
HMA50a – HMA50	3.10
WMA50a – WMA50	1.80
FWMA50a – FWMA50	5.30

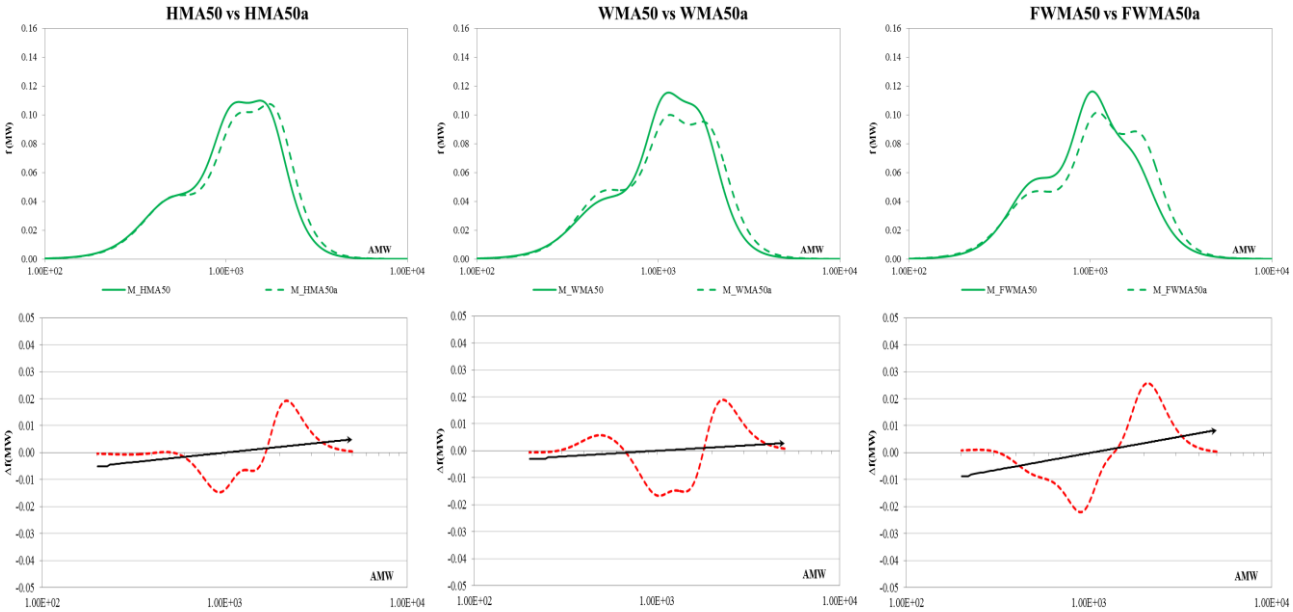


Figure 7: Effect of ageing on the MWD for HMA50, WMA50 and FWMA50

5.3.3 Effect of RAP addition

Along with the slopes presented in Table 6, the transfer from low to high molecular weight is again observed in all cases. The slope increment observed depending on the manufacturing procedure may explain the less ageing experienced by the bitumen through the foaming process compared to the surfactant or the conventional procedure. The addition of RAP affects the presence at high AMW of a peak or trend, where the clusters from absorption of resins and asphaltenes aggregate seems to appear (Figure 8).

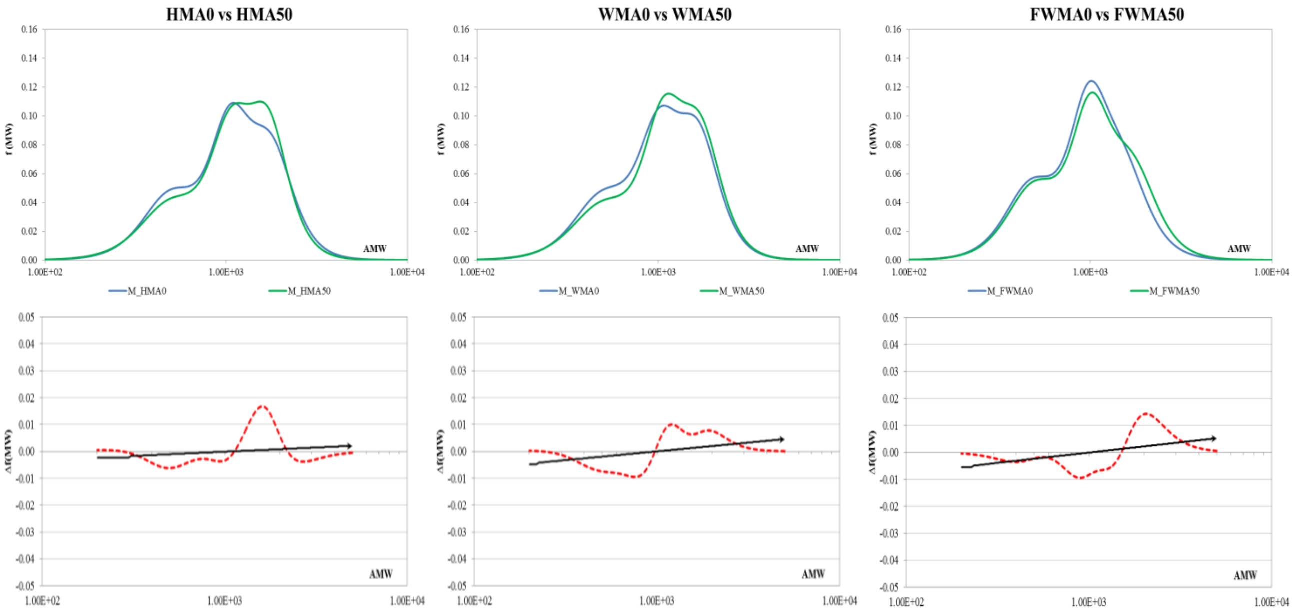


Figure 8: Effect of RAP addition on the MWD for HMA0, WMA0 and FWMA0

Table 6: Slope of MWD differences induced by the addition of RAP

Bitumen	Slope (10E-3)
HMA50-HMA0	1.31
WMA50-WMA0	2.80
FWMA50-FWMA0	3.30

5.3.4 Effect of the manufacturing procedure

The last analysis performed in this section is the influence of the manufacturing process. Figure 9 resumes the curves of the three types of bitumens without RAP, HMA0, WMA0 and FWMA0. It can be observed that compared to the FWMA0, the WMA0 and the HMA0 curves are shifted towards higher apparent molecular weight. Likewise, a peak in the low molecular weight is observed for the FWMA0 but not so neat for the WMA0 and the HMA0. This could reflect a less pronounced ageing of the bitumen [14] within the foaming process.

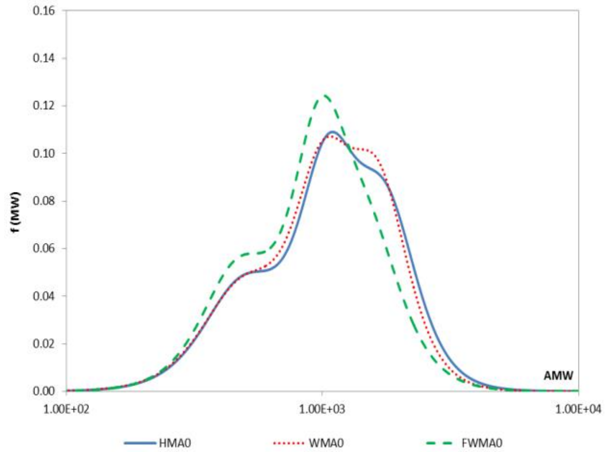


Figure 9: Effect of manufacturing procedure

The different processes are also compared for the RAP addition situation in Figure 10. The tendencies are the same as without RAP. In this case again, the shape of the FWMA50 bitumen distribution is closer to the WMA50, but still separated to the HMA50. The HMA50 distribution shows an obvious distinctive peak in the high molecular weights, not so clear for the WMA50, but indicating what would be the evolution. This could reflect an additional ageing effect due to the overheating of the virgin aggregates at 210°C for the HMA recycling process (Table 1), returning with a higher concentration of clusters.

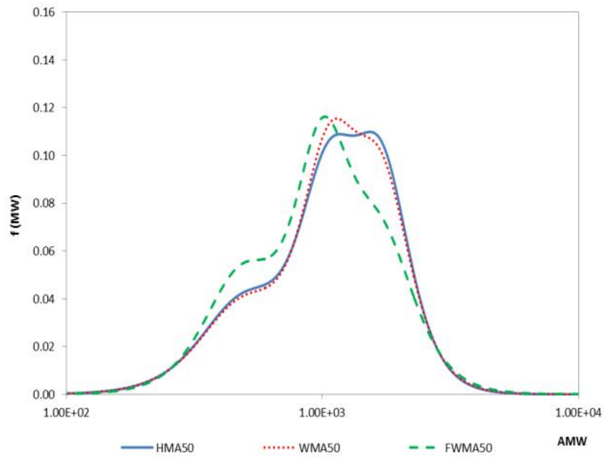


Figure 10: Effect of RAP on the manufacturing procedure

6. CONCLUSIONS AND RECOMMENDATIONS

For a better evaluation of asphalt mixes durability, where warm techniques and recycling are combined, the changes induced by ageing and recycling on the AMWD is monitored for the different manufacturing techniques. This was achieved by the application of a new method (δ-method) recently developed at IFSTTAR, that allows the calculation of an apparent molecular weight distribution from rheological measurements on bitumens.

The results obtained during the investigation led to the following conclusions:

- The application of the δ-method reveals contrasted ageing effects on the AMWD for the different processes.
- The general pattern observed is a decrease of the low molecular weight fractions and an increase of the high molecular weight fractions due to ageing for the samples with or without RAP represented by the absorption of light components by the heavy ones and the clustering produced by their aggregation.

- The WMA without RAP significantly deviates from this general pattern. The multiple transfers within the distribution suggest a more complex structural rearrangement with ageing in this case.
- The effect of RAP addition mainly seems to affect the breadth of the distributions, shifting the curves to the right. This is an effect represented by the increasing tendency of τ parameter in the model when ageing or RAP is present.
- Compared to the HMA manufacture, the FWMA production process induces a significant shift of the distribution towards higher molecular weights when ageing or RAP happens. Besides, an upcoming peak particularly appears in the high molecular weights when RAP is aged, possibly reflecting the clustering of particles.
- The comparative high molecular weights already reached by the HMA during the production process seem to explain its reduced sensitivity to further ageing. And the higher difference between warm procedures.

ACKNOWLEDGEMENTS

The research presented in this paper was carried out as part of the Marie Curie Initial Training Network (ITN) action, FP7-PEOPLE-2013-ITN. This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement number 607524.

REFERENCES

[1] Molecular weight distribution of asphaltic paving binders from phase-angle measurements, A. Themeli, E. Chailleux, F. Farcas, C. Chazallon, and B. Migault, Road Mater. Pavement Des., vol. 16, pp. 228–244, 2015
[2] Fatigue carousel at IFSTTAR Nantes, LCPC, Nantes, France, 2007
[3] Durability of hot and warm asphalt mixtures containing high rates of reclaimed asphalt at laboratory scale, M. Lopes, T. Gabet, L. Bernucci, and V. Mouillet, Mater. Struct., 2014
[4] Hot Recycling of Bituminous Mixtures," in Advances in Interlaboratory Testing and Evaluation of Bituminous Materials - State-of-the-Art, C. De La Roche, M. F. C. Van de Ven, J.-P. Planche, W. Van den Bergh, J. Grenfell, T. Gabet, V. Moullinet, L. Porot, F. Farcas, and C. Ruot, Eds. Springer, pp. 361–429, 2013
[5] Determining molecular weight distributions from viscosity versus shear rate flow curves, W. H. Tuminello and N. Cudré-Mauroux, Polym. Eng. Sci., vol. 31, no. 20, pp. 1496–1507, 1991
[6] Characterization of Polymer Molecular Weight Distribution by Transient Viscoelasticity: Polytetrafluoroethylenes, S. Wu, Polym. Eng. Sci., vol. 28, no. 8, p. 6, 1988
[7] The colloidal structure of bitumen: consequences on the rheology and on the mechanisms of bitumen modification., D. Lesueur, Adv. Colloid Interface Sci., vol. 145, no. 1–2, pp. 42–82, Jan. 2009
[8] Molecular weight and molecular weight distribution from dynamic measurements of polymer melts, W. H. Tuminello, Polym. Eng. Sci., vol. 26, no. 19, pp. 1339–1347, 1986
[9] Molecular weight distribution of regular asphalts from dynamic material functions, L. Zanzotto, J. Stastna, and S. Ho, Mater. Struct., vol. 32, no. April, pp. 224–229, 1999
[10] Etude de la structure du bitume – analyse du comportement visqueux. Rapport interne CHG01189, C. Such, 1982
[11] Analyse du comportement visqueux des bitumes. Bulletin de liaison des laboratoires des ponts et chaussées 127, C. Such, 1983
[12] Comportement thermomécanique des enrobés bitumineux à basse températures. Relations entre les propriétés du liant et de l'enrobé, F. Olard, INSA Lyon, 2003
[13] Physico-chemical analysis of five hard bitumens: Identification of chemical species and molecular organization before and after artificial aging, M. Le Guern, E. Chailleux, F. Farcas, S. Dreessen, and I. Mabille, Fuel, vol. 89, no. 11, pp. 3330–3339, 2010
[14] Durability analysis of different warm mix asphalt containing reclaimed asphalt pavement, M. Perez Martinez, P. Marsac, M. Lopes, T. Gabet, S. Pouget, and F. Hammoum, in Proc. of the XXVth World Road Congress, 2015