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Molecular weight evolution of asphaltite modified bitumens during ageing; Comparisons with equivalent petroleum bitumen

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Abstract This work focuses on the molecular structure evolution of asphaltite modified paving bitumens. In order to evaluate the ageing incidence on the molecular weight distribution (MWD), we have introduced a new parameter called the ageing distribution shift (ADS), which traduces the modification of a MWD due to ageing. The molecular evolutions of asphaltite modified bitumens during aging are compared with the molecular evolutions of pure petroleum bitumens of equivalent grade. The results show that the ADS parameter is appropriate for the evaluation of MWD modifications due to ageing. The present study shows that the asphaltite attenuates the ageing. In addition, compared to hard petroleum bitumens produced in refinery, the asphaltite modified bitumens have better ageing performance.

Keywords Asphaltite, Bitumen modification, Bitumen aging, Molecular weight distribution of bitumens

1 Introduction

In the context of a wide research project we have studied the potential of asphaltites in the production of hard bitumens [1]. Hard bitumens are of real interest in pavement engineering nowadays. They are used in the production of high modulus asphalt concretes (HMAC). HMAC allow the reduction of thickness of structural pavement layers and/or the prolongation of the pavement lifetime [2, 3].

Hard bitumens are produced in petrol refineries by processing the residue of the vacuum distillation of petrol by means of different techniques as air blowing, oxidation, solvent deasphalting etc. [4]. Access to hard bitumens is being more and more difficult and appeals are made to the careful use of this material [5]. For these reasons, several studies have been conducted or are in progress in order to develop alternatives for the production of hard bitumens from the soft petroleum ones. These alternatives very often consist in the modification of soft petroleum bitumens by various modifiers like polymers, polyphosphoric acid, rubbers, recycled plastics, fibers of various types and asphaltites [6]. Several researchers have studied the composition and mechanical properties of various modified bitumens [7-14].

In the context of bitumen modification, asphaltites have a good potential. Asphaltites are very hard natural bitumens and are chemically similar to petroleum bitumens. Due to their chemical similitude, asphaltites and petroleum bitumens have a very good compatibility.

In this paper we will focus on the ageing behavior of asphaltite modified bitumens. During ageing, the bitumen is oxidized and as a consequence the polarity of the medium increases leading to increased traction forces between the molecules. In this conditions, light molecules aggregate forming bigger molecular structures inducing important molecular changes to the bitumen’s colloidal structure [15].

The evaluation of the chemical structural evolution of asphalt during ageing, from in situ extracted sample or laboratory aged asphalt sample, is commonly carried out by standard chromatographic methods like gel permeation chromatography (GPC) [16]. However, dissolution in a solvent may induce important structural modifications resulting in a distorted view of molecular weight distributions and in an erroneous estimation of the ageing degree. For this reason, inverse mechanical approaches, which allow the determination of molecular weight distributions (MWD) from the mechanical properties of materials, would allow to overcome these difficulties. In previous publication we have put in place an innovative method, called the δ-method, which allows the back-calculation of the apparent molecular weight distribution of bitumens from phase angle measurements [17]. Based on this method, different criteria were proposed for the evaluation and quantification of the ageing state of bitumens considering the evolution of molecular populations during ageing [18].

In this paper we propose an alternative straightforward criterion for the quantification of the ageing degree. This criterion is based on the evolution of molecular weight distributions due to ageing. Both the inverse mechanical approach (δ-method) and GPC molecular distributions can be used with the proposed quantification criterion.

After a brief introduction to the δ-method, the proposed approach to quantify the ageing evolution based on molecular weight distributions will be detailed. Then, the studied materials, the experiments and the experimental results will be presented. Finally, the proposed ageing quantification method will be applied to molecular weight distribution issued by the δ-method and GPC to determine ageing evolution. The results will be compared with findings of previous studies [19].

2 Approach to quantify ageing

2.1. Calculating apparent molecular weight distribution of bitumens using the δ-method

The correlation of linear viscoelastic properties with the MWD is reported in several works [20-24]. The material can be considered as a mixture of monodisperse MW species, each of them having a single relaxation frequency. Below this frequency some species relax and makes no contribution to the mechanical response of the material. The unrelaxed species, at a particular frequency, are "diluted" by the relaxed ones **Erreur ! Source du renvoi introuvable.**[20]. As the oscillation frequency increases, smaller and smaller components will participate to the mechanical response, contributing in this way to the increase of the elastic modulus. Simultaneously, the response to the external forces becomes faster, leading to a decrease of the phase angle δ.

The phase angle is particularly sensible to molecular weight **Erreur ! Source du renvoi introuvable.**[23] and it is for this reason that this property is used here to derive the molecular weights. Adopting the picture above, δ is directly related to the cumulative molecular weight (CMW) i.e. the cumulative weight of fractions of species up to a specified MW. Here, the assumption made is that the cumulative molecular weight distribution (CMWD) curve is proportional to the δ master curve and mirror image of it. It has to be noted that the assumption of proportionality has not yet been fully demonstrated for bitumens.

For regular bitumens, Zanzotto established the following relationship between the crossover frequencies at T=0°C and the molecular weights obtained by vapor pressure osmometry **Erreur ! Source du renvoi introuvable.**[23]:

$$\log(MW) = 2.880 - 0.06768 \cdot log(\omega) \qquad [1]$$

By applying this equation to the ω axis of the phase angle master curve, we are able to plot the phase angle master curve as a function of the molecular weight. Then, making the hypothesis that the cumulative molecular weight distribution, $cumf$, is proportional to the phase angle master curve we can write:

$$cumf(MW) = A + B \cdot \delta(MW) \qquad [2]$$

Where A and B are the proportionality constants which are calculated from the following conditions:

$$for\ MW \to 0;\ \delta(MW) = 0, cumf(MW) = 0$$
$$for\ MW \to \infty;\ \delta(MW) = 90°, cumf(MW) = 1$$

From these conditions:

$$A = 0 \text{ and } B = \frac{1}{90°} \qquad [3]$$

Now, differentiating the expression 2 we obtain the differential molecular weight distribution (DMWD). The differentiation can be carried out numerically according to the equation:

$$f(MW) = \frac{dcumf(MW)}{dlogMW} \cong \frac{\Delta cumf(MW)}{\Delta logMW} \qquad [4]$$

Practically, the numerical differentiation is carried out by applying a numerical differential step of 1/3000 to the log(MW). With this resolution the convergence is achieved.

In order to enable the differentiation, the experimental data should be fitted by any rheological model. Fitting allows also the extrapolation of rheological behavior in domains experimentally inaccessible (very high and very low frequencies). The Huet-Such model [25] (1 Spring, 2 Parabolic elements and 1 Dashpot) has been chosen to fit the rheological data. This model is presented in Figure 1 and its mathematical form is given by eq. 5. In comparison to discrete models, the Huet-Such model gives more accurate results for the calculation of the apparent MWD, especially for data at very low or very high frequencies.

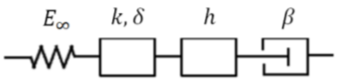


Figure 1: Analogical Huet-Such model to fit the experimental data.

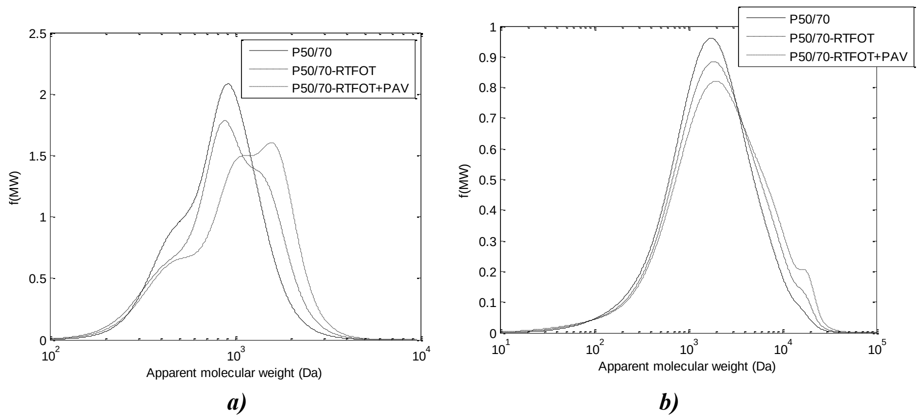
$$E^*(i\omega\tau) = \frac{E_\infty}{1 + \delta(i\omega\tau)^{-k} + (i\omega\tau)^{-h} + (i\omega\beta\tau)^{-1}} \quad [5]$$

Where ω is the radial frequency, τ is the relaxation time which is function of temperature, E_∞ is the complex modulus when $\omega\tau \to \infty$, δ, k, h and β are dimensionless parameters. τ, E_∞,δ, k, h and β are the adjustable parameters of the model.

The δ-method, is described in details and is validated in our previous publication [17].

2.2. Evolution of bitumen macromolecular structure during ageing

As stated earlier, during ageing, the bitumen is oxidized and as a consequence the polarity of the medium increases leading to increased traction forces between the molecules. In this conditions, light molecules aggregate forming bigger molecular structures. Molecular weight distributions of artificially aged bitumens (Figure 2), clearly highlight the fact that artificial ageing (RTFOT and RTFOT+PAV) induces important structural modifications. The ageing is manifested by the creation of a new molecular population and by a translation of the distributions towards higher molecular weights (Figure 2). Comparing δ-method and GPC distributions we see that qualitatively both methods give similar results. Distributions issued by both methods are center around 1000 Da. It seems however that the δ-method is more sensitive to ageing evolutions



a) ***b)***

*Figure 2: DMWD of artificially aged bitumens issued by **a)** the δ-method and **b)** by GPC.*

2.3. Quantification of ageing degree based on molecular weight distributions

Based on molecular weight distributions, the evolutions during ageing can be visualized by comparing the molecular distributions before and after ageing (Figure 3). For example, the fraction of molecules of $MW = X$ has changed from f_1 to f_2 and the evolution during ageing for $MW = X$ is $f_1 - f_2$ (Figure 3). If we extend this calculation to all the MW range, the global molecular evolution would be calculated by:

$$ADS = \int_0^\infty |f_1 - f_2| \cdot dlogAMW \qquad [6]$$

which gives the surface between the apparent molecular distributions before and after ageing. This parameter, which we will name the ageing distribution shift (ADS), is in fact directly related to the shift of the distribution toward higher molecular weights and to the creation of new molecular populations due to ageing. So, it translates the global degree of molecular associations resulting in molecular aggregation during ageing. It is clear that lower ADS values mean lower evolution of the molecular structure during ageing.

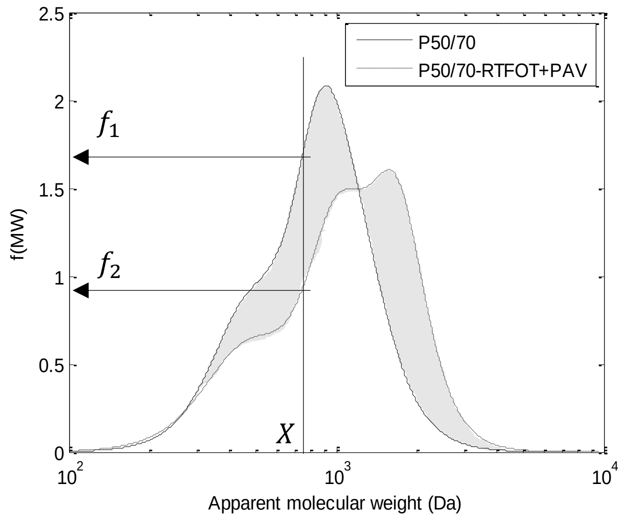


Figure 3. Principle of ageing evaluation

3 Experimental

3.1 Ageing procedures

The materials of this study are subjected to the Rolling Thin Film Oven Test (RTFOT) [26] and then to the Pressure Aging Vessel (PAV) test [27]. It is considered that the RTFOT simulates the aging of bitumens during the asphalt concrete production and the PAV test simulates the long term aging under service conditions.

3.2 Rheological measurements and modelling

3.2.1 Rheological measurements

Rheological properties of bitumens in terms of complex modulus in the linear domain are determined by oscillatory rheological tests carried out on a viscoanalyser METRAVIB. Annular shearing and traction – compression geometries were adopted for the high and the low temperature domains respectively. The complex shear modulus (G*), obtained by annular shearing is converted to complex traction – compression modulus (E*) by applying a Poisson's ratio of 0.5, thus considering the asphalt as an incompressible material above 20°C. The complex moduli of pure, modified and aged asphalts are measured from -10°C to 60°C and from 1Hz to 80Hz. These temperature and frequency ranges allow covering almost the entire viscoelastic behavior domain (phase angle from 0 to $\pi/2$) of our binders.

3.2.2 Rheological modelling

In order to enable the application of the δ-method, the isotherms, determined experimentally, are shifted to master curves at a reference temperature T_{ref}=0°C according to the LCPC method [28]. The adjustment of the model is carried out by an error minimization procedure applied simultaneously on the modulus norm and on the phase angle data. The results of the model fitting are given in section 5.1.1.

3.3 Gel permeation chromatography (GPC)

GPC analyses were carried out by means of a Waters 515 HPLC pump connected to a 500Å Waters μ-styragel-divinylbenzene column of 30cm length, 7.8mm internal diameter and particle size of 10 µm. A volume of 5µl of sample is injected in the chromatographic system *via* a Rheodyne manual injector. In order to highlight molecular associations, bitumens were analyzed under the specific conditions of high-speed size exclusion chromatography (HS-SEC) with a flow rate of 3ml/min of tetrahydrofuran (THF) and a concentration of 30g/l in THF [15, 29]. The analyses are carried out in room temperature. Polystyrene standards, with known molecular weights between 70 and 195.000Da, were used to calibrate the chromatographic column. The detection of the eluted fractions is carried out simultaneously with an UV Waters 490 detector at 340 and 350nm wavelengths and a differential refractive index detector Waters 2414. Azur software was used for the data acquisition.

4 Materials

All the materials considered in this study are referenced and described in Table 1.

Table 1. Materials considered in the study

Reference	Description
AS	Organic phase of purified asphaltite extracted in deep layers of the mine
P50/70	Petroleum bitumen of **50/70** grade
P35/50	Petroleum bitumen of **35/50** grade
P20/30	Petroleum bitumen of **20/30** grade
P10/20	Petroleum bitumen of **10/20** grade
5%AS+95%P50/70	**50/70** grade petroleum bitumen modified with **5%** of asphaltite
10%AS+90%P50/70	**50/70** grade petroleum bitumen modified with **10%** of asphaltite
15%AS+85%P50/70	**50/70** grade petroleum bitumen modified with **15%** of asphaltite

4.1 The asphaltite

The asphaltite is mined in Albania in the region of Selenizza. In its natural state it contains 15-18% of fine mineral material. The organic phase, which is used to modify the petroleum bitumen P50/70, is isolated by dissolution in tetrachloroethylene and filter-centrifugation. We have employed a purified asphaltite mined in deep layers of the mine. The composition and some basic properties of the asphaltite are given in Table 2. Comparisons are made in Table 2 with the P50/70 petroleum bitumen. The SARA fractions, the FTIR indices, the agglomerate contents and the glass transition temperatures are determined according to methods explained by Le Guern et al. [15]. As we can see in the Table 2 the asphaltite is rich in resins and asphaltenes, compounds responsible for its elevated hardness (high R&BT, high │E*│ and zero penetration).

Table 2. Some characteristics of Selenizza asphaltite

Test		AS	P50/70
c7 – precipitation (NF T60-115)	Asphaltenes c7 (%)	43.8	10.2
	Maltenes (%)	56.2	89.8
SARA fractions	Saturates (%)	1.7 ± 0.35	6.7 ± 0.65
	Aromatics (%)	24.8 ± 2.29	50.5 ± 1.81
	Resins (%)	35.1 ± 1.35	26.1 ± 1.64
	Asphaltenes Iatrosc. (%)	38.4 ± 1.88	16.7 ± 1.42
Oxidation (FTIR** indexes)	Sulfoxyde	6.36	-
	Carbonyl	3.99	-
Agglomerate content (HS-SEC*) (%)		2.4	0.92
Glass transition temperature (°C)		-1.1	-22.9
Penetrability (0.1mm) (EN 1427)		0	54
R&B Temperature (°C) (EN 1426)		119	49
│E*│(15°C, 10Hz) (Pa)		$1.23 \cdot 10^9$	$1.26 \cdot 10^8$

* High speed size exclusion chromatography

** Fourier transform infrared spectroscopy

4.2 The petroleum bitumens

The P50/70 is chosen to be modified by asphaltite (Table 1). The other petroleum bitumens, chosen for comparison, are of different (harder than P50/70) penetration grades. All the petroleum bitumens are produced in France by the same fabricant. The bitumens chosen for comparison are of the same penetration grade (35/50, 20/30, 10/20) as the bitumens obtained by asphaltite modification (Figure 4). This choice is made in order to allow pertinent comparisons between hard bitumens issued form asphaltite modification and hard bitumens produced in refinery. All the petroleum bitumens satisfy the European Norms [30, 31] and are currently used in pavement construction.

4.3 The modified bitumens

The modifying process consists in adding the fine grained asphaltite (Φ<1mm) in the preheated soft petroleum bitumen P50/70. The blend is carried out by mixing both materials with a high shear mixer for 1 hour at 180°C. These mixing conditions assure a homogeneous blend of the two components. Modification rates of 5, 10 and 15% are chosen (Table 1). The modified binders get harder with the modification rate. Starting from a soft bitumen of 50/70 grade, harder grades are obtained: 35/50, 20/30 and 10/20 with 5, 10 and 15% of asphaltite respectively. These modification rates give binders of the same penetration grade as the hard petroleum binders chosen for comparison (Figure 4). All the modified bitumens satisfy the European Norms [30, 31].

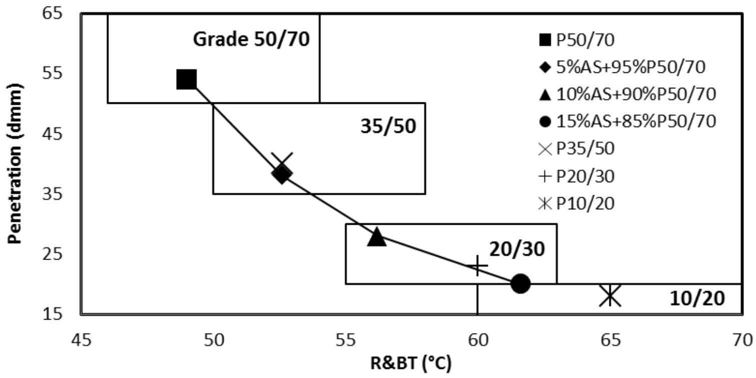


Figure 4. Penetration grades of studied bitumens

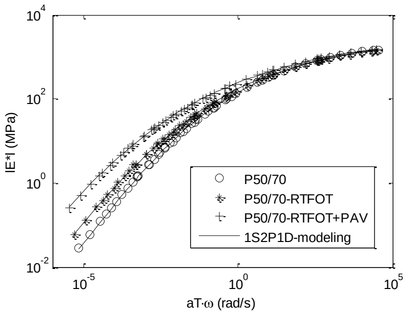
5 Evaluation of ageing degree

In this paragraph, the proposed calculation method (eq.6) based on the δ-method is employed in a first time to quantify the ageing degree of our bitumens. Then, the same calculation method (eq.6) is applied to results issued by GPC analyses. Both results are compared then between. In addition these results are compared with the results obtained in our previous publication [19].

5.1. Evaluation of ageing degree based on δ-method molecular distributions

5.1.1. Experimental data fitting

After master curve construction, the experimental measurements are fitted to the Huet-Such model (eq. 5). The fitting quality is very satisfactory (Figure 5). The minimal determination factors are R^2=0.9993 for the modulus norm and R^2=0.9932 for the phase angle. The fitted model parameters are given in Table 3.



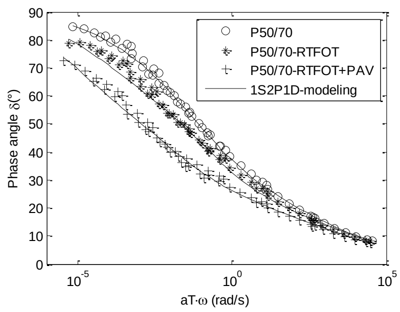


Figure 5. a) Complex modulus norm and b) complex modulus phase angle master curves at Tref=0°C of a petroleum bitumen of grade 50/70 before and after artificial ageing procedures of RTFOT and PAV

Table 3. Huet-Such model parameters of the studied bitumens

Symbol	E_{inf} (MPa)	δ	k	h	β	τ (s)
P50/70	2030	4.50	0.30	0.67	20.9	1.05E-01
P50/70 - RTFOT+PAV	2193	5.58	0.26	0.62	131	4.71E-01
P35/50	2051	4.12	0.28	0.66	26.1	2.07E-01
P35/50 - RTFOT+PAV	2120	5.70	0.26	0.63	116.0	1.44E+00
P20/30	2065	5.17	0.28	0.66	53.5	3.68E-01
P20/30 - RTFOT+PAV	2258	6.54	0.23	0.58	493.1	3.90E+00
P10/20	2161	5.11	0.26	0.64	90.0	1.21E+00
P10/20 - RTFOT+PAV	2300	5.56	0.22	0.54	899.6	9.63E+00
5%AS+95%P50/70	2074	5.18	0.30	0.69	32.4	1.96E-01
5%AS+95%P50/70 – RTFOT+PAV	2133	6.36	0.26	0.63	153.0	1.18E+00
10%AS+90%P50/70	2002	5.70	0.30	0.68	47.9	3.37E-01
10%AS+90%P50/70 – RTFOT+PAV	2175	6.22	0.26	0.62	247.8	1.53E+00
15%AS+85%P50/70	2144	5.26	0.28	0.64	94.9	4.82E-01
15%AS+85%P50/70 – RTFOT+PAV	2266	6.26	0.25	0.60	380.2	2.30E+00

5.1.2. Ageing degree calculation

δ-method apparent molecular weight distributions were calculated according to the theoretical considerations presented in section 2.1 with the fitted model parameters presented in Table 3. Ageing evaluations of the studied bitumens, calculated with the expression 6 are resumed in Figure 6. We note that the modified binders show lower molecular evolutions compared to the base petroleum bitumen P50/70. We observe that higher is the modification rate, lower is the evolution during ageing. In addition to this, comparing the evolutions of the modified binders with the evolutions of petroleum bitumens of the same penetration grade, we note that the asphaltite modified bitumens present a better aging behavior. For example the petroleum bitumen of 10/20 grade presents an ADS of 0.54 while the ADS of the modified binder at 15% of asphaltite is only 0.35.

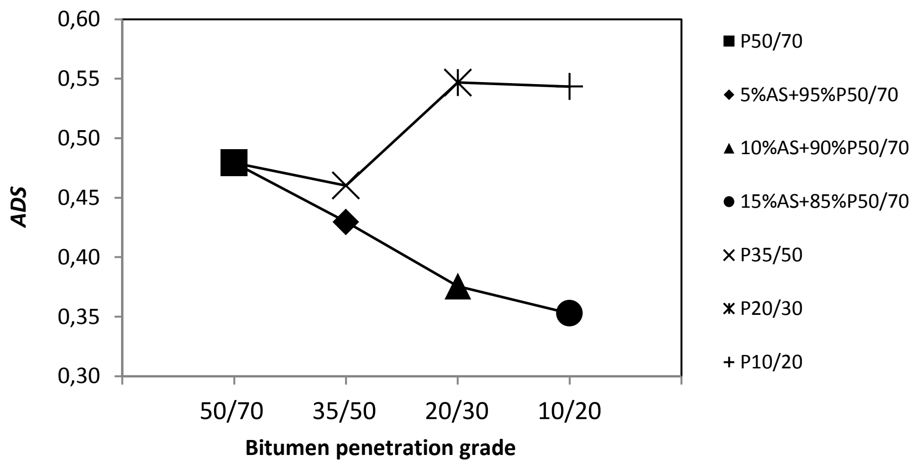


Figure 6. Molecular structure evolution of the studied bitumens after RTFOT+PAV artificial ageing; Results obtained by applying eq.6 to δ-method DMWD

5.2 Evaluation of ageing degree based on GPC analyses

GPC molecular weight distributions on non-aged and RTFOT+PAV aged bitumens were determined according to the experimental protocol given in section 3.3. ADS of the studied bitumens, calculated with the expression 6 are resumed in Figure 7. The results are qualitatively similar to the results issued by the δ-method. The modified binders show decreasing molecular evolutions with the asphaltite modification rate. In addition to this, comparing the evolutions of the modified binders with the evolutions of petroleum bitumens of the same penetration grade, we note that the asphaltite modified bitumens present a better aging behavior. For example the petroleum bitumen of 10/20 grade presents an ADS of 0.16 while the ADS of the modified binder at 15% of asphaltite is only 0.11.

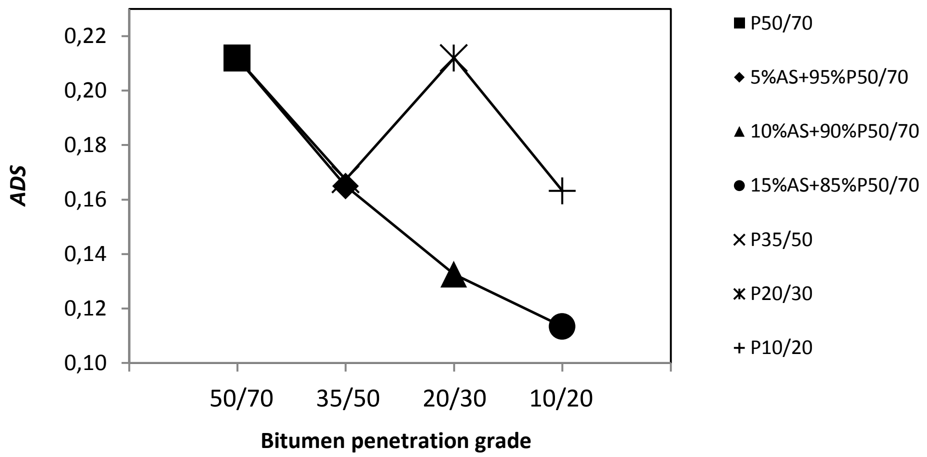


Figure 7. Molecular structure evolution of the studied bitumens after RTFOT+PAV artificial ageing; Results obtained by applying eq.6 to GPC DMWD

It is interesting to note that the results of the GPC and the δ-method analyses are in agreement. This supports the validity of the δ-method in molecular weight distribution analyses.

6 Cross-reference analysis

In our previous work [19], the ageing degree of bitumens was evaluated based on evolutions of mechanical properties during ageing by the following expression:

$$EV_x = \frac{|x^{RTFOT+PAV} - x^{New}|}{x^{New}} \cdot 100 \qquad [7]$$

Where:
x – can be the penetration, the softening point, the phase angle or the complex modulus norm measured for a given frequency, or the relaxation spectral value determined for a given relaxation time.
EV_x – The evolution of the mechanical property x
$x^{RTFOT+PAV}$ – The mechanical property after RTFOT and PAV artificial ageing
x^{New} – The mechanical property before ageing

The results presented in Figure 8, which are representative of all the results presented in [19], are in full agreement with the results of the present paper. All the interpretations made on results issued by GPC and δ-method analyses hold for results presented in Figure 8.

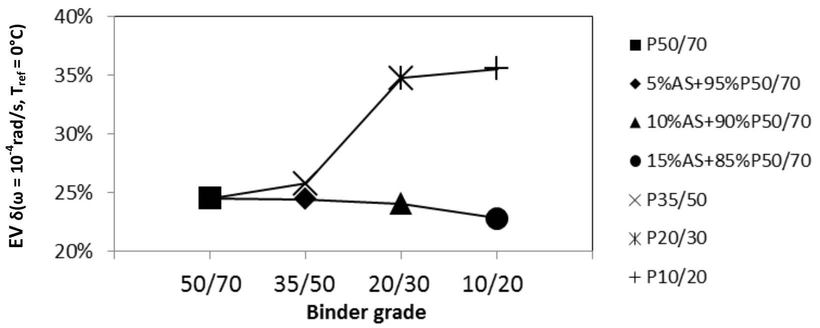


Figure 8. Evolution of complex modulus phase angle after artificial ageing RTFOT+PAV; Results obtained by applying eq.7 [19].

Contrary to evolutions calculated by eq. 7 which are based on single linear viscoelastic properties for a given frequency, the δ-method ADS (eq. 6) considers the entire spectrum of the linear viscoelastic behavior in the calculation of the ageing degree. Results issued from both mechanical (EV_x and δ-method) are in complete agreement with results issued by chromatographic analyses.

7 Conclusions

The scope of the present work was to study the molecular evolutions of Selenizza asphaltite modified bitumens during artificial ageing and to compare the ageing degree of asphaltite modified bitumens with the ageing degree of pure petroleum bitumens of equivalent grade. For comparison purposes were chosen hard petroleum bitumens produced in France by the same fabricant as the soft petroleum bitumen selected to be modified.
Molecular weight distributions before and after ageing were determined by the δ-method and by GPC analyses. A new parameter, the ageing distribution shift (ADS), is proposed here for the evaluation of molecular evolutions induced by ageing.
Both δ-method and GPC analyses give equivalent results which supports the validity of the δ-method. These results are in full agreement with previous findings [19] which means that molecular evolutions due to ageing are directly responsible for the observed evolutions of the mechanical properties. In addition the agreement of the results seems to prove the relevance of the ADS parameter proposed here for the study of the molecular evolutions during ageing.

The results of this paper show that the asphaltite behaves as an ageing inhibitor. The evolutions during ageing slow down with the modification rate. In addition to this, the comparison with the pure petroleum bitumens of the respective grade show that the asphaltite modified binders present a much more advantageous ageing behavior.

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