Effect of Ethylene Vinyl Acetate (EVA) Polymer on Rheological Properties of Bitumen Before and After Ageing

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Abstract

In road applications, bitumens are exposed to ageing processes during storage, mixing, transport and laying, as well as in service life. The oxidative ageing causes hardening of bitumens and, consequently, may make a contribution to the deterioration of asphalt pavements. Therefore, the polymer modified bitumens are recommended to increase the durability of the material. In the present work, rheology has been applied to evaluate the properties of Ethylene Vinyl Acetate (EVA) polymer modified bitumen to compare to the 35/50 penetration grade bitumen, before and after ageing. The effects of ageing on the physical and rheological properties of EVA polymer modified bitumen were evaluated using SARA analysis, penetration test, softening point test and dynamic shear rheometer test (DSR). The binders were aged by Rolling Thin Film Over (RTFOT) to simulate short-term ageing and Pressure Ageing Vessel (PAV) to simulate long-term ageing. The SARA analysis showed the expected changes in the chemical composition of binders dues to ageing process caused by RTFOT and PAV ageing. The results showed that the use of EVA polymer reduces the ageing effect on physical and rheological properties of the bitumen binder as illustrated through lower ageing index of complex modulus and an increase in tang δ indicating that the EVA polymer improve the ageing resistance of bitumen binder. In all cases, the aged modified binders showed better rheological properties than aged bitumens. The aged samples are characterized by higher stiffness and elasticity, due to an increase of the elastic modulus.

Keywords : *Polymer modified bitumen; EVA; Rheological property. RTFOT and PAV ageing*

1. Introduction

A conventional bitumen 35/50 penetration grade is commonly used in Algeria, and moreover, it is subjected to the high traffic load and hot climate. In this case, the rheological properties and durability of conventional bitumen are not sufficient to resist pavement distress. This has resulted in the need to enhance the properties of existing asphalt material. Bitumen modification offers one solution to overcome the deficiencies of bitumen and thereby improve the performance of asphalt mixtures [1, 2]

One of the principal plastomers used in pavement applications is the semi-crystalline copolymer, Ethylene Vinyl Acetate (EVA) in order to improve both the workability of the asphalt during construction and its deformation resistance in service [3].

In additional, Ageing is known as a factor influencing the performance and characteristics of bitumen binder. Many factors might contribute to this hardening of the bitumen such as oxidation, volatilization, polymerization and thixotropic [4]. Ageing significantly changed both the chemical and physical properties of asphalts. Physical properties such as penetration, softening point, ductility, viscosity, and stiffness are all affected to some extend by ageing [5].

Ageing is a very complex process in normal bitumens and the complexity increase when polymer modified bitumens (PMBs) are involved. The ageing properties of bitumens are normally characterized by measuring physical/rheological properties (e.g. penetration, softening point and viscosity) before and after artificial ageing in the laboratory. This procedure is not sufficient in the case of PMB because thermal degradation of the polymer may occur during ageing and the fragments formed may contribute to a lowering of

consistency [6]. Therefore, when assessing the ageing properties of PMB, further characteristics (e.g. viscoelasticity) have to be evaluated [7].
Bitumen ageing occurs during the mixing and construction process as well as during long-term service in road. Several methods have been proposed to replicate the effect of ageing and, therefore, to foresee bitumen behaviour during application and service life. To simulate the age hardening occurring during plant mixing and laydown the most utilized test are Rolling Thin Film Over Test (RTFOT, ASTM D-2872). To simulate long-term ageing during service the Pressure Ageing Test (PAV, AASHTO PP1) was adopted in SHRP binder specifications.

The objective is to identify the degree of ageing in physical and rheological properties of EVA modified bitumen using short-term ageing test (RTFOT) and long-term ageing test (PAV). The fundamental rheological (viscoelastic) properties of aged EVA polymer modified bitumen have been determined using the dynamic shear rheometer test (DSR). The visco-elastic properties considered in this paper are complex shear modulus, storage shear modulus, loss shear modulus and phase angle.

2. Experimental program

Investigations are carried out on the base and modified binders containing 5% of EVA before and after standard laboratory ageing (RTFOT and PAV) to evaluate the influence of ageing on the chemical, physical and rheological properties.

2.1 Materials

The base bitumen used was a 35/50 penetration grade provided by the Algerian Oil Refining Company "NAFTAL. The results of penetration grade trials and R&B softening temperature tests, according to ASTM D5 and D36, respectively, as well as chemical composition in terms of SARAs fractions are presented in table 1.

Table 1. *Physical properties and chemical characteristics of the base bitumen*

Physical properties	**Penetration (25°C; 0.1 mm)**	**41**
	Softening point (°C)	52
	Penetration index (PI)	-1.16
Chemical characteristics	Saturates (%)[a]	8.7
	Aromatics (%)[a]	36.4
	Resins (%)[a]	44.6
	Asphaltenes (%)[a]	10.3
	Colloidal index[b]	0.234

[a] Iatroscan thin film chromatography SARA analysis.
[b]Colloidal index (I_c) = (asphaltenes + saturates)/(resins + aromatics).

The thermoplastic polymer used as modifier is Ethylene Vinyl Acetate (EVA). The main characteristics of EVA polymer as given by the manufacturers are reported in table 2.

Table 2. *Main physical and chemical characteristics of EVA Polymer used as modifier for the base bitumen*

Properties	EVA Polymer
Physical aspect	Granular
Molecular structure type	Linear
Vinyl acétate (wt.%)	18 %
Density (ASTM D792)	0.939 g-cc
Viscosity	1.25 Pa.s
Tensile strength (ASTM D412)	31 MPa
Elongation at break (ASTM D412)	>800 %
Hardness shore (A) (ASTM D2240)	90
Melt flow index (ASTM D1238)	1-2g /10 min

2.2 Preparation of EVA modified bitumens

The modified binders were prepared at 180°C and a speed of 600 rpm using a high shear mixer. While preparing SEBS modified binders, 600 g of the bitumen was melted and poured into a 2000 ml spherical flask. Upon reaching 175°C, the EVA polymer was added to the bitumen. After reaching 180°C, the mixing was continued at the temperature for two hours. The mixer speed was maintained through the mixing process. After completion, the EVA-bitumen was removed from the flask and divided into small containers. The blend was cooled to room temperature, sealed with aluminum foil and stored for further testing. The EVA concentrations in the base bitumen was chosen as 5% by weight. The uniformity of dispersion in the base bitumen was confirmed by passing the mixture through an ASTM 100# sieve. After completion, the different samples were cooled to room temperature, covered with aluminum foil and stored for testing.

2.3 Conventional bitumen tests

The base bitumen and the polymer modified bitumens were subjected to the following conventional binder tests: penetration, softening point temperature. Penetration test was used to determine the consistency of a bitumen binder according to ASTM D5 by measuring the depth in tenths of a millimeter to which a standard loaded needle will penetrate vertically in 5 seconds. The softening temperature is an important performance criterion for bituminous materials because it characterizes the resistance of asphalt to rutting (permanent deformation). The test was performed according to ASTM D36.
In addition, the temperature susceptibility of the modified bitumen samples was calculated in terms of penetration index (PI) using the results obtained from both penetration and softening point temperature tests. Temperature Susceptibility

is defined as changes in the consistency parameter as a function of temperature. A classical approach related to PI calculation has been given in the Shell Bitumen Handbook [8].

$$PI = \frac{1952 - 500 \times \log(Pen_{25}) - 20 \times TBA}{50 \times \log(Pen_{25}) - TBA - 120} \quad (1)$$

2.3 Ageing procedures

Ageing of bitumen is induced by chemical and physical changes that occur during the production of the pavement and throughout its service life. The process is usually accompanied by hardening of the binder, which general influences the deterioration of the asphalt pavement [5].

The samples were aged using the standard Rolling Thin Film Over Test (RTFOT, ASTM D 2872) at a temperature of 163°C for 75 min as short-term ageing and Pressure Ageing Vessel (PAV, AASHTO PPI) at 100°C and an air pressure of 2.1 Mpa for 20 hours to simulate the long-term ageing. To investigate the influence of oxidative ageing on physical and rheological changes of bitumen binders, the age hardening is evaluated by measuring penetration test (ASTM D5), softening point test (ASTM D36), and dynamic shear rheometer (DSR).

2.3 Dynamic Shear Rheometer Test (DSR)

Dynamic mechanical analysis (DMA) was performed on the base bitumen and EVA modified bitumens, to determine their rheological properties using dynamic shear rheometer (DSR). The dynamic shear rheometer (DSR) was adopted to characterize the viscoelastic behavior of bitumens binders at low and intermediate to high service temperatures. The DSR provides an indication of the rutting resistance of bitumen immediately following construction. Resistance to rutting at high service temperatures in the early stages of pavement life is also evaluated [9, 10].
The principal rheological parameters obtained from DSR were complex shear modulus (G*) and phase angle (δ). G* is defined as the ratio of maximum shear stress to maximum strain and provides a measure of the total resistance to deformation when the bitumen is subjected to shear loading [11]. The phase angle is the phase shift between the applied shear stress and shear strain response during a test and is a measure of the viscoelastic balance of the material behavior.The test method requires that a thin bitumen specimen be sandwiched between two parallel metal plates held in a constant temperature medium. The DSR tests reported in this paper were performed under controlled-strain loading conditions using frequency sweeps between 0.01 and 10 Hz at temperatures between 20°C and 80ºC. The tests were undertaken with parallel plates testing geometry. Diameter of plates was 25 mm with 1 mm gap. For specification purposes, the frequency is 10 radians per second which has been related to a traffic speed of 100 km/h.

3. Results and discussion

3.1 Chemical characterization of the effect of ageing

The most important changes that cause hardening of the binder in pavements are the changes in the composition of the bitumen molecules from reaction with oxygen, molecular growth (forming of asphaltenes) and molecular structuring that produces different rheological behavior [12,13].

One method that used to study the changes associated with ageing of paving grade bitumen is to determine the generic composition of the aged bitumen. The changes in the percentages of the Saturates, Aromatics, Resins and Asphaltenes (SARA), obtained from Iatroscan thin layer chromatography, of the base bitumen and PMBs after RTFOT and PAV ageing are shown in table 3. This table also reports the values of the colloidal instability index (CI), which is defined by :

CI = (asphaltenes + saturates) / (resins + aromatics) [11].

The CI were calculated in order to determine the potential compatibility of the base bitumens to polymer modification. In general, a CI higher than 0.28 predicts compatibility problems (phase separation) between the bitumen and the polymer [11].

Table 3*: Changes in chemical composition due to ageing for base bitumen and EVA PMB*

Binder	Condition	S (%)	A (%)	R (%)	As (%)	Colloidal index IC
Base bitumen	Unaged	8.7	36.4	44.6	10.3	0.234
	RTFOT	8.2	27.4	47.9	16.5	0.321
	PAV	6.8	24.2	50.1	18.9	0.345
5% EVA PMB	Unaged	8.9	41.6	36.8	12.7	0.275
	RTFOT	8.8	39.7	36.7	14.8	0.309
	PAV	8.1	34.5	40.8	16.6	0.328

The analysis of the chemical composition of the base bitumen and the polymer modified samples indicates a similar decrease in aromatics with an increase in asphaltenes and resins with the percentage mass of saturates remaining fairly constant after ageing. The base bitumen and PMB, therefore, showed the expected changes in their chemical composition due to the ageing process caused by RTFOT and PAV ageing.

The SARA data also indicates that the magnitude of increase in asphaltenes and resins and decrease in aromatics after ageing is greater in the presence of polymer in the bituminous matrix. This is explained by the shifting of lower molecular weight fractions towards higher molecular weight fractions (oils towards resins and resins towards asphaltenes) [1].
The changes in chemical composition of the base bitumen and the polymer modified samples are more important after PAV ageing compared to that after RTFOT ageing. This is understandable due to the severe oxidative ageing that occurs during PAV ageing.
The data indicate that the CI values of the EVA PMB are below 0.28 before ageing. These results can be related to the good compatibility between the bituminous matrix and the EVA polymer. Moreover, the CI values obtained after ageing are higher than 0.28 resulting in the reduction of the compatibility between the bitumen and the polymer.

3.2. Influence of ageing on the conventional properties of the PMB

The effect of ageing on the penetration and softening point of base bitumen and the EVA PMB's can be seen in table 4. Temperature susceptibility of PMB's is evaluated by the determination of the penetration index (PI), which is defined as the change in the consistency parameter as a function of temperature [14]. Higher penetration index (PI) indicates less temperature susceptibility and more rubbery elastic behavior.

Table 4*: Changes in conventional test data due to ageing for base bitumen and EVA PMB 's*

	Base bitumen			5% EVA PMB		
	Before	RTFOT	PAV	Before	RTFOT	PAV
Pen (mm)	41	25	13,5	18	15	9,7
Soft.Pt (°C)	52	57	63,4	68,7	71,2	75,6
(PI)	-1,16	-1,06	-0,94	0,39	0,45	0,37

The results in table 4, indicate a decrease in penetration and an increase in softening point for base bitumen and EVA PMB after ageing. This indicates a hardening of the binders and corresponds to the oxidative processes identified by SARA analysis. In addition, the EVA polymer modified bitumen shows lower penetration, higher softening point and higher penetration index when compared to base bitumen. The EVA PMB shows better resistance to ageing compared to base bitumen as evident from small decrease in penetration and small increase in softening point.

From table 4, the increase in penetration index (PI) observed for the EVA PMB shown that the EVA polymer modifier significantly reduces the temperature susceptibility of the base bitumen before and after ageing. This clearly shows that polymer modification induces a rubbery elastic behavior conferring to the bitumen better resistance to low temperature cracking and permanent deformation [15]. However, the increased penetration index (PI) observed after PAV ageing, is less important for both the unmodified bitumen and the EVA PMB after RTFOT ageing.

3.3. Ageing indices

Ageing index measurement is one of the most popular procedures used to determine ageing susceptibility and provides ranking of different bitumen binders. Ageing index is defined as the ration of physical or rheological parameter of the aged bitumen to that of the original bitumen as shown in (1).

$$Ageing\ index = \frac{Bitumen\ property\ after\ ageing}{bitumen\ property\ before\ ageing} \quad (1)$$

The penetration and softening point-ageing indices for base bitumen and EVA PMB after RTFOT and PAV tests are presented in table 5.

Table 5*: Changes in ageing index for EVA PMB's*

Bitumens	Penetration Ageing Index		Softening point Ageing Index	
	$\frac{RTFOT}{Unaged}$	$\frac{PAV}{Unaged}$	$\frac{RTFOT}{Unaged}$	$\frac{PAV}{Unaged}$
Base bitumen	0.61	0.33	1.09	1.22
5% EVA PMB	0.83	0.37	1.09	1.18

The results showed a decrease in penetration and increase in softening point of unmodified bitumen and EVA polymer modified bitumen after the two different ageing. In addition, the ageing indices indicate that the changes in the traditional, empirical tests are greater after PAV ageing compared to those after RTFOT ageing. However, the relative magnitude of the ageing indices indicate that the effect of ageing on the physical performance of EVA PMB is less important from that found for unmodified base bitumen. Thus, the EVA polymer addition led to improving the binder resistance to oxidative ageing.

3.4. Influence of ageing on the rheological properties of the PMB

In this study, DMA was employed to characterize the rheology of the base bitumen and the modified binder containing 5% of EVA before and after laboratory ageing

(RTFOT and PAV). Dynamic Shear Rheometer test was conducted by using a temperature sweep starting from 20°C to 100ºC at a constant frequency of 10 rad/s on the entire samples. The tests were undertaken with parallel plates testing geometry. Diameter of plates was 25 mm with 1 mm gap. For specification purposes, the frequency is 10 radians per second which has been related to a traffic speed of 100 km/h. The most frequent graphical representation used to characterize residue rheological behavior is the complex modulus G* and the phase angle δ.

In DMA, complex modulus G* is defined as the ratio of maximum (shear) stress to maximum strain and provides a measure of the total resistance to deformation when the bitumen is subjected to shear loading. The phase angle δ is the phase shift between the applied shear stress and shear strain response during a test and is a measure of the viscoelastic balance of the material behavior. A higher *G** and a lower δ are desired for rutting resistance. The bitumen with a high *G** is stiffer and provides increased resistance to deformation. The bitumen exhibiting a lower δ has a greater elastic component, thus allowing more of the total deformation to be recovered.

The main curve of the complex modulus for base bitumen and modified bitumen, against temperature was obtained, as illustrated in figures 1.

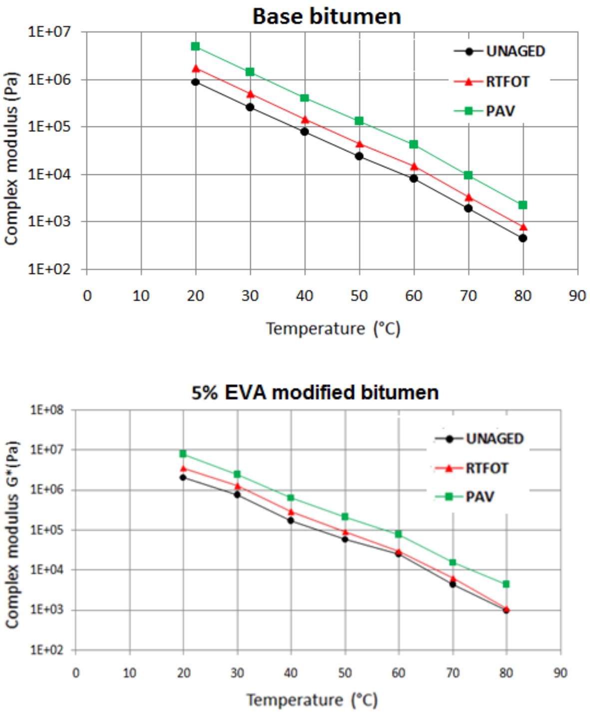

Figure.1. *Complex modulus as function of temperature at 10 rad s^-1^ for base bitumen and 5% EVA modified bitumen before and after ageing.*

As illustrated in figure 1, at the frequency studied, ageing increases the complex modulus of base bitumen and of the modified binder containing 5% EVA. The increase in temperature is followed by a decrease in the complex modulus; this is observed for aged and unaged binders. The increase in G* after PAV ageing is understandably greater than after RTFOT ageing due to the prolonged ageing process in the PAV. An increased complex modulus is observed for the aged BMP as compared with the original one before and after ageing. Lower slope of complex modulus means that the asphalt is softer, also higher complex modulus have benefit since it reduce rutting problems in the asphalt. This phenomenon is identical to that seen for the base bitumen and confirms the hypothesis that the increase in G* is attributed solely to the oxidative ageing of the base bitumen in the PMB and that the bitumen phase in the PMB is aged in a similar to that of an unmodified bitumen.

The main curve of the phase angle, for base bitumen and modified bitumen, against temperature was obtained, as illustrated in figures 2.

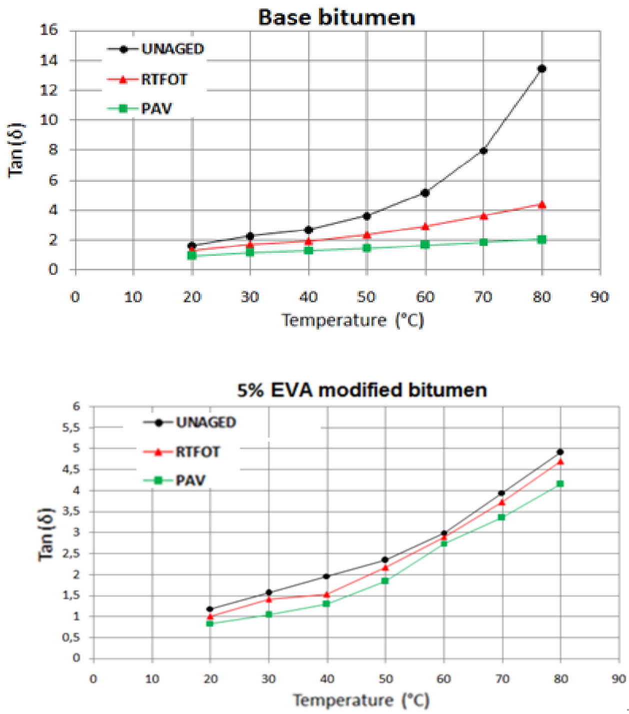

Figure 2. *Phase angle as function of temperature at 10 rad s^{-1} for base bitumen and 5% EVA modified bitumen before and after ageing*

Figure 2 reveals changes in the viscoelastic properties of the binders during ageing. As can be seen, the elasticity of the base bitumen and modified binders is increased by ageing, as indicated by a decrease in phase angles in the temperature range. Owing to ageing, the recorded decrease in phase angles suggests that a variation from a more viscous to more elastic behavior occurs.

The decrease in phase angles for the base bitumen and the modified bitumen binder was more pronounced after PAV test compare to RTOT test. For the base bitumen and 5 %

EVA modified bitumen, complex modulus is increased and phase angle is reduced through ageing.
The results obtained indicate that the aged EVA modified bitumen display better rheological properties than the corresponding base bitumen. In practice, this should be favorable for long-term durability of asphalt pavements.

4. Conclusion

The addition of EVA polymer to bitumen, in order to improve its performance for pavement applications has been studied. The rheological investigation of the EVA polymer modified bitumens, by means of empirical methods and dynamic shear rheometry, has shown that there is a considerably difference in behaviour between the base bitumen and the EVA modified binders.
The addition of EVA polymer to the bitumen results in the improvements in the basic properties like penetration and softening point, which demonstrated the increased stiffness (hardness). Based on PI, the addition of EVA to bitumen improves temperature susceptibility of bitumen.
Considering the results obtained by DSR test, it is seen EVAMBs binder exhibits increases complex modulus (G*) and has more decreased phase angle values, consequently, using the EVA polymer is considerably improves the elastic properties and rutting resistance of bitumen.
This study showed that the fundamental rheological characterization of binder properties is superior to the conventional empirical measures. These empirical measures cannot be directly related to the improved binder properties resulting from polymer modification. However, the fundamental rheological characterization could be used directly to predict binder performance.

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