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Influence of thermo-oxidative aging on chemical composition and physical properties of polymer modified bitumens

Nadjet Dehouche [a,*], Mustapha Kaci [a], Khadija Ait Mokhtar [b]

[a] *Laboratoire des Matériaux Organiques, Faculté de la Technologie, Université Abderrahmane Mira, Bejaia 06000, Algeria*
[b] *Laboratoire des Routes et Aérodromes, Faculté de Génie Civil, USTHB, Alger, Algeria*

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This paper presents some experimental results on property changes due to thermo-oxidative aging of bitumen modified by styrene–butadiene–styrene (SBS) and ethylene vinyl acetate (EVA) copolymer incorporated at various concentrations, i.e. 3, 5 and 7 wt.%. The chemical compositions, the properties and the morphology of the samples have been determined and characterized using SARA (saturates, aromatics, resins and asphaltenes) analysis, conventional test methods and optical microscopy, respectively.

The study reveals that polymer modification globally improves the conventional properties of the base bitumen as evidenced by a decrease in penetrability, an increase in softening point and a reduction in temperature susceptibility inducing a rubbery elastic behavior to the base bitumen. This effect is dependent on both the type and the content of polymer used. Moreover, samples prepared with SBS show better improvement as compared with EVA modified bitumens. The morphological analysis shows that there is a clear difference between the SBS and EVA modified bitumens. For 3 wt.% SBS modified bitumens, the polymer phase is homogenously dispersed in a continuous bituminous matrix consisting of polymer particles swollen by the solvating phase of the bitumen. In the case of EVA modified bitumen with the same polymer content, much finer dispersion of EVA particles is observed. After thermo-oxidative aging, the results clearly indicate a hardening of samples, being more pronounced for the base bitumen and those modified with EVA.

For all samples, aging reduces the content of aromatics and at the same time increases the contents of resins and asphaltenes, while changes in the content of saturates are almost negligible. These structural modifications may result from oxidation of the bitumen and some chemical interactions with the polymers.

1. Introduction

Asphalt is widely used as an adhesive material, especially in pavement construction [1]. However, during the “in life” service of asphalt binders, there are many types of failures, i.e. high temperature rutting, low thermal cracking and fatigue cracking which can reduce the quality and performance of pavements and subsequently limit its further application [2,3]. In addition, during the bitumen processing steps including production, storage, lying, and compaction of asphalt mixtures, material degradation occurs. Further, the exposure of bitumen to oxygen for a long time may also result in degradation which can be influenced by many factors such as the binder properties and the morphology [4].

One of the most promising methods for improving the performances of asphalt is to incorporate polymers in percentages ranging from 3 to 7 wt.% [2,4]. Indeed, blending small amounts of polymer into asphalts partially alleviates rutting and thermal cracking [5]. Block copolymers are recognized as especially effective asphalt modifiers due in large part, to the thermoplastic elastomeric properties of this class of materials [5–9].

Currently, the most commonly used polymers for bitumen modification is the styrene–butadiene–styrene (SBS) followed by other polymers such as styrene butadiene rubber (SBR), ethylene vinyl acetate (EVA) and polyethylene [10]. The main advantage of SBS is that it has a two-phase morphology consisting of glassy micro-domains made of polystyrene connected to rubber polybutadiene segments, exhibiting cross-linked elastomer behavior. This allows the polystyrene domains to maintain a morphological structure and this partial solubility is a key factor in making SBS a good asphalt modifier [11].

EVA is also used in road construction in order to improve both the workability of the asphalt during construction and its deformation resistance in service. In fact, the literature [12] reported that EVA provides the modification of bitumen throughout the

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* Corresponding author.
E-mail address: dehouche_nadjet@yahoo.fr (N. Dehouche).

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crystallisation of rigid three-dimensional networks within the bitumen, which improve permanent deformation and thermal cracking.

The knowledge of the thermo-oxidative degradation of the polymer modified bitumens during the blend preparation and under aging treatment is necessary to predict the performance of the bituminous system [13]. In addition, polymer modified bitumen is usually thermodynamically unstable, and phase separation readily occurs during their storage at high temperatures, giving rise to transportation problems [14].

Numerous studies have been carried out on different aspects of compatibility and interactions between the polymers and the base bitumen aiming to improve the performances of the modified materials. However, the data dealing with the aspect of bitumen aging is rather scarce making this research area still interesting to be studied.

This paper aims to characterize the properties of the SBS and EVA modified bitumens by using conventional and empirical test methods as well as to evaluate the morphology by assessing the state of dispersion of SBS and EVA polymer and bitumen phases. The chemical composition and the main physical characteristics of the asphalt mixtures prepared with the modified bitumen samples have also been investigated after thermo-oxidative aging using the Rolling Thin Film Oven Test (RTFOT).

2. Experimental

2.1. Materials

Asphalt grade is specified in terms of softening point temperature and penetration value [13]. In the present study, the base bitumen was a 35/50 penetration grade kindly provided by the Algerian Oil Refining Company "NAFTAL". The main physical properties of the bituminous material are the following: penetration (at 25 °C 1/10 mm) = 40.5, softening point temperature = 52.3 °C and ductility at 25 °C $\geqslant$ 150 cm.

The polymers used as modifiers are styrene–butadiene–styrene block copolymer (SBS) supplied by Shell Chemicals Company (Netherlands) and commercialized under the trade name Kraton D-1101. Ethylene vinyl acetate copolymer (EVA) was supplied by OMYA PERALTA Gmbh (Germany) under the grade name Miravithen D 18001. The main physical and chemical properties of the two thermoplastics as given by the manufacturers are reported in Table 1.

2.2. Preparation of polymer modified bitumens

Polymer modified bitumens were prepared using a high shear mixer at 180 °C and a speed of 600 rpm. Initially, 600 g of bitumen were heated to fluid condition and poured into a 2000 ml spherical flask. Up on reaching 175 °C, SBS and EVA copolymers were added slowly to the bitumen, thus preventing any polymer aggregate formation during the mixing process. Mixing was then continued at 180 °C for 2 h to produce polymer modified bitumens (PMAs). Various blend compositions based on bitumen/SBS and bitumen/EVA were prepared according to the following content rates: 3, 5 and 7 wt.%.

To confirm the uniform dispersion of the polymer modifiers in the bitumen matrix, the mixture was passed through an ASTM 100# sieve. After completion, the different samples were removed from the flask and poured into small containers. The whole samples were cooled to room temperature, covered with aluminum foil and stored for testing.

Table 1
Main physical and chemical characteristics of SBS and EVA copolymers used as modifiers for the base bitumen.

Properties	Polymers	
	SBS	EVA
Physical aspect	Porous and granular	Granular
Molecular structure type	Linear	Linear
Polystyrene (wt.%)	31	/
Vinyl acetate (wt.%)	/	18
Density (ASTM D792)	0.94	0.939
Stress at break (ASTM D412)	33 MPa	38 MPa
Elongation at break (ASTM D412)	880%	>800%
Hardness shore (A) (ASTM D2240)	72	90
Melt flow index (ASTM D1238)	<1 g 10 min^{-1}	1–2 g 10 min^{-1}
Processing temperature	150–170 °C	64 °C

2.3. Aging experiment

The accelerated thermal aging under oxygen of both PMAs and neat bitumen was carried out using the Rolling Thin Film Oven Test (RTFOT) according to ASTM D1754 [14]. The RTFOT is used to simulate the effect of occurring short-term ageing in the mixing process [13]. This was performed using glass containers heated to 163 °C for about 20 min before loading the sample. After this, the aging process continues for 75 min at 163 °C. The aged binders were evaluated by measuring the penetration at 25 °C and the softening point temperature [3,9,10].

2.4. Techniques

The polymer modified bitumens were tested using empirical tests of softening point temperature, penetration and ductility before and after RTFOT. For comparative purposes, tests were also conducted on the neat bitumen.

Penetration test was used to determine the consistency of a bitumen binder according to the following procedure [17]: bitumen is placed in a standard cup at 25 °C. A needle is then allowed to fall into the bitumen under a 100 g load for 5 s. The length the needle penetrates into the bitumen during this time is expressed in units of 0.1 mm. Soft bitumens exhibit high penetrations and harder bitumens low penetration values.

The softening point 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. The heated bitumen sample is placed in each of two brass rings. The rings are then placed in a bath of demineralised water/glycerol and a ball bearing is placed on each. The water/glycerol is heated at a rate of 5 °C/min until the binder deforms due to its decreasing viscosity with increasing temperature. The softening point temperature was taken as the temperature at which the sample became soft enough to allow the ball, enveloped in the sample material, to fall a distance of 25.4 mm. This was recorded as the ring and ball softening point temperature.

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 the change in the consistency parameter as a function of temperature. A classical approach related to PI calculation is reported in the Shell Bitumen Handbook as shown with the following equation [10]:

$$\mathrm{PI} = \frac{1952 - 500 * \log(\mathrm{Pen}_{25}) - 20 * \mathrm{SP}}{50 * \log(\mathrm{Pen}_{25} - \mathrm{SP} - 120)}$$

where P_{25} is the penetration at 25 °C and SP is the softening point temperature of the modified bitumen samples. Lower values of PI indicate higher temperature susceptibility.

The ductility of both unmodified and modified bituminous samples was measured according to ASTM D113-86. The test consists of measuring the distance to which the bituminous sample will elongate before breaking when two ends of a briquette specimen of the material are pulled apart at 5 cm/min and 25 °C.

Storage stability (toothpaste tube test) was determined according to ASTM D5892. The bituminous sample was placed in a tube (cylindrical mold of 32 mm diameter and 160 mm height) and stored vertically into an oven at 163 ± 5 °C for 48 h. The tube was then cooled to room temperature and stored in a freezer. It was cut into three equal parts. The upper and lower parts were then melted and poured into the rings for the ring and ball softening point temperature test. The difference in °C between the softening point temperature of respective top and bottom samples was reported [5,8,10,15].

SARA characterization was used in this study to determine the chemical composition of both the neat bitumen and the polymer modified bitumens before and after aging. Bitumen is often conveniently characterized by its chromatographic fractions, the maltenes and the asphaltenes, which are respectively soluble and insoluble in *n*-heptane. The maltenes can be fractionated further in classes of compounds called saturates, aromatics and resins. For this purpose, both microdeasphalting and TLC–FID (Thin Layer Chromatography with Flame Ionization Detection) methods were used to precipitate the asphaltene fraction and to fractionate the remained part (maltene) to saturates, aromatics and resins, respectively. In the first step, 0.4 g of the sample was added to 20 ml of *n*-heptane to precipitate asphaltenes. The mixture was heated for 30 min. Heating helps in formation of larger aggregates of asphaltene precipitates. Stirring and shaking the mixture are necessary to prevent precipitation of resins and other molecules. After this step, the samples were left to cool down and then filtered to separate asphaltene precipitates from the maltene phase. The filtration was done under vacuum using a membrane of 0.45 μm size. The mass of the membrane was measured earlier. The membrane was left to dry for 10 min and then weighted again. The difference between the two weights was reported as the mass of the asphaltene fraction in the sample. The maltene phase which contains saturates, aromatics and resins was then analyzed with the TLC–FID method for SAR analysis. In this method, first, 10 mg of the maltene phase were added to 1 ml of chloroform. A very tiny amount of this diluted sample was put on a special quartz rod which in fact is a capillary tube covered with the silica gel provided for the chromatography purposes. The procedure was repeated for each sample on three rods for more accuracy and the average of