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Ageing by UV radiation of an elastomer modified bitumen

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Abstract

Laboratory methods to simulate the short- and long-term ageing occuring during the service life of pure and polymer modified bitumens in a pavement are standardized but none of them takes into account the influence of UV radiations. If the impact of thermal ageing on the degradation of SBS elastomers in bitumens has been extensively studied, there is not study dealing with the photo-oxidation of these copolymers in a bituminous matrix. So, the aim of our study was to investigate, by FTIR spectrometry and SEC chromatography, whether the architecture of elastomers (linear or radial) might have any influence on their ageing by UV radiation in a bituminous matrix. The results show that the elastomers oxidation kinetic, unlike the disappearance kinetic of *trans*-butadiene double bond, does not depend on their architecture. But, when putted into the same base bitumen, the two copolymers show exactly the same oxidation kinetic and the same decreasing kinetic of *trans*-butadiene double bond. So, this study has revealed that inside the bituminous matrix, on the one hand, the elastomers architecture does not influence on its degradation when submitted to UV radiation and, on the other hand, there is a "protection" of the elastomers by the studied bitumen towards UV radiation.

Keywords: Modified bitumen; Elastomers; Photo-oxidation; Fourier Transform infrared spectrometry; Size exclusion chromatography

1. Introduction

Bitumen has been used in the construction of asphalt pavements for more than a century. As a viscoelastic material, bitumen plays a prominent role in determining many aspects of road performance. For example, a bituminous mixture needs to be flexible enough at low service temperatures to prevent pavement cracking and to be stiff enough at high service temperatures to prevent rutting [1].

However, because of continuously increasing traffic volumes and axle loads, bituminous mixtures containing conventional bitumens do not always perform as expected. Consequently, for certain applications, properties of bitumens need to be improved with regard to performance-related properties, such as resistance to permanent deformation, low temperature cracking, load-associated fatigue, wear, stripping and ageing [2]. The first way of achieving better asphalt pavement is to use a better arrangement of aggregates, binder and void contents. When all these parameters are adequately selected, the second step is to use a better binder with higher performance than pure bitumen. Such an enhanced binder is often a polymer modified bitumen (PmB) obtained by the incorporation of a polymer in the bitumen using mechanical mixing and/or chemical reaction [3]. The properties of PmBs are dependent on polymer characteristics and content, bitumen nature, as well as the blending process [4–6]. Despite the large number of polymeric products, mostly two classes of polymers are suitable and typically used in bitumen modification, elastomers and plastomers. Polymer modification, developed in France in the late seventies, is now widely used in road construction [7].

However, the enhanced properties of these PmB's can evolve as a result of ageing during mixing, storage and

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application in service [8]. Ageing is already a very complex process in conventional bitumens and the complexity increases when polymer modified bitumens are involved. It is well known that the principal cause of ageing in service of bituminous binders is the oxidation by oxygen from the air of certain molecules. This oxidation results in the formation of highly polar and strongly interacting oxygen containing functional groups [9–11]. This mechanism of thermal oxidation by air oxygen is well-known for both pure and modified bitumens.

On the other hand, although the influence of solar radiation on bituminous binders has been known for some considerable time [12], the influence of ultraviolet (UV) light on bitumen ageing is often ignored in laboratory simulations of ageing due to the fact that UV radiation only affects the upper layers of the pavement surfacing [12–14]. In the 1950s, an ‘‘Exposure test’’ [15] was developed which showed that the effect of solar radiation depended on the nature of the bitumen [16]. The photo-oxidation of bituminous binders, carried out according to the same experimental conditions than the ones described in the European standard of paint ageing [17], lead to the same conclusions.

The mechanisms of photo- and thermal ageing of elastomers are well-described in the literature [18–22]. Even if the impact of thermal ageing on the degradation of SBS elastomers in the bitumens has been extensively studied [8,11,12,24,25], however there is not studies dealing with the photo-oxidation of these copolymers in a bituminous matrix.

So, this paper describes a study that investigates whether the architecture of elastomers might have any influence on their ageing by photo-oxidation in a bituminous matrix. This influence was studied for a blend of a same base bitumen with two elastomers showing different architectures.

2. Experimental

2.1. Materials

The studied base bitumen B was a 35/50 penetration grade according to NF EN 12591 standard. In order to be closer to the ageing conditions during road service life, the photo-ageing tests were performed on binders previously submitted to the Rolling Thin Film Oven Test (RTFOT) (NF EN 12307-1), claimed to simulate ageing at the jobsite (i.e. mixing with aggregates and laying on the road).

The penetration at 25 °C (NF EN 1426) and the softening point (NF EN 1427) of the unaged pure bitumen and the aged binder after RTFOT as well as their evolution expressed according to the normalized ways (ratio of retained penetration and difference in softening point as in EN 12591 standard) are listed in Table 1.

Table 1
Conventional characteristics of the unaged and aged base bitumen B

Base bitumen	Ageing	Penetration at 25 °C[1] (1/10 mm)	Retained penetration (%)	Softening point[2] (°C)	Softening point increase (°C)
B	Origin	53	64	49,3	5,1
	RTFOT	34		54,4	

[1] According the NF EN 1426 standard.
[2] According the NF EN 1427 standard.

Table 2
Generic fraction of the unaged and aged base bitumen B determined by IATROSCAN

Base bitumen	Ageing	Saturated (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)
B	Origin	8	39	34	19
	RTFOT	8	36	37	19

Generic fractions of the base bitumen B, measured with the IATROSCAN MK5, by successive elution in *n*-heptane, toluene/*n*-heptane (80/20), dichloromethane/methanol (95/5), are listed in Table 2. Details of the methods are provided in the literature [26].

Two physical polymer modified bitumens (PmBs) were manufactured at the laboratory by adding 4% of two elastomers, either a linear styrene/butadiene/styrene (l-SBS) or a radial styrene/butadiene/styrene (r-SBS) to the base bitumen B. Both blends were obtained after 1 h of moderated shear stirring (300 rpm) and under normal air pressure, at 180 °C.

The molecular weights of the linear and radial SBS copolymers, with 30% of styrene, are about 155,400 (M_w). They were determined by size exclusion chromatography (SEC) according to the experimental procedure described further.

2.2. Ageing methods

Short-term ageing was addressed by the Rolling Thin Film Oven Test (RTFOT) as described in the European standard NF EN 12607-1. This technique has been validated for some time for unmodified bitumens for which it is considered to be more severe than actual jobsite conditions [27]; in the case of modified bitumens, its validity is still open to doubt. However, in the absence of anything better, it has been used with considerable success [28,29] to compare different PmBs during laboratory studies.

Photo-ageing tests were performed in an UV weathering oven. According to Montepara [30,31], the binder film was aged by RTFOT test before UV exposure. Pieri's ‘‘dry slide’’ technique was used to prepare the binder film [32]: 25 μL of binder in a 170 g L^{-1} solution of dichloromethane were deposited on a slide suitable for transmission Fourier Transform InfraRed (FTIR) measurement (NaCl). The solvent was eliminated by natural evaporation and FTIR spectrometry was used to check its complete absence. From both the deposited volume and the area of the residual film, these films can be considered to be approximately 10 μm