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Infrared microscopy investigation of oxidation and phase evolution in bitumen modified with polymers

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Abstract

Increase in traffic volume has led to a wider use of Polymer modified Bitumens (PmB's) in road construction. Although the mechanical properties of such materials have been widely studied, their change with time in service, also called ageing, is yet to be fully understood.

One of the most important issues is to identify the process involved: is PmB ageing a consequence of bitumen ageing, polymer ageing or both at the same time? Moreover, most PmB's feature a two-phase structure made of polymer rich areas along with polymer poor regions, depending on the bitumen chemistry, the polymer nature and content. It is therefore important to take this peculiar structure into consideration when trying to sort out the respective effect on ageing of the polymer and the bitumen. Infrared microscopy allows characterizing separately different phases in heterogeneous products; therefore it is appropriate for PmB's.

In this paper, PmB's were studied in their original state and after conventional tests claimed to simulate the ageing during the mixing process and several years of road service (RTFOT + PAV). The PmB's included plastomers and elastomers, some of them being *in situ* crosslinked. Infrared microscopy was used to determine for each phase the polymer rate and functional indices characterizing the bitumen such as aromaticity, aliphaticity and condensation, and also to map the polymer distribution in the PmB.

The characterization of PmB in their original state points out which species of the bitumen are involved in the polymer swelling and the effect of the polymer nature. The characterization of the same PmB's after the RTFOT + PAV ageing shows how the bitumen species responsible for the swelling evolve during ageing. In addition, kinetic studies were performed using an heating cell fitted to the IR microscope. They confirmed the tendencies obtained with the conventional ageing tests.

These studies come to the conclusion of an interdependence of the ageing of the different constitutive phases in a PmB and of chemical exchanges between them. They make clear the micro-morphological modification induced by ageing in a PmB. They finally help to better understand the effect of a crosslinking on the PmB microstructure and its ageing mechanism.

Keywords: Polymer modified Bitumens; Infrared microscopy; Ageing; Simulation techniques

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.

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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 and 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 theses parameters are adequately selected, the second step is to use a better binder with higher performance than neat 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 application in service [8]. The knowledge of the change with time in service of such materials still remains insufficient at the present time. Consequently, ageing is one of the important issues being discussed to set up performance-related test methods and then specifications in Europe [9]. One of the key issues is, in fact, to describe the process involved: is PmB's ageing a consequence of bitumen ageing, polymer ageing or a combination of both?

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 [10,11]. The ageing is generally assessed by conventional ageing tests such as Rolling Thin Film Oven Test (''RTFOT'', norm EN 12607-1) and Pressure Ageing Vessel (''PAV'', norm EN 14769). RTFOT and PAV are expected to simulate, respectively, short term ageing during mixing and long term ageing in the field [12,13].

Because the main cause for ageing of bituminous binders is oxidation, the chemical transformations of the binders during ageing can be determined by analytical techniques such as the infrared spectroscopy, which informs on the nature and concentration of functional and structural groups [14].

However, the infrared spectroscopy developed for conventional bitumens that are relatively homogeneous materials at this scale is not sufficient to characterize PmB's, due to their heterogeneous microstructure. Indeed, PmB's generally display a biphasic microstructure with polymer nodules dispersed in a continuous bitumen phase, or a bitumen phase dispersed within a continuous polymer phase, or even two interlocked continuous phases [15].

Consequently, microscopy techniques are suitable to study PmB's such as UV fluorescence microscopy [6]. In another study, infrared microscopy was chosen because it simultaneously allows visualising the PmB's microstructure and chemically characterizing the visualized micro-phases [16].

Moreover, this technique associated with an ageing cell, specially developed to fit the infrared microscope [17], permits to follow continuously *in situ* the oxidation of PmB's through the visualization and chemical characterization of the different micro-phases without modifying the internal equilibrium between polymeric and bituminous phases.

The goal of this particular study was to understand the chemical mechanisms of PmB's ageing during continuous oxidation under the microscope and to compare them with more conventional ageing test methods used by the industry.

Another aim of this study was to bring new information to durability studies in progress within current national and European standardization frameworks.

2. Materials and procedures

2.1. Materials

The base bitumen Bc was a 70/100 penetration grade bitumen according to NF EN 12591 standard obtained from a TOTAL refinery. The penetration at 25 °C (NF EN 1426) and the softening point (NF EN 1427) of the unaged neat bitumen and the aged binder after RTFOT + PAV are listed in Table 1, as well as their evolution expressed according to the normalized ways (percent of retained penetration and difference in softening point as in EN 12591).

Generic fractions of the base bitumen measured with the CORBETT method by successive elution in heptane, toluene/*n*-heptane (80/20), dichloromethane/methanol (95/5), are listed in Table 2.

Two physical PmB's were manufactured at the laboratory by adding 6% of two different copolymers, either an unsaturated elastomer (linear styrene/butadiene/styrene, SBS) or a saturated plastomer (ethylene/vinyl acetate, EVA) to the base bitumen Bc. Both blends were obtained after 2 h of moderate shear stirring (300 rpm) and under normal air pressure, at 180 °C for the bitumen modified with unsatured elastomer SBS and at 160 °C for the one involving the saturated plastomer EVA.

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

Base bitumen	Ageing	Penetration at 25 °C (1/10 mm)/retained penetration (%)		Ring and Ball softening point (°C)/R&B increase (°C)	
Bc (conventional)	Origin	78	41	46.5	Δ= 11.5
	RTFOT + PAV	32		58.0	