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Molecular structure evolution of asphaltite-modified bitumens during ageing; Comparisons with equivalent petroleum bitumens

Andrea Themeli [a,b,c,*], Emmanuel Chailleux [b,*], Fabienne Farcas [c], Cyrille Chazallon [a], Bernard Migault [a], Nadège Buisson [b]

[a] ICUBE (UMR 7357, CNRS, National Institute of Applied Sciences), 24, Boulevard de la Victoire, F-67084 Strasbourg Cedex, France
[b] LUNAM Univ., IFSTTAR, MAST, MIT, Route de Bouaye, BP 4129, F-44341 Bouguenais, France
[c] Univ. Paris-Est, IFSTTAR, MAST, CMPD, 14-20 Boulevard Newton, Champs-sur-Marne, F-77447 Marne-la-Vallée, France

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Abstract

This work focuses on the molecular structure evolution of asphaltite-modified paving bitumens during ageing. In order to quantify the effect of ageing on the molecular weight distribution (MWD) of bitumens, a new parameter, called hereafter the ageing molecular-distribution shift (AMDS), is introduced. The molecular evolutions of asphaltite-modified bitumens during aging are compared with the molecular evolutions of pure petroleum bitumens of equivalent grade. The results based on AMDS confirm previous research showing that the asphaltite attenuates the ageing and, compared to hard petroleum bitumens produced in refinery, the asphaltite-modified bitumens present a better ageing performance. The AMDS parameter reveals appropriate for the evaluation of evolutions due to ageing.

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 which allow material economies on 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].

The asphaltites, natural bitumens chemically similar to petroleum bitumens, have a good potential as bitumen modifiers. 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

* Corresponding authors at: IFSTTAR-Nantes, Route de Bouaye, BP 4129, 44341 Bouguenais Cedex, France.
E-mail addresses: andrea.themeli@yahoo.com (A. Themeli), emmanuel.chailleux@ifsttar.fr (E. Chailleux), fabienne.farcas@ifsttar.fr (F. Farcas), cyrille.chazallon@insa-strasbourg.fr (C. Chazallon), bernard.migault@insa-strasbourg.fr (B. Migault), nadege.vignard@ifsttar.fr (N. Buisson).

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oxidizes and as a consequence the polarity of the medium increases leading to increased traction forces between the molecules. In this conditions, light molecules aggregate and form bigger molecular structures inducing important molecular changes to the bitumen's colloidal structure [15].

The evaluation of the chemical structural evolution of bitumens during ageing, from in situ extracted samples or laboratory aged bitumen samples, 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 (MWD) and in an erroneous estimation of the ageing degree. For this reason, inverse mechanical approaches, which allow the determination of MWDs from the mechanical properties of materials, would allow to overcome these difficulties. In previous publications we have put in place a new 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 the MWD 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 of the δ-method, the proposed approach for ageing quantification based on the MWD evolution, will be detailed. Then, the studied materials, the experimental procedures and the experimental results will be presented. Finally, the proposed ageing quantification criterion will be applied to molecular weight distributions issued from the δ-method and GPC to determine evolutions due to ageing. The results will be compared with findings of previous studies [19].

2. Ageing quantification approach

2.1. Apparent molecular weight distribution of bitumens by the δ-method

The correlation of linear viscoelastic properties of materials with their MWD is reported in several works [20–24]. The material can be considered as a mixture of species of monodisperse molecular weight (MW), each of them having a single relaxation frequency. Below this frequency some species relax and make no contribution to the mechanical response of the material. The unrelaxed species, at a particular frequency, are "diluted" by the relaxed ones [20]. As the oscillation frequency increases, smaller and smaller components 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.

Adopting the picture presented above, the δ can be 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. This method is inspired by previous works effectuated on polymers and polymers blends for which inverse mechanical approaches are demonstrated as valid [20,21].

However, it is to be noted that the assumption of proportionality has not yet been fully demonstrated for bitumens.

The phase angle (δ) is particularly sensitive to the molecular weight of bitumens [23] and it is for this reason that this property is used here to derive the molecular weights. For regular bitumens, Zanzotto established the following relationship between the crossover frequency at T=0°C and the molecular weights obtained by vapor pressure osmometry [23]:

$$\log(MW) = 2.880 - 0.06768 \cdot log(\omega) \quad (1)$$

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. According to the hypothesis that the cumulative molecular weight, $cumf$, is proportional to the phase angle, we can write:

$$cumf(MW) = A + B \cdot \delta(MW) \quad (2)$$

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

$$for\ MW \to 0; \delta(MW) = 0, cumf(MW) = 0$$

$$for\ MW \to \infty; \delta(MW) = 90^{\circ}, cumf(MW) = 1$$

From these conditions:

$$A = 0\ and\ B = \frac{1}{90^{\circ}} \quad (3)$$

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

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

Practically, the numerical differentiation is carried out by applying a numerical differential step of 1/3000 to thelog(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