

## Bitumen modifiers for reduced temperature asphalts: A comparative analysis between three polymeric and non-polymeric additives



A.A. Cuadri, V. Carrera, M.A. Izquierdo, M. García-Morales\*, F.J. Navarro

Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro<sup>2</sup>TecS), Campus de 'El Carmen', Universidad de Huelva, 21071 Huelva, Spain

### HIGHLIGHTS

- Three bitumen modifiers for warm mix asphalts in the paving industry.
- Binders with low viscosity at the mixing/lay-down/compaction temperatures.
- Important increases in viscosity binders as a consequence of ambient curing.
- Non-polymeric derivatives create hydrogen-bond network with bitumen.
- Reactive prepolymer involves reactions between isocyanate groups and ambient water.

### ARTICLE INFO

#### Article history:

Received 23 May 2013

Received in revised form 31 October 2013

Accepted 1 November 2013

Available online 21 November 2013

#### Keywords:

Modified bitumen

Thiourea

Thiourea dioxide

Isocyanate

Warm mix asphalts

### ABSTRACT

This study presents three bitumen modifiers which may find successful application in the fabrication of binders for warm mix asphalt in the paving industry. In that sense, two non-polymeric additives, thiourea and thiourea dioxide, along with a reactive isocyanate-terminated prepolymer have been evaluated. Viscous flow and linear viscoelasticity tests, at 60 °C, reveal bituminous modified binders which evolve towards highly viscous materials when subjected to ambient curing. However, at 135 °C, they show lower viscosity than a typical 3 wt.% SBS binder used as reference. These results suggest modified binders with low viscosity which may contribute to reduce the mix asphalt temperature. On the contrary, they are expected to undergo an important increase in viscosity when the asphalt is in-service, which would contribute to improve further their performance. Low temperature performance and effects of short-term and long-term aging were not considered in this study.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

Bitumen is usually defined as a dark brown to black material, mainly obtained from crude oil distillation. It is widely used as a binder of mineral aggregates in road pavements [1], as well as waterproofing material, joint sealant and for roofing applications [2,3].

Bitumen shows quite a high chemical complexity. It contains different types of molecular species, which are classified (in terms of solubility in *n*-heptane) into two major fractions, maltenes and asphaltenes. The asphaltenes (As) consist of highly condensed planar and heteroatom polar groups, polar aromatic ring systems and large amounts of heteroatom polar functional groups [4]. Based on differences in solubility and polarity, the maltene fraction can be further divided into three groups: saturates (S), aromatics (A) and resins (R) [5]. Thus, bitumen physico-chemical and rheo-

logical properties strongly depend on both temperature and the relative proportion of those four "SARAs" fractions [6,7].

Bitumen is the only deformable component and the continuous phase in asphalt mixtures. In this sense, the viscoelastic properties of bitumen, over a wide range of temperatures and loadings, are of major importance when predicting roads performance [8]. Any bitumen additive should improve the binder properties at high and/or low in-service temperatures, depending on the requirements demanded [9]. Consequently, it should be strong enough to withstand traffic loads at high temperature, which may cause rutting or permanent deformation. On the contrary, it may be necessary high flexibility at low temperatures, in order to avoid excessive thermal stresses.

Polymeric additives have been widely used to enhance the in-service properties of bitumen [3,10–12]. Polymers commonly used to modify bitumen include styrene-butadiene-styrene copolymer (SBS), styrene-butadiene rubber (SBR), ethylene vinyl acetate (EVA), polyethylene (LDPE, HDPE, etc.) and waste polymers (plastics from agriculture, crumb tire rubber, etc.) [3,13–16]. The

\* Corresponding author. Tel.: +34 959 21 82 07; fax: +34 959 21 93 85.

E-mail address: [moises.garcia@diq.uhu.es](mailto:moises.garcia@diq.uhu.es) (M. García-Morales).

characteristics of their mixing with bitumen may significantly affect the technical properties of the resulting blend, as well as the costs of the whole operation [17]. Thus, for example, bitumens modified with high molecular weight polymers may yield a significant phase separation during their storage at high temperatures [18].

Desirably, a modifying agent of bitumen for warm climate countries should meet the following features: (a) easy to incorporate; (b) homogeneously dispersed during storage; (c) adequate viscosity at high in-service temperatures, which increases resistance to permanent deformation; but (d) low viscosity at the mix asphalt temperatures, which permits energy saving operations. In relation to this last demand, production temperatures corresponding to traditional hot mix asphalt (HMA) requires materials to be heated between 135 and 180 °C, as polymer modified bitumens present very high values of viscosity at lower temperatures. The success of warm mix asphalt (WMA) technologies, emerged over the last years, relies on the development of binders which exhibit low viscosity during the asphalt production. This allows for the adequate coating of mineral aggregates and the consequent benefit for the lay-down and compaction operations.

On these grounds, a modified bitumen with low viscosity (which facilitates the asphalt mixing and compaction) which evolves towards a highly modified bitumen by means of ambient curing may represent a promising binder for the WMA technology. With this aim, this work proposes three bitumen modifiers which, through chemical reactions involving bitumen, may result of special interest in reducing the asphalt production/application temperatures: (a) two non-polymeric chemical agents, like thiourea and thiourea dioxide; and (b) a low molecular weight reactive isocyanate prepolymer. Out of scope of this article are the low temperature properties and the effects of short-term and long-term aging.

## 2. Experimental

### 2.1. Materials

Bitumen with penetration grade 150/200 was used as base material for the bitumen modification. The results of penetration grade (EN 1426:2007 [19]), softening temperature tests (EN 1427:2007 [20]) and "SARAs" fractions (procedure outlined elsewhere [21]) are shown in Table 1 (average values with their corresponding standard deviations).

Three different chemical modifiers are proposed. The two first, thiourea dioxide and thiourea, are non-polymeric substances, whilst the last one is a polyol functionalized with isocyanate groups. Detailed information on these modifiers is given below:

1. Thiourea dioxide ("ThD," hereinafter) has been described as a reducing agent used for vat dye, reduction of ketones to alcohols and hydrocarbons, reduction of conjugated unsaturated acids to the corresponding saturated acids, etc. So, bitumen modification by ThD is expected to occur on a strong reducing action. It was supplied by Sigma Aldrich, melts between 124 and 127 °C and has a molecular weight of 108.12 g/mol.
2. Thiourea ("Th," hereinafter) has been previously used as an additive to improve coating quality and to inhibit corrosion in several applications. It was supplied

by Sigma Aldrich, has a molecular weight of 76.12 g/mol and its melting point lies within the interval 175–179 °C.

Both of these substances, thiourea dioxide and thiourea, are white powders, soluble in water and polar organic solvents, but insoluble in non-polar solvents. Their structural formulae have been included in Fig. 1.

3. A polypropylene-glycol functionalized with polymeric 4,4'-diphenylmethane diisocyanate (henceforth MDI-PPG). This prepolymer was synthesized by reaction of Alcupol D-0411 (polyol donated by Repsol YPF, Spain) and polymeric MDI (supplied by T.H. Tecnica, Spain). The reaction conditions were: a PPG:MDI molar ratio of 1:5; N<sub>2</sub> atmosphere; temperature of 40 °C; 48 h of mild agitation. The resulting prepolymer, with a molecular weight of 925 g/mol, is a light brownish liquid.

In order to establish a comparative analysis with a non-reactive additive, the commercial thermoplastic elastomer "Kraton D-1101," which belongs to the category of physical modification, has been also studied. This triblock copolymer of styrene-butadiene-styrene (SBS), provided by Shell Chemical Company U.K., is able to modify through physical dispersion in bitumen. It has a molecular weight of  $1.5 \cdot 10^5$  g/mol and a styrene content of 31 wt.%.

### 2.2. Modified binders

Blends of bitumen with the different modifiers were carried out by means of an IKA RW-20 stirring device (Germany) equipped with a four-blade turbine, which has previously shown to produce the adequate mixing of bitumen with these three modifiers. A glass vessel (60 mm diameter; 140 mm height) containing bitumen was dipped into a bath with circulating oil and heated up to the processing temperature. Once this was reached, the modifier was added and the blend was stirred under the conditions described in Table 2. Regarding the non-polymeric substances, both of them are in molten state at their selected processing temperature (130 °C for ThD and 180 °C for Th). As for the polymeric additive, this is a liquid with very low viscosity at the processing temperature of 90 °C. For these reasons, a four-blade turbine rotating at 1200 rpm for 1 h is enough so that a proper dispersion can be achieved. After preparation, the binders were divided into two parts: (a) one part was tested as such (referred to as "fresh" binder); and (b) the another part was poured onto aluminium foil, forming a thin layer which was exposed to ambient under free access of air/moisture ("ambient cured" binder).

Regarding the SBS binder, blending was conducted with a Silverson L5M (Silverson Machines Ltd., U.K.) homogenizer under the conditions detailed in Table 2, as this rubber requires of more severe conditions to obtain a proper homogeneous dispersion.

### 2.3. Tests and measurements

Viscous flow measurements, at 60 °C, were carried out in a controlled-strain ARES rheometer (Rheometric Scientific, USA). Temperature sweep tests in oscillatory shear, using a continuous heating ramp of 1 °C/min, a frequency of 10 rad/s, and 1% of strain, were conducted in a controlled-stress rheometer PHYSICA MCR-301 (Anton Paar, Austria) between 20 and 95 °C. Before testing, samples were equilibrated for 30 min at the starting temperature. Plate-and-plate geometry (25 mm diameter and 1 mm gap) was always used. In order to ensure accurate results, at least two replicates were conducted for every sample.

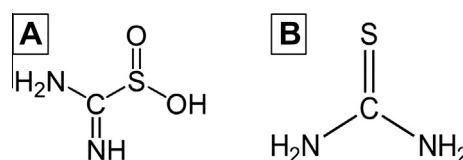


Fig. 1. Structural formulae of: (A) thiourea dioxide and (B) thiourea.

**Table 1**  
Penetration values, Ring & Ball softening temperatures, "SARAs" fractions and colloidal index value for the neat bitumen used.

	Values
Penetration (dmm)	168(5) <sup>a</sup>
R&B softening point (°C)	41.0(2.0) <sup>a</sup>
Saturates (wt.%)	7.4(0.5) <sup>a</sup>
Aromatics (wt.%)	57.6(2.1) <sup>a</sup>
Resins (wt.%)	15.1(1.2) <sup>a</sup>
Asphaltenes (wt.%)	19.9(1.5) <sup>a</sup>
Colloidal Index (C.I.)	0.38

<sup>a</sup> Values given as: mean (standard deviation).

**Table 2**  
Processing conditions used for the modified bituminous binders.

Modifier agent	Concentration (wt.%)	Proc. temperature (°C)	Proc. time (h)	Agitation speed (rpm)
Thiourea dioxide (ThD)	3 and 9	130	1	1200
Thiourea (Th)	3 and 9	180	1	1200
Reactive prepolymer (MDI-PPG)	4	90	1	1200
Styrene-butadiene-Styrene (SBS)	3	180	2	2500

Download English Version:

<https://daneshyari.com/en/article/257952>

Download Persian Version:

<https://daneshyari.com/article/257952>

[Daneshyari.com](https://daneshyari.com)