



Processing of bitumens modified by a bio-oil-derived polyurethane



A.A. Cuadri, M. García-Morales, F.J. Navarro, P. Partal *

Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro²TecS), Campus de 'El Carmen', Universidad de Huelva, 21071 Huelva, Spain

HIGHLIGHTS

- Polyurethane modified binders with improved end-performance.
- Natural polyol as a sustainable alternative to the use of petro-chemical stuff.
- Binder's properties highly influenced by both processing and post-treatment.
- Important changes in the binder's microstructure after modification.

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ABSTRACT

Castor oil (CO) functionalized by isocyanate groups ($-NCO$) is proposed as a novel bio-based reactive polyurethane (PU) for bitumen modification. This work presents a comparative analysis conducted on blends of bitumen and 2 wt.% of a PU prepolymer prepared by NCO-functionalization of castor oil. Four preparation procedures were evaluated, which resulted from the combination of two processing times (1 h or 24 h, at 90 °C) followed by two different post-treatments (water addition or ambient curing for up to 6 months). It was found that the degree of modification attained after post-treatment depends on the previous processing conditions. Thus, short processing times are required if the binder is further subjected to ambient curing. Instead, the success of the water-addition modification falls on a previous long processing step. As revealed by rheological tests, ambient curing was seen to be by far a more efficient way of modification if compared to direct addition of water, and makes clear that the resulting binder evolves towards a better performance when in-service. In that sense, Thin Layer Chromatography tests, Modulated DSC and AFM images demonstrated a more complex microstructure characterized by the presence of a larger content of molecules with higher polarity, size and molecular weight.

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1. Introduction

Bitumen, residue from crude oil distillation, is a complex material basically composed of hydrocarbons along with some other molecules which contain small percentages of heteroatoms (sulphur, nitrogen and oxygen). Bitumen compounds can be classified by chromatographic techniques into four different fractions (usually referred to as SARAs): saturates (S), aromatics (A) and resins (R), which make up the maltenes, and asphaltenes (As). The complexity, aromaticity, heteroatom content, and molecular weight increase in the order $S < A < R < As$ [1]. A colloidal model, consisting of asphaltenes being dispersed into an oily matrix of maltenes and peptized by resins, is traditionally used to describe bitumen behaviour [2,3].

On account of its properties, bitumen is the most suitable material to be used as a binder of mineral aggregates for paving

applications [4]. In bituminous asphalt mixes, mineral fillers (with a particle size below 75 μm) typically represent from 2 to 12 wt.% on their total mineral matter [3]. Hence, a bitumen/filler blend (commonly referred to as mastic) naturally forms when bitumen and aggregates are mixed. In that sense, mastic is the actual product used to hold coarser aggregates particles together in the asphalt mixtures [5]. Consequently, bitumen is the only deformable component and forms the continuous matrix of the mastic (and, therefore, of the asphalt mixtures) contributing significantly to road performance [6].

Unfortunately, even the best designed and constructed road pavements deteriorate over time under the combined effects of traffic loading and weathering. The most common distresses are: (a) rutting, or permanent deformation at high temperatures [7]; (b) thermal cracking, or thermal fracture due to lack of flexibility at low temperatures [8]; and (c) fatigue cracking, or series of longitudinal interconnected cracks caused by the repeated applications of wheel loads [4]. Hence, different blends of bitumen with a large variety of modifiers have been studied [9,10]. The polymers

* Corresponding author. Tel.: +34 959 21 99 89; fax: +34 959 21 93 85.

E-mail address: partal@uhu.es (P. Partal).

used for the modification can be divided into three categories, namely thermoplastic elastomers, plastomers and reactive polymers [11,12]. However, the two first classes of polymers usually present a limited compatibility with bitumen. The addition of reactive polymers, which contain functional groups able to react with certain bitumen compounds, may yield some advantages in the resulting binder [11–14].

Interestingly, the use of polyurethane prepolymers presents, among others, two significant benefits. First, these prepolymers are liquids which facilitate their blends with bitumen at low temperature (i.e., 90 °C). Second, the low concentration of additives required to achieve binders with enhanced rheological properties would result in a price reduction of the resulting product.

On the other hand, the utilization of renewable raw materials in polyurethane (PU) formulations has become of increasing interest recently. Moreover, apart from the environmental benefits, the prepolymers thermal stability has been found to improve when castor oil, instead of a polyethylene glycol (PEG), is used [15]. Bitumen modification with this type of prepolymer is expected to take place by reaction of the free –NCO groups in the prepolymer and bitumen pendant groups which contain active atoms (–OH mainly, typically present in the asphaltenes) [16,17]. However, previous studies on NCO-functionalized polyether prepolymers [18–20] point out that this type of bitumen modification is a complex process, greatly influenced by a post-process curing which involves ambient moisture. Thus, during the material's service-life, water from the air is able to slowly diffuse into bitumen and react with –NCO groups in excess (“ambient” modification). Interestingly, this route has been simulated by direct addition of water to fresh material (“added-water” modification).

The goal of the present work is explore the effect of processing on the rheological behaviour of bituminous products modified with isocyanate-functionalized castor oil. Furthermore, we aim to understand the microstructural changes behind “ambient” and “added-water” modifications with this type of prepolymers. Accordingly, different rheological tests and some other supporting techniques (TLC/FID, MDSC and AFM) have been conducted.

2. Experimental

2.1. Materials

Bitumen with a penetration grade of 100/150 was used as base material for the modification. Details of technological properties (penetration grade and R&B softening temperature, according to ASTM D5 and D36, respectively) and chemical composition, in terms of SARAs fractions, are shown in Table 1.

Two different types of polymers, which correspond to “active” (chemical modification) and “passive” (physical modification) categories, respectively, have been considered:

- (a) Castor oil (designated as CO) supplied by Guinama (Spain), with hydroxyl index of 125 mg KOH/g (measured according to standard ASTM D1957), was functionalized with

isocyanate groups, by its reaction with a polymeric 4,4'-diphenylmethane diisocyanate (–NCO content of 31 wt.%) provided by T.H. TECNIC, S.L (Spain). This reaction was carried out at 60 °C, for 48 h, under agitation and with N₂ blanketing. In order to ensure an excess of non-reacted –NCO groups in the reaction product, an equivalent ratio –NCO/–OH of 8:1 was selected. This ratio was found optimal in a previous work [15]. The resulting reactive prepolymer (referred to as MDI-CO) has an average molecular weight of 2640 g/mol, and is expected to bring about “chemical” modification of bitumen, via –NCO groups.

- (b) For the sake of comparison, the commercially available SBS triblock copolymer “Kraton D-1101” (31 wt.% styrene; M_w of $1.5 \cdot 10^5$ g/mol) was used to carry out “physical modification”, through mere physical dispersion in bitumen.

2.2. Sample preparation

MDI-CO/bitumen blends were prepared in a batch mixer composed of a glass vessel (60 mm diameter and 140 mm height), an IKA RW-20 (Germany) stirring device and a four-blade turbine. Bitumen modification, always with 2 wt.% PU prepolymer, was performed by the following two different procedures:

- (i) In the first procedure, bitumen and MDI-CO were mixed for 1 h, at 90 °C and 1200 rpm, and the resulting modified bitumen was then divided into three parts: (a) one was used as such (“non-treated” or fresh binder); (b) the second one was mixed with 2 wt.% water for 45 min at 90 °C (“added-water” binder); and (c) the third part was poured onto aluminium foil, forming a thin layer which was exposed for up to 6 months to ambient conditions (“ambient” binders). All these samples will be referred to as “1 h-processing” samples.
- (ii) In the second procedure, prepolymer and bitumen were mixed for 1 h and then the blend was set inside an oven for 24 h at 90 °C; afterwards, the resulting binder was divided into the same three parts as above. All these samples will be referred to as “24 h-processing” samples.

In addition, a bituminous reference sample with 3 wt.% of SBS (formulation typically used in paving) was prepared for 1.5 h, at 180 °C, with a Silverson homogenizer.

Finally, two samples of neat bitumen subjected to the above processing protocols (i) and (ii) did not show any relevant change in their rheological response if compared to the original neat bitumen.

2.3. Testing procedures

Different rheological tests were conducted in a controlled-stress rheometer Physica MCR-301 (Anton Paar, Austria): (a) viscous flow measurements, at 60 °C; and (b) temperature sweep tests in oscillatory shear, between 30 and 100 °C, at a heating rate of 1 °C/min, a frequency of 10 rad/s and deformation of 1% strain (within LVE interval). A plate-and-plate geometry (25 mm diameter; 1 mm gap) was always used. In order to ensure the repeatability of the results, all the tests were carried out at least twice.

Modulated Differential Scanning Calorimetry (MDSC) was performed with a TA Q-100 (TA Instruments, US). Samples (5–10 mg) were subjected to the following testing procedure: temperature interval between –50 and 90 °C; heating rate of 5 °C/min; amplitude of modulation of ± 0.5 °C; period of modulation of 60 s; and nitrogen as purge gas, with a flow rate of 50 mL/min. In order to provide the same recent thermal history, all the modified

Table 1
Penetration values, R&B softening temperatures and SARAs fractions for the neat bitumen studied.

	Bitumen 100/150
Penetration (1/10 mm)	114
R&B softening point (°C)	40
Saturates (wt.%)	7
Aromatics (wt.%)	61
Resins (wt.%)	20
Asphaltenes (wt.%)	12

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