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Effect of processing on the rheological properties of poly-urethane/urea bituminous products

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ABSTRACT

In this work, bitumen modification, by "in situ" formation of poly-urethane/urea-based polymers in the bituminous matrix, has been studied. This procedure consisted of a first modification by the addition of MDI-PPG reactive prepolymer (polypropylene-glycol, PPG, functionalized by polymeric MDI, 4,4′-diphenylmethane diisocyanate), in a first stage, and a further modification of the new bitumen-MDI-PPG molecules as water was added, in a second stage. Thin layer chromatography, TLC–FID, and infrared spectroscopy, FTIR, techniques have been used to follow the reactions occurring in four different types of bitumen. Rheological measurements have demonstrated that the resulting bitumen modification strongly depends on the processing conditions selected during the first stage. Thus, bitumen modification degree after water addition increases as processing time does. Furthermore, water addition has been found to promote bitumen foaming at low processing temperatures, which could be used in novel applications where a foamed binder is required. As a result, a reactive bitumen modification mechanism, involving a set of three chemical reactions, has been proposed.

1. Introduction

Bitumen is a colloidal dispersion obtained from crude oil distillation. The chemical composition and colloidal nature of bitumen mainly depend on the crude oil source and refining processes involved. Its composition is usually given in terms of the relative quantities of the SARAs fractions (Saturates, Aromatics, Resins and Asphaltenes) [1]. Bitumen physico-chemical behaviour depends on the relative concentration of its different fractions. Thus, a variation in its composition strongly affects its mechanical properties and chemical reactivity [2,3].

Conventional bituminous materials have found satisfactory use in highway pavement and airfield runway applications, due to some bitumen properties such as impermeability, adhesiveness, elasticity and ductility [4]. However, nowadays, the need to enhance bitumen properties has grown due to the combined action of heavy truck traffic, dramatic changes of temperature, and increase in axle loads. Hence, different blends of bitumen with a large variety of modifying agents have been studied [5,6]. Among them, bitumen modification with polymers may help to overcome road distresses such as rutting at high temperature, fatigue cracking or thermal cracking [7,8]. The polymers used for bitumen modification can be divided into three broad categories, namely thermoplastic elastomers, plastomers, and reactive polymers [9,10]. Thermoplastic elastomers are able to endow the pavement with higher flexibility at low temperatures, while plastomers and reactive polymers are added to confer rigidity and reduce deformations under load. However, the two first classes of polymers usually present a very low compatibility with bitumen. The addition of reactive polymers, containing functional groups supposedly able to chemically interact with certain bitumen compounds, may yield some advantages in the resulting binder [2,3,9,11].

In this sense, a MDI-PPG (polypropylene-glycol functionalized with 4,4′-diphenylmethane diisocyanate) prepolymer has been used in this research. Bitumen modification with this prepolymer is expected to take place by reaction of the isocyanate groups of the prepolymer with functional groups containing active hydrogen atoms (mainly, –OH), typically present in the asphaltene micelles [12,13]. However, studies on roofing membranes and bituminous binders for paving applications [14–16] have pointed out that bitumen modification with MDI functionalized prepolymers is a much more complex process, which also involves curing processes due to air moisture (i.e. water in the environment). Thus, once the material is in use, water from the air is able to diffuse and react with the remaining isocyanate groups. Recent results on bitumen modification by PEG functionalized with isocyanate groups [14] proved the existence of an optimum temperature interval for processing, established at 90–120 °C.

Aiming to proceed further with this investigation and as an attempt to spare the curing stage described before, the aim of this work was to promote "in situ" formation of poly-urethane/urea-based polymers in the bituminous matrix during the binder mixing process, by the addition of a small amount of water to a MDI-PPG/bitumen mixture. As a result, instead of the slow curing process previously commented [14–16], the addition of water to a mixture of isocyanate-based prepolymer and

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bitumen could be used for the design of tailored polymer-modified bituminous products (i.e. poly-urethane/urea-based modified binders) with improved properties. This paper explores the effect of processing on the rheological behaviour of the resulting modified bitumen. On the other hand, the final characteristics of the modified binders seemed to be strongly dependent on the crude oil source and the processing conditions. Moreover, water addition has been found to promote bitumen foaming at low processing temperatures, which could be used in novel applications where a foamed binder is required.

2. Experimental

Four bitumen samples from different sources, referred to with letters A to D, were used as base materials for water-polymer modification. The results of penetration grade trials, according to ASTM D5 [17] and ring and ball (R&B) softening temperature tests, determined according to ASTM D36 [18], are presented in Table 1.

A low molecular weight reactive polymer was used as modifying agent. The polymer was a polypropylene-glycol (PPG) functionalized by polymeric MDI (4,4′-diphenylmethane diisocyanate), henceforth MDI-PPG. It shows an average M_w of 2800 g mol^{-1}, a polydispersity (M_w/M_n) of 1.33 (both determined by GPC, with the apparatus Waters 2414 Refractive Index Detector, the column Styragel® HR 4E and THF as solvent), and an average functionality of 2.8. This polymer was synthesized by reaction of PPG, Alcupol D-0411 (donated by Repsol YPF, Spain) and polymeric MDI (supplied by Dow Chemical, Spain), selecting a PPG-MDI molar ratio of 1:3, in N_2 atmosphere, at 40 °C for 48 h and under agitation. The resulting polymer is a light brownish liquid. For the sake of comparison, styrene–butadiene–styrene copolymer, SBS, (typically used in the paving industry) was also utilized as a modifying agent (characteristics are presented in Table 1).

MDI-PPG bitumen blends were processed in a batch mixer (a cylindrical vessel of 60 mm diameter and 140 mm height), using an IKA RW-20 stirring device (Germany) equipped with a four-bladed 45°-pitched turbine. Since both neat bitumen samples and MDI-PPG prepolymer viscosities at 90 °C are low enough as to carry out a proper mixing process, the procedure proposed aims to prevent bitumen from severe processing conditions that could lead to primary ageing. Bitumen modification with 4 wt.% MDI-PPG and 2 wt.% water was performed by following two different procedures: i) Firstly, bitumen and MDI-PPG were mixed for 1 h, at 90 °C and 1200 rpm, followed by water addition and mixing for 45 min at the same temperature and speed; ii) In the second procedure, polymer and bitumen were mixed for 1 h and stored in an oven for 24 h at 90 °C; afterwards, water was added and the whole blend mixed for 45 min. The development of the foamed bitumen, observed after water addition, was assessed through readings taken by a DLS-C 15 Distance Laser Sensor (Dimetrix AG, Switzerland), set above the mixing vessel which allowed the evolution of foam height with time to be recorded. For the sake of clarity, samples prepared according to procedure i) will, henceforth, be referred to as “1 h processing” and those corresponding to procedure ii) as “24 h processing”.

Viscous flow measurements, at 60 °C, were carried out in a controlled stress RS-150 rheometer (Haake, Germany), using a plate-and-plate geometry (35 mm diameter, 1 mm gap). Temperature sweep tests in oscillatory shear, according to AASHTO TP5 [19]. (1 °C/min heating rate, 10 rad/s and 1% strain), were conducted in a Gemini rheometer (Bohlin, UK) between 10 and 110 °C. At least two replicates of each test were done.

Bitumen SARAs fractions were determined by thin layer chromatography coupled with a flame ionization detector (TLC/FID), using an Iatroscan MK-6 analyzer (Iatron Corporation Inc., Japan). Elution was performed in hexane, toluene and dichloromethane/methanol (95/5), following the procedure outlined elsewhere [20].

FTIR spectra were obtained with a Digilab FTS3500ARX (Varian, USA) apparatus. Two sets of MDI-PPG-water modified binder solutions were prepared by dissolving 0.7 g of each binder in 25 mL of toluene and dichloromethane, respectively. Toluene was chosen as a solvent because of its lack of absorbance in the spectral region of interest (NCO band at 2273 cm^{-1}). On the other hand, the binders were also dissolved in dichloromethane, which does not show any relevant peak between 1600 and 2000 cm^{-1} (urea/urethane C O bands). The measuring cell, consisting of two KBr disks (32 × 3 mm) with a Teflon spacer in between (path length of 1 mm) placed into the appropriate sample holder, was filled with the different solutions prepared. The spectra were obtained in a wavenumber range of 400–4000 cm^{-1} at 4 cm^{-1} resolution in the transmission mode.

3. Results and discussion

3.1. Polymer modification and processing

Fig. 1 shows the viscous behaviour of MDI-PPG-water modified bitumen samples, at 60 °C, manufactured following procedures i) (1 h processing) and ii) (24 h processing). Viscous flow curves corresponding to neat bitumen B and 3 wt.% SBS modified bitumen B (formulation commonly employed in the paving industry) have also been included for the sake of comparison. The remaining neat bitumen samples have not been included in Fig. 1, because they show a very similar viscous behaviour to neat bitumen B. It can be observed that bitumen reactive modification by MDI-PPG and water

Table 1
Penetration values and R&B softening temperatures for the different neat bitumen samples studied, as well as some characteristics of the SBS used in the reference sample.

	Bitumen A		Bitumen B		Bitumen C		Bitumen D	
	neat	24 h	neat	24 h	neat	24 h	neat	24 h
Penetration (dmm)	145	84	160	57	111	47	165	106
R&B softening point (°C)	41.5	48	39.5	64	45.5	70.5	38	45.5

SBS Kraton D-1101CS

Supplier	Shell Chemical Company (U.K.)
Styrene content (wt.%)	31
Density ISO 2701 (kg/m^3)	940
Tensile strength[a] (MPa)	33
Modulus, 300% (MPa)	2.9
Ultimate elongation (%)	880

[a] Stress–strain data measured on films cast from toluene.

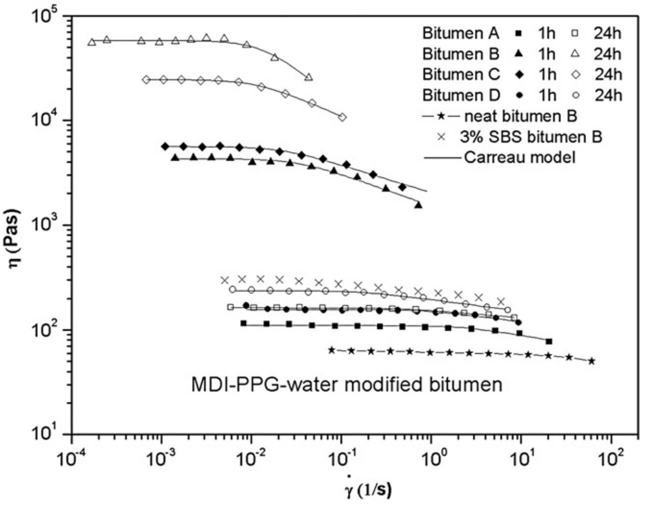

Fig. 1. Viscous flow curves, at 60 °C, for neat bitumen B, 3% SBS modified bitumen B, and MDI-PPG-water modified binders (from bitumen A, B, C and D) after 1 h and 24 h processing.