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Use of a MDI-functionalized reactive polymer for the manufacture of modified bitumen with enhanced properties for roofing applications

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Abstract

In this study, the suitability of a reactive polymer, synthesized by reaction of 4,4′-diphenylmethane diisocyanate (MDI) with a low molecular weight polyethylene-glycol (PEG), as a modifying agent for the manufacture of bitumen-based waterproof membranes, was evaluated. With that purpose, rheological and thermal analysis tests, and microstructural observations by AFM were carried out on different samples of modified bitumen having a MDI–PEG content ranging from 0 to 10 wt.%, cured at room temperature for a period of time within 0–30 days. The results obtained demonstrate that the addition of the reactive polymer proposed in this work to bitumen is very suitable at high in-service temperatures, because a noticeable increase in the values of viscosity, at 60 °C, of the resulting modified bitumen samples is observed on a timescale of days. AFM observations, carried out at 50 °C, evidenced that the reactive polymer MDI–PEG leads to a new microstructure, displaying a higher level of stiffness. Therefore, this polymer should be seriously taken into consideration as a modifier of bituminous coatings for the waterproofing industry.

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Keywords: Modified bitumen; Reactive polymer; Rheology; Roofing membrane; Product design

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1. Introduction

Bitumen, a residue from crude oil distillation [1,2], is a complex mixture of four main families of compounds, referred to as SARAs fractions (saturates, aromatics, resins and asphaltenes). It can be considered as a colloidal system in which micelles of high molecular weight organic molecules (asphaltenes), surrounded by a shell of resins, are dispersed in an oily phase (maltenes), consisting of low molecular weight saturated and aromatic hydrocarbons together with the remaining resins [3–5]. Bitumen behaviour depends on the relative concentration and the chemical features of asphaltenes and maltenes; thus, a variation in its composition strongly affects its mechanical properties.

Bitumen presents a large set of interesting potential properties: impermeability, ductility, adhesivity,

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resistance to the effect of weathering and chemicals, etc. They all have favoured the development of a wide field of applications that ranges from the construction of road pavements [6] to more specialised purposes, such as waterproof membranes for the roofing industry [7]. The performance of bitumen has been questioned over the last decades, given that it does not present a satisfactory behaviour as a consequence of extreme temperatures, severe temperature fluctuations between day and night, and the application of heavy loads. In that sense, the addition of different types of polymers to bitumen has been shown to improve its performance in a broad range of in-service temperatures [8].

Polymers that have been commonly used to modify bitumen include styrene–butadiene–styrene copolymer (SBS), styrene–butadiene rubber (SBR), tire rubber, ethylene vinyl acetate (EVA), polyethylene, and others [8–12]. Plastomers and elastomers are physically dispersed into bitumen, giving rise to a modified binder consisting of scattered domains of swollen polymer all over a bituminous continuous phase, with improved mechanical properties as a result of weak physical interactions between the polymer domains and the bitumen compounds. However, the above listed polymers usually present a very low compatibility with bitumen, and phase separation may eventually occur in the event of the blend being stored at high temperature in absence of stirring [13]. 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 [14–17], regarding both improved storage stability and enhanced in-service performance.

A MDI-functionalized polyethylene-glycol (MDI–PEG) was considered in the present work. Isocyanate groups are known to react under mild conditions with all compounds that contain 'active' hydrogen atoms (alcohols, amines, carboxylic acids, or water) to form urethane, urea and amide linkages [18,19]. Consequently, MDI–PEG modification of bitumen is expected to occur by reaction of the isocyanate groups of the polymer with most of the polar groups (–OH; >NH) of asphaltenes and resins [18,20–22].

In the present paper, we investigate the rheological and thermal behaviour of blends of bitumen with different concentrations of a MDI-functionalized polyethylene-glycol, for bitumen-based coating material applications. In that sense, bitumen/MDI–PEG blends, with a polymer content ranging from 0 to 10 wt.%, were prepared and let cured, at room temperature, for up to 30 days. The results obtained from rheological tests, as well as from thermal and microstructural analysis, are reported. With the purpose of assessing the modification ability of this reactive polymer, the results have been compared with those obtained with a selected SBS-modified bitumen (12 wt.% polymer), formulation widely used in roofing applications.

2. Experimental

2.1. Materials

Bitumen with a penetration grade of 150/200, provided by Cepsa (Spain), was used as base material for polymer modification. The results of selected technological tests carried out on bitumen samples, and the ASTM standards used are presented in Table 1.

Two different types of polymers have been used as modifying agents: the first one, belonging to the category of the so-called 'reactive polymers', because of the presence of isocyanate groups, was a polyethylene-glycol functionalized by polymeric MDI (4,4′-diphenylmethane diisocynate), henceforth MDI–PEG, with an average M_w of 784 g mol^{-1}, polydispersity (M_w/M_n) of 1.8 and an average functionality of 2.8. This polymer was synthesized by reaction of PEG (donated by Repsol YPF, Spain) and polymeric MDI (supplied by Bayern AG, Germany), selecting a molar ratio PEG/MDI of 1:5, in N_2 atmosphere, at a temperature comprised between 30 and 40 °C, for 48 h and under agitation. The resulting polymer was in liquid form with light brownish colour (Newtonian viscosity of 182 mPa s at 25 °C and 10.9 mPa s at 90 °C).

The second one was a styrene–butadiene–styrene (SBS) triblock copolymer, Kraton D-1101, provided by Shell Chemical Company (UK) (31 wt.% styrene content, $M_w = 1.5 \times 10^5$ g mol^{-1}, and $M_n = 8.98 \times 10^4$ g mol^{-1}).

Table 1
Some physico-chemical characteristics of the bitumen studied

	ASTM standard	Value
Penetration grade (dmm)	D5	200
Asphaltene content (wt.%)	D3279	22.3
R&B softening temperature (°C)	D36	46
Ductility at 25 °C (cm)	D133	100

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