

Bitumen modification with a low-molecular-weight reactive isocyanate-terminated polymer

F.J. Navarro, P. Partal *, M. García-Morales, F.J. Martínez-Boza, C. Gallegos

Departamento de Ingeniería Química, Facultad de Ciencias Experimentales, Campus de 'El Carmen', Universidad de Huelva, 21071 Huelva, Spain

Received 16 November 2006; received in revised form 17 January 2007; accepted 18 January 2007

Available online 21 February 2007

Abstract

A low-molecular-weight polyethyleneglycol functionalized with a polymeric MDI (4,4'-diphenylmethane diisocyanate) was used as a modifying agent for a 60/70 penetration grade bitumen. The rheological properties of the resulting modified binder, at both low and intermediate temperatures, before and after curing at room temperature were studied and compared with those corresponding to a SBS modified bitumen. The analysis showed that the addition of a small quantity of this reactive polymer leads to enhanced rheological properties mainly at high in-service temperature (50 °C). However, modification was found to be rather slow during binder curing at room temperature. Moreover, storage stability analysis showed that phase separation did not take place after bitumen storage at 163 °C, though storage at high temperature affects the modification capability of the reactive polymer. Atomic force microscopy measurements showed that the reactive polymer addition leads to asphaltene-rich regions with lower thermal susceptibility, which are present even at high temperature, yielding an improved bitumen viscosity in this range of in-service temperatures.
© 2007 Elsevier Ltd. All rights reserved.

Keywords: Modified bitumen; MDI-functionalized polymer; Rheology; Storage stability

1. Introduction

Asphaltic bitumen, from crude oil distillation processes, is widely used as a binder in road surfacing. It is generally believed that it can be pictured as a colloidal dispersion where the components of highest molecular weight, the asphaltenes, are dispersed into a medium constituted by the remaining components, the maltenes. The maltenic fraction can still be divided into three generic groups of different molecular weight and aromaticity (in decreasing order of these features): resins, aromatics and saturates [1,2].

However, the performance of asphaltic bitumen is questioned, given that they are brittle and hard in cold environments and soft in hot environments [3]. These deficiencies of bitumen can be overcome by the addition of polymers,

which is known to endow bitumen improved viscoelastic behaviour [4–7]. Polymer modified bitumens, henceforth PMBs, are designed to prevent the three main causes of poor performance and loss of structural integrity of asphalt pavements: rutting, as a consequence of the accumulated plastic deformation due to both high loads and/or high temperatures; fatigue cracking, caused by repetitive loading; and thermal cracking due to embrittlement caused by low temperature [6,8–10].

For any meaningful study on the efficiency of PMBs, it is necessary to understand the quality improvements associated with individual polymers [11]. Three main categories of polymers are generally considered as PMBs modifiers: thermoplastic elastomers, plastomers and reactive polymers. Thermoplastic elastomers are able to confer good elastic properties, while plastomers and reactive polymers are added to improve rigidity and reduce deformations under load [12].

However, most of the polymers used present a low compatibility with bitumen. After the manufacturing of the

* Corresponding author. Tel.: +34 959 21 99 89; fax: +34 959 21 99 83.
E-mail address: partal@uhu.es (P. Partal).

polymer-bitumen blends, phase separation may eventually occur as the blend is stored at high temperature (160–200 °C) in absence of stirring [13]. Pavement construction techniques require the binder to remain stable previously and during the application on the road [13]. A possible solution to the above mentioned storage stability problem is the use of the so-called ‘reactive polymers’, containing functional groups supposedly able to bond with bitumen molecules [12,14].

A MDI (4,4'-diphenylmethane diisocyanate) functionalized polymer was considered in the present work. It is well-known that isocyanate groups react under mild conditions with all compounds that contain ‘active’ hydrogen atoms (alcohols, amines, carboxylic acids and water) to form urethane, urea and amide linkages [15,16]. Consequently, MDI-polymer modification of bitumen is expected to take place by reaction of isocyanate groups of the polymer with most of polar groups (–OH, –NH) of asphaltenes and resins [3,15,17,18].

This paper deals with the modification ability of a MDI-functionalized polymer of low molecular weight (polyethyleneglycol, PEG). Rheological properties in a wide range of temperatures, storage stability and microstructure (analysed by atomic force microscopy, AFM) of the modified bitumen are reported. These results have been compared with those obtained for a selected SBS-modified bitumen formulation.

2. Experimental

2.1. Materials

A 60/70 penetration grade bitumen, provided by Construcciones Morales S.A. (Spain), was used as base material for polymer modification. Bitumen composition, determined by Iatroscan MK-6s (Mitsubishi Kagaku Iatron Inc., Japan), penetration grade according to ASTM D5 [19], R&B softening point, determined according to ASTM D36 [20], and viscosity, at 50 °C, of the base bitumen are shown in Table 1.

Two different polymers were used in this study. The first one, belonging to the category of the so-called ‘reactive polymers’, because of the presence of isocyanate groups, was a polyethyleneglycol functionalized with polymeric MDI (4,4'-diphenylmethane diisocyanate), 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 Bayer AG, Germany), selecting a molar ratio of 1:5, in N₂ atmosphere, between 30 and 40 °C, for 48 h and under agitation. The resulting polymer was in liquid form with light brownish colour. The second one was a styrene-butadiene-styrene (SBS) triblock copolymer, Kraton D-1101CS, provided by Shell Chemical Company (UK). Some properties of the latter product are shown in Table 1.

Table 1

Some physical and compositional characteristics of the bitumen and SBS used

<i>Bitumen</i>	
$\eta^{50\text{ °C}}$ (Pa s)	3.59×10^3
Penetration (dmm)	56
R&B softening point (°C)	53.5
Asphaltenes content ^a (wt%)	15.5
Resins content ^a (wt%)	64.2
Aromatics content ^a (wt%)	14.4
Saturates content ^a (wt%)	5.9
<i>SBS</i>	
Styrene content (wt%)	31
Solution viscosity SMS2406 ^b (Pa s)	4.0
Density ISO 2701 (kg m ⁻³)	940
Hardness, Shore A (30 s)	72
Tensile strength ^c (MPa)	33
Modulus, 300% (MPa)	2.9
Ultimate elongation (%)	880

^a Determined by Iatroscan.

^b Measured on 25 wt% solution in toluene at 25 °C.

^c Stress–strain data measured on films cast from toluene.

2.2. Modified bitumen processing

Blends of bitumen and MDI-PEG, at three different concentrations (0.5, 1.0 and 1.5 wt%), were prepared in an open batch vessel, using an IKA RW-20 stirring device (Germany) and a four-blade impeller. Samples were processed for 30 min, at 90 °C and agitation speed of 1200 rpm, using silicone oil as heating fluid. A processing temperature of 90 °C prevents the modified bitumen from oxidation. In addition, such a temperature does lead to a satisfactory mixing, given that a low viscosity liquid polymer is employed as a modifier. A blend of bitumen and 3 wt% SBS was also prepared using the same processing device, for 3 h, at 180 °C and the same agitation speed as before. After processing, curing at room temperature for up to 9 months was carried out on the MDI-PEG modified bitumen samples.

2.3. Tests and measurements

Viscous flow measurements, at 50 and 135 °C, and frequency sweep tests, at –20 °C, within the linear viscoelastic region, were carried out with the controlled-stress rheometer Haake RS150 (Germany), using plate-and-plate geometries (10, 20 and 35 mm diameter; 1 mm gap). Time sweep tests, at a stress constant value within the low-shear-rate Newtonian viscosity region of the material, were performed with a controlled-stress Haake RS100 rheometer (Germany), coupled with a heating system Haake TC501, using plate-and-plate geometries (20 and 35 mm diameter; 1 mm gap).

Storage stability tests on MDI-PEG and SBS modified bitumen samples were carried out according the procedure outlined in AASHTO PP5 [21].

The microstructural characterization of the samples was carried out by means of atomic force microscopy (AFM)

Download English Version:

<https://daneshyari.com/en/article/208195>

Download Persian Version:

<https://daneshyari.com/article/208195>

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