



Research article

Physico-chemistry control of the linear viscoelastic behaviour of bitumen/montmorillonite/MDI ternary composites: Effect of the modification sequence



F.J. Ortega^a, C. Roman^a, F.J. Navarro^{a,*}, M. García-Morales^a, T. McNally^b

^a 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

^b International Institute for Nanocomposites Manufacturing (IINM), WMG, The University of Warwick, CV4 7AL Coventry, United Kingdom

ARTICLE INFO

Article history:

Received 22 September 2015

Received in revised form 9 November 2015

Accepted 18 November 2015

Available online 10 December 2015

Keywords:

Bitumen

Clay

Composite

MDI

Isocyanate

Microstructure

ABSTRACT

Binary bituminous composites consisting of asphaltic bitumen and 10 wt.% organically modified montmorillonite (OMMT) Cloisite 20A®, and ternary composites, also containing 2 wt.% polymeric MDI (diphenylmethane diisocyanate), were prepared by melt blending. In order to appraise the effect that the order of addition of bitumen modifiers has on the composites rheological properties, dynamic shear temperature sweep measurements were conducted. If the MDI curing was prolonged for up to 24 h, quite notable differences were observed between ternary blends at which the OMMT was added before and after MDI modification. On the one hand, a later MDI addition increased the binary composite linear viscoelastic (LVE) moduli at low-to-intermediate temperatures, but provoked a marked reduction at the highest temperatures studied. By contrast, an inversion in the order of addition showed to enhance the rheological response in the entire range of temperature studied. Optical microscopy observations and, mainly, atomic force microscopy (AFM) scans suggest the reactive agglomeration of OMMT into large domains if MDI is added in a second step. However, if MDI is firstly added, the reactive modification is mainly targeted at the bitumen matrix and then at the interaction between that and the hydroxyl groups located in the MMT.

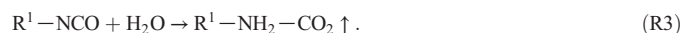
© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Bitumen is the heaviest fraction resulting from crude oil distillation. It is a complex material mainly composed of aliphatic, aromatic and naphthenic hydrocarbons, in addition to other molecules containing some heteroatoms (e.g. sulphur, nitrogen and oxygen) [1].

Desirable properties such as impermeability, ductility, adhesiveness, elasticity or resistance to weathering and chemicals make it suitable for a wide range of applications, mostly related to the fields of pavement construction and roofing membrane manufacture [1]. However, it shows strong susceptibility to temperature, which dramatically changes its in-service behaviour from a viscoelastic liquid, at medium-high temperatures, to a brittle solid at low temperatures. Such variable behaviour leads to problems like rutting (permanent deformation), thermal cracking or fatigue cracking in targeted engineering applications [1,19]. In order to overcome these problems and achieve the desired properties, bitumen is usually modified with different types of polymeric materials. In this sense, bitumen modifiers can be classified into two main categories: non-reactive polymers (e.g. thermoplastics elastomers, plastomers); and reactive polymers (e.g. anhydrides, isocyanates, epoxides), which contain groups suitable to react with specific bitumen molecules. Among these,

reactive isocyanate-based polymers have shown to highly enhance bitumen properties. Isocyanate groups react under mild conditions with functional groups containing active hydrogen atoms, such as alcohols, sulphhydryls, amines, carboxylic acids or water, creating urethane, urea and amide linkages. In previous works [2,17–19,30], the use of MDI (4,4'-diphenylmethane di-isocyanate) remarkably enhanced bitumen properties, as a result of the reactive interaction between the —NCO groups of the oligomer and the most polar groups (mainly —OH and —NH, but also —SH and —COOH) of asphaltenes and resins in bitumen [30], influenced by air moisture, through reactions involving water, due to some intake of air while stirring during bitumen processing. Accordingly, the following set of NCO-involved reactions might develop when MDI is added to bitumen:



Additionally, heat, oxygen diffusion or UV radiation may also affect bitumen properties, due to changes in its chemical composition [6],

* Corresponding author.

E-mail address: frando@uhu.es (F.J. Navarro).

leading to hardening and ageing [1]. In this regard, layered silicates (nanoclays), which have largely been used in the modification of polymers, are also being studied in the modification of bitumen, targeted at improving thermal, mechanical and barrier properties [3–7,22]. Montmorillonites (MMT), a type of naturally occurring mineral consisting of layers of silica SiO_4 tetrahedron sheets bonded to alumina AlO_6 octahedron sheets, can be highly intercalated or partly exfoliated in a polymer matrix, or similarly when added to bitumen. However, in order to increase the degree of compatibility with bitumen, these nanoclays, including montmorillonite, are normally subjected to an ion exchange process in which organic cations from a quaternary alkylammonium salt substitute the inorganic cations located in the gallery space between layers [3,4,8,22].

For the sake of improving bitumen performance, the combined effect of polymeric MDI and the commercially available modified montmorillonite Cloisite® 20A were evaluated in a previous work [10]. Bitumen modified with 10 wt.% Cloisite® 20A showed noticeably enhanced viscoelastic properties, marked shear-thinning flow behaviour and less thermal susceptibility. However, when 2 wt.% MDI was further added to this binary system, the linear viscoelastic moduli experienced a dramatic drop at the highest temperatures studied after curing for 24 h. This result was attributed to the disruption of the clay-based structural reinforcement, assumed to have been formed at shorter curing times, due likely to the re-aggregation/agglomeration of clay tactoids/platelets, facilitated by NCO-involving reactions.

On account of this and in order to gain a deeper insight into the reactive interaction between bitumen, OMMT and MDI in ternary blends, a different approach has now been followed. Bitumen was firstly modified with MDI before Cloisite® 20A was added, and the order of addition in bitumen/MDI/C20A ternary blends compared with respect to previous formulations. Linear rheology, X-ray diffraction, and optical and atomic force microscopy shed some light into the physico-chemistry behind the modification observed, and its relation with the structures obtained on the micro- and nano-metre length scales.

2. Experimental

2.1. Materials

Bitumen with penetration grade within the range 160/220 was used as the base bitumen for the composite formulations. Bitumen specifications, shown in Table 1, correspond to the values of penetration grade (EN 1426:2007), softening temperature (EN 1427:2007) and composition, given in terms of the “SARAs” fractions.

The following additives were used as modifying agents:

- Cloisite® 20A (“C20A”, hereafter), corresponds to an off-white, natural montmorillonite (MMT) modified with N,N-dimethyl dihydrogenated tallow (C_{14} – C_{18}) quaternary ammonium chloride. The cation exchange capacity is 92.6 meq/100 g clay and the hydrogenated tallow is composed of a combination of octadecyl (65 wt.%), hexadecyl (30 wt.%) and tetradecyl (5 wt.%) groups. Chemically, in addition to the organic cation between the platelets, clays naturally contain hydroxyl groups on the edge of the platelets, which are available for

further interaction with other functional groups. Regarding particle specifications, the weight loss on ignition was 38 wt.%, with moisture content lower than 2 wt.%. Dry particle sizes range from values lower than 2 μm (10 vol.%), to lower than 13 μm (90 vol.%), with an average value of 8 μm . The platelets are approximately 1 nm in thickness, yielding aspect ratio values higher than 50, and according to XRD, the interlayer spacing is 2.42 nm.

- Polymeric MDI (4,4'-diphenylmethane diisocyanate), supplied by T.H. Tecnic (Spain). It consists of an oligomeric mixture of 4,4'-diphenylmethane di-isocyanate, 2,4' and 2,2' isomers, and condensation products with more than two aromatic rings. A typical polymeric MDI contains approximately 50 wt.% pure MDI, 30 wt.% tri-isocyanate, 10 wt.% tetra-isocyanate, 5 wt.% penta-isocyanate and 5 wt.% higher homologues. The polymeric MDI used is characterized by an —NCO content of 30 wt.% [9].

2.2. Sample processing

Depending on the formulation, two different processing devices were used: first, a low-shear mixer, composed of a 50 mm four-bladed impeller coupled to the blending device “IKA RW20”, with stirring speeds of 800–1000 rpm; secondly, an “IKA Ultraturrax™ T25” high-shear homogenizer, based on the rotor-stator principle, equipped with a dispersing accessory with a 25 mm diameter stator, with rotation speed ranging from 16,000 to 18,000 rpm. Samples were processed in metal containers (109 mm diameter and 131 mm height) immersed in a recirculating oil digital bath “J.P. SELECTA” with immersion thermostat “J.P. SELECTA DIGITERM 200”.

Previous results demonstrated the reaction between —NCO in the polymeric MDI and —OH in the C20A can be equivalently expressed as 1.33 g of polymeric MDI per 10 g of C20A [10]. Thus, for a formulation with 10 wt.% C20A, a value of 2 wt.% polymeric MDI was chosen in order to provide 2/3 —NCO for C20A and 1/3 —NCO excess, ensuring the desired reaction with the bituminous matrix. Regarding the processing times, and with a view to a potential application, the aim was to contrast the benefits/disadvantages of different mixing times. In order to establish a comparative analysis, the modification of bitumen was carried out by applying different orders of addition, which resulted in the set of systems listed in Table 2, in accordance with the following two processing sequences:

Sequence A). — C20A-MDI modification.

A.1) — C20A pre-dispersion: in order to favour high-shear dispersion, 10 wt.% C20A was firstly blended with bitumen at low shear (≈ 1000 rpm), at 150 °C for 10 min. A part of the so-called “bitumen/C20A pre-dispersion” was used as such, whereas the rest of the product was subjected to the following stage, A.2).

A.2) — High shear blending: the previous sample was submitted to high-shear blending (18,000–20,000 rpm), at 150 °C for 20 min (“bitumen/C20A composite”). After this, the sample was separated in three parts: a part was used as such; another part was kept under low-shear stirring for 1 h and 24 h, resulting in what are termed the “1 h-bitumen/C20A” and “24 h-bitumen/C20A” composites, respectively; and the remaining part was subjected to stage A.3).

A.3) — Reaction with MDI: 2 wt.% polymeric MDI was blended at low-shear (≈ 1000 rpm) with the bitumen/C20A composite, at 150 °C, being allowed to cure for 1 h and 24 h, and termed accordingly “1 h-bitumen/C20A/MDI” and “24 h-bitumen/C20A/MDI” composites.

Sequence B) — MDI-C20A modification.

B.1) — Reaction of bitumen with MDI and curing for 1 h and 24 h; followed by B.2) — C20A pre-dispersion, for 10 min.; and concluded by B.3) — high-shear blending for 20 min to give the “1 h-bitumen/MDI/C20A” and “24 h-bitumen/MDI/C20A” composites.

For the purpose of clarity, note that nomenclature indicates the order of modifier addition.

Table 1
Penetration, R&B softening temperature and composition (SARAs fractions) values for base bitumen.

Specifications	Bitumen 160/220
Penetration (1/10 mm)	162
R&B softening point (°C)	42.4
Saturates (wt.%)	6.0 (0.8) ^a
Aromatics (wt.%)	59.9 (1.7) ^a
Resins (wt.%)	19.8 (2.2) ^a
Asphaltenes (wt.%)	14.3 (1.1) ^a

^a Values given as mean (standard deviation).

Download English Version:

<https://daneshyari.com/en/article/209214>

Download Persian Version:

<https://daneshyari.com/article/209214>

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