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STATE OF THE ART

An overview of the use of nanoclay modified bitumen in asphalt mixtures for enhanced flexible pavement performances

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Bitumens are complex materials, produced mainly from crude oil as a by-product of petroleum refineries, but may also be obtained from bio-oils or solid hydrocarbons. Bitumen specifications have become stringent, mainly because they are used as binders in asphalt mixtures that have to offer good resistance to weather and traffic erosion. There are many different types of additives that can be used to improve bitumen properties and, consequently, asphalt mixtures performance. Nanoclays are one of the newest additives being used in paving grade bitumens to increase their in-service performance. This paper covers the main aspects of asphalt mixtures with nanoclays, including constituent materials, mix design and mechanical performance issues, as well as technical specifications.

Keywords: asphalt mixtures; bitumen; fatigue life; nanoclay; permanent deformation; stiffness

Highlights

• Nanoclays can be used to enhance the mechanical properties of bitumens and asphalt mixtures at a reasonable cost.
• The mixing process of nanoclays with bitumen is generally easy, before its mixture in asphalt concrete.
• Hot and warm mix asphalts (HMA and WMA) with nanoclays can use a mix design similar to those of traditional mixtures.
• Nanoclays mixed in different types of bitumens (with or without polymers) offer good mechanical performance.
• Since long-term performance is still unknown, no life-cycle cost analysis is available.

1. Introduction

The main aim of this review is to cover the use of nanoclays in hot mix asphalt (HMA) and in warm mix asphalt (WMA), focusing especially in the laboratory mix design and the mechanical performance of those materials. HMA are mixtures of several ingredients, including binders, fillers, aggregates and other additives (Figure 1). WMA differ from HMA in that the former are produced and laid down at temperatures 20–40°C lower.

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Over the last two decades, the immense industry of production and lay-down of asphalt mixtures (Asphalt Institute & Eurobitume, 2015) have developed and applied many innovations, in order to meet economic and environmental objectives (Capitão, Picado-Santos, & Martinho, 2012). The industry has been focused specially on improving the in-service mechanical performance of the asphalt mixtures. In addition, other aspects, such as the energy consumption reduction and the minimisation of the environmental impacts (during the asphalt mix production and its transport and application), are receiving greater attention. To this end, new binders (including bitumens, as called in Europe or asphalts in North America) have been developed.

The most common base bitumens are complex mixtures of aliphatic, aromatic and naphthenic hydrocarbons. The chemical components of these bitumens are usually grouped into two categories: asphaltenes and maltens (Jahromi & Khodaii, 2009). Asphaltenes contain high-molecular weight phenols and heterocyclic compounds, while maltens (the de-asphalted fraction of bitumen) are divided into saturates (the fraction eluted with \( n \)-pentane), aromatics (the fraction eluted with benzene) and resins (those adsorbed on clays or eluted from silica gel by polar eluents) (Garcia, 2014).

Many additives have been developed to minimise certain pathologies which take place during the in-life service of asphalt mixtures, such as, for example, cracking, permanent deformation and erosion (Zhu, Birgisson, & Kringos, 2014). Some of them allow the adjustment of various properties of the binders, such as their softening temperature and viscosity. For example, the binder/aggregate adhesivity may be chemically improved by adding surfactants. Such additives also enable to the reduction of the mixing temperature and the compaction in the layers of flexible pavements (Abdullah, Zamhari, Hainin, Oluwasola, Hassan, et al., 2016; Abdullah, Zamhari, Hainin, Oluwasola, Yusoff, et al., 2016; Capitão et al., 2012).

As pointed out by Zhu et al. (2014), although these modifying agents improve many bitumen properties, they also introduce some drawbacks, such as stability problems in the storage of blends, a lower resistance to ageing and higher cost. Nevertheless, the main advantages of modified bitumen justify their use in asphalt mixtures, especially, when higher gas barrier properties, enhanced mechanical behaviour and better thermal properties are achieved.

One of the most recent strategies to improve the performance of asphalt concrete mixtures consists in adding nanomaterials to the binders. In particular, it has been described that some
properties of the binders can be strongly improved by mixing small amounts of nanoclays, dispersed at nanometer level (Galooyak, Dabir, Nazarbeygji, & Moeini, 2010; Jahromi & Khodaii, 2009; Liu, van de Ven, Wub, Yu, & Molenaar, 2011).

Table 1 summarises the testing procedures mentioned in the next sections and in the literature, the applicable European Norms and their corresponding ASTM and AASHTO standards.

1.1. Bitumens
The world use of bitumen in 2015 was approximately 87 million tons per year (Asphalt Institute & Eurobitume, 2015). The paving industry represents the main area of all applications (with 85% of the total). The size of this market has stimulated the scientific community to better understand the composition and the rheological behaviour of the different kinds of binders that can be used in asphalt mixtures.

Bitumens (or asphalts) are complex materials, produced mainly from crude oil (as a by-product of oil refineries). They can also have other origins (Garcia, 2014), such as biomass pyrolysis (bio-oil and bio-char) or solid hydrocarbons (Gilsonite). The complexity of these materials is linked to the fact that bitumens are composed of numerous hydrocarbons. Depending on the chemical species resulting from its constitution and preparation process (saturate, cyclic or aromatic), these materials are classified as paraffinic, naphthenic or aromatic (Guern, Chailleux, Farcas, Dreessen, & Mabille, 2010).

Bitumens have not only very different chemical compositions, but also a wide range of molecular weights. These molecular weights were pointed by Jahromi and Khodaii (2009) as being in the range of 1000–100,000 for asphaltenes, 500–50,000 for resins, 300–20,000 for aromatics and 300–1500 for saturates. However, other authors argue that those weights are not so elevated, considering values of up to 2000 g/mol (Redelius, 2009), 3500 g/mol (Paliukaite, Vaitkus, & Zofka, 2014) or 7000 g/mol (Weigel & Stephan, 2017), such as summarised in Table 2.

Tendentially, binders with greater amounts of resins and asphaltenes have a greater stiffness and tensile strength (TS), when compared to those with more saturates and aromatics. These results suggest that it is fundamental to know and compare the chemical composition of binders in many cases, especially for those which include recycled or aged binders or binders with rejuvenators (Sultana & Bhasin, 2014).

Redelius and Soenen (2015) classified asphaltenes by their solubility. Asphaltenes contain the molecules with the strongest dispersive interactions in bitumen, as well as the strongest $\pi-\pi$ (pi–pi) interactions.

The chemical composition of bitumens also shows that up to 10 wt.% comprises sulphur, nitrogen and oxygen, while the remaining portion includes essentially carbon and hydrogen (Polacco, Filippi, Merusi, & Stastna, 2015).

1.2. Nanomaterials and nanoclays
According to the European Union Recommendation 2011/696/EU, nanomaterials are materials which contain particles, “in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm” (or from $10^{-9}$ up to $10^{-7}$ m).

Some nanomaterials have been used to develop a generation of high-performance materials with impact in many sectors, including the paving of transport infrastructures (Jamshidi, Hasan, Yao, You, & Hamzah, 2015). One of the most promising materials for construction is polymer matrix nanocomposites (PMCs), thanks to their remarkable mechanical, thermal and durability properties. Polymer-layered silicate nanocomposites, in particular, have been studied
Table 1. Some of the European Norms (EN) used and corresponding ASTM and AASHTO standards.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Properties</th>
<th>Main test methods/procedures</th>
<th>Test ref.</th>
<th>Parameters</th>
<th>EN standard</th>
<th>ASTM standard</th>
<th>AASHTO standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binders</td>
<td>Penetration grade</td>
<td>Penetration</td>
<td>PG</td>
<td>Pen</td>
<td>EN 1426</td>
<td>D 5</td>
<td>T 49</td>
</tr>
<tr>
<td></td>
<td>Softening point</td>
<td>Ring and ball temperature</td>
<td>SP</td>
<td>R&amp;B</td>
<td>EN 1427</td>
<td>D 36</td>
<td>T 53</td>
</tr>
<tr>
<td></td>
<td>Viscosity</td>
<td>Dynamic viscosity</td>
<td>RV</td>
<td>η</td>
<td>EN 13302</td>
<td>D 2196/D 4402</td>
<td>T 316/TP 48</td>
</tr>
<tr>
<td></td>
<td>Permanent deformation/</td>
<td>Dynamic shear rheometer</td>
<td>DSR</td>
<td>G*, δ, Rj</td>
<td>EN 14770</td>
<td>D 7175</td>
<td>T 315/TP 5-97</td>
</tr>
<tr>
<td></td>
<td>stiffness/ low-temperature</td>
<td>Bending beam rheometer</td>
<td>BBR</td>
<td>S(t)</td>
<td>EN 14771</td>
<td>D 6648</td>
<td>T 313</td>
</tr>
<tr>
<td></td>
<td>cracking</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Compliance and recovery</td>
<td>Multiple stress creep and</td>
<td>MSCR</td>
<td>Jnr, R, Jnr, diff</td>
<td>EN 16659</td>
<td>D 7405</td>
<td>T 350/TP 70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>recovery</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Short-term ageing</td>
<td>Elastic recovery</td>
<td>ER</td>
<td>RE</td>
<td>EN 13398</td>
<td>D 6084/D 113</td>
<td>T 51</td>
</tr>
<tr>
<td></td>
<td>Long-term ageing</td>
<td>Rolling thin-film oven test</td>
<td>RTFOT</td>
<td>—</td>
<td>EN 12607-1</td>
<td>D 2872</td>
<td>T 240</td>
</tr>
<tr>
<td></td>
<td>Stability and flow</td>
<td>Pressure ageing vessel</td>
<td>PAV</td>
<td>—</td>
<td>EN 14769</td>
<td>D 6521</td>
<td>R 28</td>
</tr>
<tr>
<td></td>
<td>Water sensitivity</td>
<td>Marshall test</td>
<td>MT</td>
<td>MS, F</td>
<td>EN 12697-34</td>
<td>D 6927//D 1559</td>
<td>T 245</td>
</tr>
<tr>
<td></td>
<td>Low-temperature cracking</td>
<td>Indirect tensile strength test</td>
<td>ITS</td>
<td>ITSR</td>
<td>EN 12697-23</td>
<td>D 6931/D 4867</td>
<td>T 283</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tensile stress restrained</td>
<td>TSRST/UTST/RT Tr.temp, Fr.temp.</td>
<td>EN 12697-46</td>
<td>TP 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>specimen test/uniaxial</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>tensile stress test/relaxation test</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stiffness</td>
<td>Flexural loading/tension-</td>
<td>e.g. 4PB</td>
<td>E*, δ</td>
<td>EN 12697-26</td>
<td>D 4123</td>
<td>T 342</td>
</tr>
<tr>
<td></td>
<td></td>
<td>compression/diametric</td>
<td></td>
<td>ε6</td>
<td>EN 12697-24</td>
<td>D 7460</td>
<td>T 321</td>
</tr>
<tr>
<td></td>
<td>Resistance to fatigue</td>
<td>Wheel-tracking test/Hamburg</td>
<td>WTT/HWT</td>
<td>RD, PRD, WTS</td>
<td>EN 12697-22</td>
<td></td>
<td>T 324</td>
</tr>
<tr>
<td></td>
<td></td>
<td>wheel-track</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cyclic compression test</td>
<td>CCT</td>
<td>fc</td>
<td>EN 12697-25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Bitumen: characterisation of its fractions.

<table>
<thead>
<tr>
<th>Bitumen compounds</th>
<th>Color</th>
<th>Physical state</th>
<th>Content in bitumen (wt.%)</th>
<th>Molecular weight (g/mol)</th>
<th>Density @ 20°C (g/cm³)</th>
<th>Solubility parameter (MPa 0.5)</th>
<th>H/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maltenes</td>
<td></td>
<td></td>
<td>[1] [2]</td>
<td>[1] [2]</td>
<td>[1]</td>
<td>[1]</td>
<td>[1]</td>
</tr>
<tr>
<td>Saturates (paraffins)</td>
<td>White</td>
<td>Liquid</td>
<td>05–15 05–20</td>
<td>≈ 600</td>
<td>470–880</td>
<td>≈ 0.90</td>
<td>15.0–17.0</td>
</tr>
<tr>
<td>Aromatics (or naphthene aromatics)</td>
<td>Dark brown</td>
<td>Liquid</td>
<td>30–45 30–65</td>
<td>≈ 800 (avg.)</td>
<td>570–980</td>
<td>≈ 1.00</td>
<td>17.0–18.5</td>
</tr>
<tr>
<td>Resins (or polar aromatics)</td>
<td>Dark brown</td>
<td>Solid or semi-solid</td>
<td>20–35 30–45</td>
<td>300–2000</td>
<td>780–1400</td>
<td>≈ 1.07</td>
<td>18.5–20.0</td>
</tr>
<tr>
<td>Asphaltenes (insolubles in hexane and heptane)</td>
<td>Black</td>
<td>Solid</td>
<td>05–25 05–25</td>
<td>800–3500</td>
<td>400–7000</td>
<td>≈ 1.15</td>
<td>17.6–21.7</td>
</tr>
</tbody>
</table>

since the 1990s (Silvestre, Silvestre, & Brito, 2015). However, though some authors expect nanoclay composites to replace mineral fillers in asphalt mixtures (Iskender, 2016), their use has been hindered by the fact that these clays are hydrophilic, thus difficult to use as fillers in most polymer matrices.

Natural nanoclays are one of the most common, safe (if properly handled), inexpensive and sustainable layered silicates, with montmorillonite (MMT) being the most used (Bonati et al., 2013). Other natural clays, like hectorite, saponite (Silvestre et al., 2015) and kaolinite (Zhu et al., 2014), have also been extensively studied for use in composites.

Cloisite, an organically modified montmorillonite (OMMT), is a quaternary ammonium salt-modified natural MMT with a 2:1 layer structure and high surface charge (Farias et al., 2016; Walters et al., 2014). The other well-known nanoclay, kaolinite, has a 1:1 layer structure and very low surface charge. MMT has a 2:1 layered structure with two silica tetrahedron layers sandwiching an alumina octahedron layer (Bonati et al., 2013) (Figure 2).

In order to increase its specific surface area, MMT is generally subject to a surface treatment to separate the individual clay sheets, known as exfoliation (Figure 2(B)). The exfoliation of MMT is determined by its capacity to exchange ions. In the case of MMT, the cation exchange capacity (CEC) ranges from 80 to 120 meq/100 g (milli-equivalents per 100 g), while in kaolinite these values are between 3 and 5 (Jahromi & Khodaii, 2009).

Considering the capacity of the silicate particles to disperse into individual layers, nanoclay nanocomposites can be organised into three groups: flocculated (immiscible), intercalated and exfoliated (Silvestre et al., 2015). The characteristics of each of these groups are illustrated in Figure 3, which includes examples of typical wide-angle X-ray scattering (WAXS) spectra and transmission electron microscopy (TEM) images.

In the exfoliated nanocomposites the individual layers of clay are dispersed in a continuous polymer matrix and are spaced apart at a distance dependent on the clay loading (Silvestre et al., 2015). Intercalated nanocomposites are systems where the polymer has penetrated the galleries between silicate sheets, but has not completely delaminated them. In these nanocomposites there is a significant interaction between silicate layers, but the structure is not wholly exfoliated. Flocculated (immiscible) nanocomposites have predominantly the same structure as an intercalated nanocomposite, but some silicate layers are flocculated due to hydroxylated edge–edge interaction.

In exfoliated clays the separation of clay sheets results in a nanoclay with an extensive active surface area (in the range 700–800 m²/g). This helps create a better intensive interaction between the nanoclays and the bitumen matrix (Jahromi & Khodaii, 2009), and thus enhance the behaviour of asphalt mixtures.

OMMT is typically prepared by cation exchange between Na-MMT galleries and a surfactant, such as cetyltrimethyl ammonium bromide (CTAB) (Haerudin et al., 2010). Recent works have
shown the synergic effects obtained by mixing alkaline fillers with layered silicates. In particular, OMMMT allows the reduction of the total filler amount, which represents an economical advantage (Bonati et al., 2013), when compared to other additives that do not lead to any reduction in this fraction.

Mohammadiroudbari, Tavakoli, Aghjeh, and Rahi (2016) studied the effect of nanoclays on the morphology of polyethylene-modified bitumen and the results showed that the content of the polymeric phase, the functionality of the polyethylene and the process used for mixing the components has a strong influence on the state of nanoclay intercalation or exfoliation.

Nanoclays are already used in many nanocomposites in the building industry, namely in polymeric coatings and foams (Silvestre et al., 2015) and in the production of asphalt mixtures for flexible pavements (Abdullah, Hainin, Yusoff, Zamhari, & Hassan, 2016; Abdullah, Zamhari, Hainin, Oluwasola, Hassan, et al., 2016; Abdullah, Zamhari, Hainin, Oluwasola, Yusoff, et al., 2016; Ameri, Vamegh, Imaninasab, & Rooholaminib, 2016; Ashish et al., 2016; Babagoli, Mohammadi, & Ameri, 2017; Blom, De Kinder, Meeusen, & Van den Bergh, 2017; Ezzat, El-Badawy, Gabr, Zaki, & Breakah, 2016; Farias et al., 2016; Galooyak et al., 2010; Iskender, 2016; Jahromi & Khodaii, 2009; Jamshidi et al., 2015; Liu et al., 2011; Silvestre et al., 2015).

2. Nanoclay-modified bitumens

2.1. Modified bitumens and nanoclays

Bitumen modifications help achieve the desired properties required in the asphalt pavements and have been commonly performed with the addition of thermoplastic or elastomeric polymers. Different types of polymers are used in polymer-modified bitumens (PMB) to produce enhanced asphalt mixtures, increasing the mechanical performance and durability of pavement,
and reducing its maintenance operations (thus, offsetting the higher initial investment) (Polacco et al., 2015).

Technical developments in the field of bitumen polymer modification during the last four decades include the application of several plastomers, such as polyethylene (PE), polypropylene (PP), poly(ethylene-r-vinyl acetate) (EVA) and poly(ethylene-co-butyl-acrylate) (EBA), and thermoplastic elastomers, such as poly(styrene-b-butadiene-b-styrene) block copolymer (SBS), poly(styrene-b-isoprene-b-styrene) (SIS) and poly(styrene-b-ethylene-butene-b-styrene) (SEBS) (Ameri, Mohammadi, Vamegh, & Molayem, 2017; Aziz, Rahman, Hainin, & Bakar, 2015; Babagoli et al., 2017; Li, Wu, Liu, Cao, & Amirikhian, 2017; Zhu et al., 2014).

Different solutions have also been studied in order to minimise the drawbacks of many polymer modifiers, among which, saturation, the need for functionalisation (including the application of reactive polymers) and the use of extra additives (sulphur and antioxidants). In contrast, there are only a few studies of bitumen blends with innovative modifiers (Munera & Ossa, 2014). Among these, clay minerals are especially interesting to use with PMB (Zhu et al., 2014), due to their lower cost, hydrophobicity and the ability to be dispersed at the nanoscale.

Regarding the costs, Hossain et al., cited by Ashish et al. (2016) and by Li, Xiao et al. (2017), reported that two nanoclay-modified bitumens (NMB) were “22 and 33%” less expensive than the similar PMB. In another study, Farias et al. (2016) were more expressive and pointed to a reduction of “approximately 36%” when clay can replace polymer. However, based on our experience, this is an excessive percentage which may be connected with the low MMT unit price considered.

Dispersed hydrophobic clay minerals can have an intercalated or exfoliated structure (Jasso, Bakos, Stastna, & Zanzotto, 2012), with the latter being more efficient for use with PMB. Among other benefits, the addition of exfoliated hydrophobic clays can increase the storage stability, viscosity, stiffness and rutting resistance of PMBs (Zhu et al., 2014).

However, Zhu et al. (2014) noted that completely exfoliated hydrophobic clay minerals structures in PMB are difficult to achieve, and therefore, only partial improvements in the properties at low temperatures are obtained, namely ductility. These factors may limit the use of hydrophobic clay minerals in PMB. Furthermore, Yao et al. (2013) showed that depending on how the modification of the asphalt binders is preformed, the nano- or micro-materials can suffer both chemical reactions and physical dispersion when mixed in bitumen.

Although bitumens modified with a physical mixture of polymer and clay may be nonhomogeneous, the use of the clay can still have a positive effect on the material. Jasso et al. (2012) tested a PMB containing 3 wt.% of OMMT and the results showed an internal network stronger than the equivalent PMB without the clay. One of the most important advantages of using OMMT is enhancing the storage stability of PMBs (which depends on the bitumen, polymer and modification process) (Polacco et al., 2015). Galooyak et al. (2010) found that by adding a suitable amount of exfoliated nanoclay to SBS-modified bitumen, not only the performance of PMBs was improved, but also the storage stability. As well as, the use of nanoclays may allow a reduction in the consumption of polymer, as shown by Farias et al. (2016) who compared a PMB (4% of SBS) with an SBS/nanoclays bitumen.

The addition of clay as a third constituent into PMB with linear and branch SBS block copolymer was investigated by Golestani, Nejad, and Galooyak (2012). In their study the samples were processed by melt blending (MB) with different amounts of OMMT and the results showed improvements in the physical properties, rheological behaviour and the storage stability of the PMB. However, these authors also observed that the high-temperature storage stability decreased with the total amount of OMMT added. The same conclusion was presented by Ilyin, Arinina, Mamulat, Malkin, and Kulichikhin (2014) when meta-kaolin was used. Ortega, Navarro, García-Morales, and McNally (2015) also noticed a degradation in the visco-elastic behaviour in
some conditions, although the addition of 10 wt.% nanoclay improved the bitumen rheological response.

In another study, Jahromi and Khodaii (2009) proposed an approach where bitumen was modified with only a small amount of nanoclay, and its physical properties were effectively improved when the clay was spread at the nanoscopic scale. They mention that those particles, when compared with Cloisite particles, were more curly and smaller.

Although the preparation of PMB using traditional methods has been amply reported, the influence of some parameters, such as temperature, shearing speed and processing time, has not been generally investigated in detail. Fang, Yu, Liu, and Li (2013) focused on the processes for dispersing a large amount of nanoparticles into bitumen and enhancing the compatibility of the different phases. Iskender (2016) states that nanoclay materials can replace mineral fillers, but the use of clay minerals in large amounts may spoil the elastic properties of PMB, such as observed by Golestani et al. (2012). Nazzal, Kaya, Gunay, and Ahmedzade (2012) also observed that the addition of nanoclays in the asphalt binder amplifies the adhesive strengths, although there is a slight decline in cohesive forces.

El-Shafie, Ibrahim, and El Rahman (2012) show that the physical and mechanical properties of binders are frankly improved by an efficient dispersion of the clay, due to the large surface area and the stiffening effect of the nanoclay (by forming bond chains within the binder), and increase the softening temperature (up to 12°C relative to the base asphalt binders). Jahromi and Khodaii (2009) also demonstrated that a small percentage of nanoclay mixed in the bitumen causes significant changes in rheological parameters, decreasing ductility and penetration, as well as the enhancement of the resistance to ageing and softening point.

Golestani et al. (2012) through the addition of OMMT to PMBs showed that the softening point and the viscosity increased, while the penetration decreased, with important effects on elastic recovery and ductility. El-Shafie et al. (2012) used nanoclays that were organically modified, obtained from macroclay, to conclude that the kinematic viscosity value, at 150°C, increases 145% when compared with the control binder. Ziari, Babagoli, and Akbari (2015) claim that the use of Bentonite (BT) for the modification of bitumen can increase the viscosity. Walters, Fini, and Abu-Lebdeh (2014) also confirm that the viscosity of a bio-modified binder with bio-char and nanoclay was found to be clearly higher than without the nanoclay.

Different aspects of the use of nanocomposites in asphalt binders were also studied by Yao et al. (2013), who confirmed that the addition of selected nano- or micro-materials enhances anti-oxidation effects on the modified asphalt binder, and by Li, Wu et al. (2017), who used an OMMT to prove that its addition can minimise the volatile organic compound (VOC) emission of bitumen (due to the fact that the interlayer space of the nanoclays was filled by the light components of bitumen).

In Table 3 and Figure 4 we show some information on recently reported experiments regarding different types of bitumen (all, except two, with a penetration grade over 50 dmm), nanoclay content (from 2 to 30 wt.% of bitumen), methods of the preparation and blending (mainly the melt-intercalated (MI) process and shear mixing procedure) and the kinds of structures obtained (mainly intercalated).

The information in Table 3 shows that several authors also used blends of polymers (such as SBS, EVA and SEBS) and nanoclays. In one of those cases (Galooyak et al., 2010), the authors prepared an OMMT/SBS blend by using the MI technique and obtained an exfoliated structure, which promote the homogenous distribution of OMMT in PMB. However, Zhu et al. (2014) state that hydrophobic clay minerals are hard to be perfectly exfoliated.

There are great differences in the mixing parameters (temperature, speed and duration) used (Table 3 and Figure 5), probably due to differences in bitumen chemistry and in their penetration
Table 3. Nanoclay-modified binders and asphalt mixtures evaluated – some recent experience.

<table>
<thead>
<tr>
<th>Years</th>
<th>Reference</th>
<th>Materials</th>
<th>Commercial name</th>
<th>Structure type</th>
<th>Bitumen type</th>
<th>Nanoclay content (wt. % of bitumen)</th>
<th>Blending of nanoclays with bitumen</th>
<th>Nonoclays preparation or blending methods</th>
<th>Mix temp. (°C)</th>
<th>Mix speed (rpm)</th>
<th>Duration (min)</th>
<th>Binder</th>
<th>Asphalt mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>2017</td>
<td>[1]</td>
<td>Org. mod. mont.</td>
<td>OMMT</td>
<td>I/E</td>
<td>67 dmm</td>
<td>2%, 5% and 10%</td>
<td>MB</td>
<td>160</td>
<td>2500</td>
<td>120</td>
<td>P</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[2]</td>
<td>Montmorillonite + SBS</td>
<td>MMT + fibers</td>
<td>I/E</td>
<td>60/70</td>
<td>2–5%</td>
<td>MI</td>
<td>160</td>
<td>5000</td>
<td>60</td>
<td>P</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[4]</td>
<td>Organophilic nanoclay</td>
<td>OMMT</td>
<td>I/E</td>
<td>50</td>
<td>3%</td>
<td>MB</td>
<td>145</td>
<td>5000</td>
<td>P</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2016</td>
<td>[5]</td>
<td>Montmorillonite + fibers</td>
<td>MMT + fibers</td>
<td>I/E</td>
<td>60/70</td>
<td>2%, 4% and 6%</td>
<td>PM</td>
<td>155</td>
<td>5000</td>
<td>120</td>
<td>P</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[6]</td>
<td>Org. mod. mont.</td>
<td>OMMT</td>
<td>I/E</td>
<td>58-22</td>
<td>2% and 6%</td>
<td>Ultrasonic mixer @65 W</td>
<td>150</td>
<td>20</td>
<td>P</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[7]</td>
<td>Org. mod. mont.</td>
<td>Bentonite</td>
<td>I/E</td>
<td>86 dmm</td>
<td>2%, 4% and 6%</td>
<td>MB</td>
<td>155</td>
<td>4000</td>
<td>120</td>
<td>P</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[8]</td>
<td>Org. mod. mont. + SBS</td>
<td>OMMT + SBS</td>
<td>I/E</td>
<td>50/70</td>
<td>4%</td>
<td>Dispersed in toluene with SBS</td>
<td>160</td>
<td>2000</td>
<td>120</td>
<td>P</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>2015</td>
<td>[9]</td>
<td>Montmorillonite</td>
<td>MMT</td>
<td>I/E</td>
<td>PG64-28</td>
<td>2% and 4%</td>
<td>Dispersed in organic solvent</td>
<td>160</td>
<td>2500</td>
<td>180</td>
<td>P</td>
<td>P/N</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[10]</td>
<td>Nanoclay</td>
<td>OMMT + SBS</td>
<td>I/E</td>
<td>60/70</td>
<td>2% and 4%</td>
<td>Dispersed in organic solvent</td>
<td>160</td>
<td>2500</td>
<td>180</td>
<td>P</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[12]</td>
<td>Montmorillonite</td>
<td>MMT</td>
<td>I/E</td>
<td>70/100</td>
<td>3%</td>
<td>SM + SP</td>
<td>150</td>
<td>1550</td>
<td>90</td>
<td>P</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[13]</td>
<td>Nanoclay</td>
<td>PG 58-22</td>
<td>I/E</td>
<td>3% and 6%</td>
<td>SM + SP</td>
<td>150</td>
<td>1550</td>
<td>90</td>
<td>P</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[14]</td>
<td>Nanoclay</td>
<td>Bentonite</td>
<td>60/70</td>
<td>10%, 15%, 20%, 25% and 30%</td>
<td>MB</td>
<td>140</td>
<td>4000</td>
<td>15</td>
<td>P</td>
<td>P</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[15]</td>
<td>Nanomer nanoclays</td>
<td>PG58-34</td>
<td>2% and 4%</td>
<td>MB</td>
<td>130</td>
<td>4000</td>
<td>120</td>
<td>P</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>[16]</td>
<td>Org. mod. mont. + MDI</td>
<td>OMMT + MDI</td>
<td>Cloisite</td>
<td>I</td>
<td>160/220</td>
<td>10%</td>
<td>Dispersed in toluene with MDI</td>
<td>150</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>2014</td>
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<tr>
<td>[17]</td>
<td>Org. mod. mont.</td>
<td>OMMT</td>
<td>Cloisite</td>
<td>E</td>
<td>44 dmm</td>
<td>3% to 6% (100/10-100/30 SEBS-C15A ratios)</td>
<td>PM</td>
<td>145–155</td>
<td>4000</td>
<td>60</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[18]</td>
<td>Org. mod. mont. + SEBS</td>
<td>OMMT + SEBS</td>
<td>Cloisite</td>
<td>E</td>
<td>PG 64</td>
<td>3–5%</td>
<td>MB</td>
<td>160 ± 5</td>
<td>6000</td>
<td>25</td>
<td>P</td>
<td></td>
<td></td>
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<tr>
<td>2014</td>
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<tr>
<td>[19]</td>
<td>Montmorillonite</td>
<td>MMT</td>
<td>PG 58-34</td>
<td>2% and 4%</td>
<td>MB</td>
<td>130</td>
<td>4000</td>
<td>120</td>
<td>P</td>
<td></td>
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</tr>
<tr>
<td>[21]</td>
<td>Nanomer nanoclays</td>
<td>PG 58-34</td>
<td>2% and 4%</td>
<td>MB</td>
<td>130</td>
<td>4000</td>
<td>120</td>
<td>P</td>
<td></td>
<td></td>
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<tr>
<td>[22]</td>
<td>Org. mod. mont.</td>
<td>OMMT</td>
<td>E</td>
<td>80/100</td>
<td>3.0%, 5.0% and 9.0%</td>
<td>PM</td>
<td>150</td>
<td>2000</td>
<td>60</td>
<td>P</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[23]</td>
<td>Org. mod. mont.</td>
<td>OMMT</td>
<td>Cloisite</td>
<td>E</td>
<td>50/70</td>
<td>3.33%</td>
<td>MB</td>
<td>160 ± 5</td>
<td>4000</td>
<td>30</td>
<td>P</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td></td>
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</tr>
<tr>
<td>[25]</td>
<td>Org. mod. mont. + surfact.</td>
<td>OMMT</td>
<td>SPREA MISR</td>
<td>I</td>
<td>60/70</td>
<td>2%, 4%, 6% and 8%</td>
<td>MB</td>
<td>160</td>
<td>120</td>
<td>P</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[26]</td>
<td>Org. mod. mont.</td>
<td>OMMT</td>
<td>Cloisite</td>
<td>200/300</td>
<td>SBS/OMMT = 3%/ (1–2%)</td>
<td>MB</td>
<td>&gt; 180</td>
<td></td>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[27]</td>
<td>Org. mod. mont. + SBS</td>
<td>OMMT + SBS</td>
<td>Cloisite</td>
<td>I</td>
<td>85/100</td>
<td>SBS/OMMT = 100/12.5 to 100/50%</td>
<td>MB</td>
<td>180 ± 5</td>
<td>4000</td>
<td>45</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[28]</td>
<td>Org. mod. mont. + SBS</td>
<td>OMMT + SBS</td>
<td>I</td>
<td>60/80</td>
<td>4% (SBS) + 3% (OMMT)</td>
<td>MB</td>
<td>180</td>
<td>2000</td>
<td>30</td>
<td>P</td>
<td></td>
<td></td>
<td></td>
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</table>

(Continued)
<table>
<thead>
<tr>
<th>Years</th>
<th>Reference</th>
<th>Materials</th>
<th>Abbrev.</th>
<th>Commercial name</th>
<th>Structure type</th>
<th>Bitumen type</th>
<th>Nanoclay content (wt. % of bitumen)</th>
<th>Nanoclay preparation or blending methods</th>
<th>Mix temp. (°C)</th>
<th>Mix speed (rpm)</th>
<th>Duration (min)</th>
<th>Binder</th>
<th>Asphalt mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>[29]</td>
<td>Nanoclay</td>
<td>Organic modified</td>
<td>OMMMT</td>
<td>I</td>
<td>PG 64-28</td>
<td>2% and 4%</td>
<td>Dispersed in organic solvent</td>
<td>160</td>
<td>2500</td>
<td>180</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[30]</td>
<td>Organic modified</td>
<td>OMMMT + EVA</td>
<td>Cloisite/Dellite</td>
<td>I</td>
<td>70/100</td>
<td>4%</td>
<td>Treated with cation exchange reaction</td>
<td>180</td>
<td>4000</td>
<td>60</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>2010</td>
<td>[31]</td>
<td>Organic modified</td>
<td>Bentonite</td>
<td>E</td>
<td>50/70</td>
<td>2% and 4%</td>
<td>PM/Mba</td>
<td>180</td>
<td>4000</td>
<td>60</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[32]</td>
<td>Organic modified</td>
<td>OBT</td>
<td>E</td>
<td>60/70</td>
<td>1%, 2%, 4%, 5% and 6%</td>
<td>SM + SP</td>
<td>160</td>
<td>4000</td>
<td>60</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2009</td>
<td>[34]</td>
<td>Organic modified</td>
<td>OMMMT + SBS</td>
<td>Nanofil</td>
<td>(OMMT), I (MMT)</td>
<td>85/100</td>
<td>2%, 4% and 7%</td>
<td>MI</td>
<td>180</td>
<td>4000</td>
<td>120</td>
<td>P</td>
<td></td>
</tr>
</tbody>
</table>


grades, that lead to significant variations on the final properties of NMB. This represents a serious obstacle when looking for direct correlations among the reported results.

2.2. Asphalt mixtures with nanoclay-modified bitumen

A recent justification for the use of higher performance binders in enhanced asphalt mixtures (as is the case of NMB) is related with the bitumen consumption reduction during the infrastructure lifecycle. This fact also contributes to decrease fossil fuel consumption and global emissions, as supported by the Paris Agreement (signed during the Conference of Paris, held in December 2015).

Cheng, Shen, and Xiao (2011) found that WMA which incorporated Sasobit (a synthetic wax obtained by the Fischer–Tropsch process from syngas) and a nano-size hydrated lime had an important increment in the indirect tensile strength (ITS), stiffness and flow number (both in dry and wet conditions), when compared to samples that include micro-size hydrated lime. The use of additives in WMA, for example, chemical surfactants or organic waxes (such as Sasobit), allow their handling (mixing, spreading and compaction) at lower temperatures (Capitão et al., 2012), facilitating the incorporation of nanoclays (Abdullah, Hainin, et al., 2016; Abdullah, Zamhari, Hainin, Oluwasola, Hassan, et al., 2016; Abdullah, Zamhari, Hainin, Oluwasola, Yusoff, et al., 2016; Cheng et al., 2011).

Yao et al. (2013) found that asphalt binders which incorporate non-modified nanoclay and polymer-modified nanoclay (PMN) have a lower deflection and a higher stiffness than samples prepared with only asphalt binder, resulting in a better permanent deformation resistance.

Polacco et al. (2015) confirmed that organo-modified clays are typically more compatible with bitumen than with the polymers. This impacts the results obtained in different preparation methods. In the physical mix method, only a small portion of the clay acts as a surfactant in improving the bitumen/polymer contact, whereas in the master-batch method the polymer/clay premix allows a better interaction between the additives, resulting in a more durable binding.
Those authors also stated that one of the main drawbacks of bitumen/polymer/clay system is related with the binder viscosity gain attributable to the clay. Consequently, higher temperatures may be required during the handling of the asphalt mixtures, in contrast with the actual tendency to privilege the use of WMA (Abdullah, Hainin, et al., 2016; Abdullah, Zamhari, Hainin, Oluwasola, Hassan, et al., 2016; Abdullah, Zamhari, Hainin, Oluwasola, Yusoff, et al., 2016; Capitão et al., 2012; Cheng et al., 2011).

Abdullah, Zamhari, Hainin, Oluwasola, Hassan, et al. (2016) mixed a 80/100 penetration grade bitumen with a MMT clay surface modified with two different chemical compounds: dimethyl dialkyl amine (35–45 wt.%) and octadecylamine (35–45 wt.%) plus aminopropyl-triethoxysilane (0.5–5.0 wt.%). They concluded that the nanoclay which includes the first compound increases significantly the viscosity, while the latter compound reduces the viscosity of the base bitumen and offers the same performance as a chemical WMA-modified asphalt binder.

A different method, plasma modification, was also used by Karahancer et al. (2014) to enhance the performance of HMA. They modified the surface of limestone mineral filler by plasma processing, using three different components: hexamethyldisiloxane (HMDSO), methylmethacrylate (MMA) and silicon tetrachloride (SiCl₄), concluding that plasma modification is a sustainable technique to get better asphalt mixtures.

Finally, Zapién-Castillo, Rivera-Armenta, Chávez-Cinco, Salazar-Cruz, & Mendoza-Martínez (2015) used mixtures of MMT nanoclay with a block SEBS copolymer (in the range from 3% to 6% of SEBS/nanoclay modifier) to study the phase segregation problem, achieving a better field behaviour of the asphalt mixture.

3. Design and characterisation of asphalt mixtures with nanoclays

3.1. Introduction

Some asphalt mixtures design methods are empirical and based on volumetric properties. Meanwhile, advanced systems consider not only these properties, but also the mechanical performance of binders and mixtures. A wide characterisation of all materials (aggregates, filler, bitumen and additives) used to produce asphalt mixtures (HMA or WMA) must be made and correlated with the performance required for pavements where they will be applied.

In Table 4 we show a brief overview of tests performed by different authors for the characterisation of binders and modified binders.

In the next subsections are presented and analysed some considerations on the design and characterisation of modified binders and asphalt mixtures, including NMB.

3.2. Design and characterisation of modified binders

The development of specifications for binders and mixtures tests goes back to the early decades of the twentieth century and was based on indirect measurements using classical tests, such as penetration or ring and ball tests. These tests are still used, but do not provide a direct quantification of the additive segregation in the samples tested (Polacco et al., 2015). For example, Munera and Ossa (2014) studied multicomponent (MC) bitumen blends and characterised them by penetration and softening point, but added rheological tests to evaluate the response of each property in function of the amount of polymer used. However, Jamshidi et al. (2015) claim that some traditional rheological properties, such as viscosity and the plastic component of the complex modulus ($G^\ast \sin\delta$), should be used to study the consequences of nanomaterials incorporation.
Table 4. Characterisation of binders – some tests used.

<table>
<thead>
<tr>
<th>Test ref.</th>
<th>Test/procedure</th>
<th>Usefulness</th>
<th>Advantages</th>
<th>Drawbacks</th>
<th>Some references</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG</td>
<td>Penetration grade</td>
<td>Used to determine the penetration grade of binders at 25°C</td>
<td>Inexpensive test with a simple preparation. Bitumen grade in terms of its hardness. Good measure of predicting rutting resistance</td>
<td>The amount of bitumen used may not represent well the rest of the tank. Results are very sensitive to the test conditions and bitumen specimen preparation.</td>
<td>Ezzat et al. (2016), Guern et al. (2010), Munera and Ossa (2014), Li, Wu et al. (2017), Iskender (2016), Abdullah, Zamhari, Hainin, Oluwasola, Hassan, et al. (2016), Jahromi and Khodaii (2009)</td>
</tr>
<tr>
<td>SP</td>
<td>Softening point</td>
<td>Used to determine the softening point of binders (ring and ball apparatus) = temperature at which the binder has a penetration grade of ≈ 800 dmm</td>
<td>Inexpensive test with a simple preparation. It permits the classification of bitumens and it gives an indication of its tendency to flow at elevated temperatures when it is in service</td>
<td>The amount of binder used may not represent well the rest of the tank. It is not suitable for PMB, in particular for highly modified PMB.</td>
<td>Ezzat et al. (2016), Guern et al. (2010), Munera and Ossa (2014), Li, Wu et al. (2017), Iskender (2016), Abdullah, Zamhari, Hainin, Oluwasola, Hassan, et al. (2016), Jahromi and Khodaii (2009)</td>
</tr>
<tr>
<td>RV</td>
<td>Rotational viscosity</td>
<td>Used to determine the viscosity of binders at several temperatures. Can measure viscosities of opaque, settling or non-Newtonian fluids</td>
<td>Quick test with a simple preparation which requires a small amount of binder. It is sufficient to represent the workability of the binder</td>
<td>The small amount of binder used may not represent well the rest of the tank. Binders with a high concentration of additives may have variations in results.</td>
<td>You et al. (2011), Ezzat et al. (2016), Jamshidi et al. (2015), Li, Wu et al. (2017), Babagoli et al. (2017)</td>
</tr>
<tr>
<td>DSR</td>
<td>Dynamic shear rheometer</td>
<td>Used to describe the linear visco-elastic properties of bitumen over a range of frequencies and temperatures. It gives the complex shear modulus, ( G^* ), the phase angle, ( \delta ), and its components</td>
<td>Simple preparation. It allows to inferred some parameters like deformation ( [G^<em>/\sin(\delta)] ) and fatigue ( [G^</em> \times \sin(\delta)] ) behaviours</td>
<td>The precision of this test has not yet been established</td>
<td>You et al. (2011), Jamshidi et al. (2015), Santagata, Baglieri, Tsantili, and Chiappinelli (2015), Yao et al. (2013), Mollenhauer, Tušar, and Eberl (2016), Li et al. (2017), Zare-Shahabadi et al. (2010), Batista et al. (2016)</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Test ref.</th>
<th>Test/procedure</th>
<th>Usefulness</th>
<th>Advantages</th>
<th>Drawbacks</th>
<th>Some references</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBR</td>
<td>Bending beam rheometer</td>
<td>Used to test asphalt binders at low temperatures in order to determine their susceptibility to thermal cracking</td>
<td>Largely software controlled. Good reproducibility in general</td>
<td>Available experience mainly in USA and Canada. Some uncertainties in modified bitumen</td>
<td>Mollenhauer et al. (2016), Li, Wu et al. (2017), Weigel and Stephan (2017), Abdullah, Zamhari, Hainin, Oluwasola, Hassan, et al. (2016), Pei et al. (2015), Zare-Shahabadi et al. (2010)</td>
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<tr>
<td>RTFOT</td>
<td>Rolling thin-film oven tests</td>
<td>Permits the artificially short-term ageing of binders and the determination of its resistance to hardening under the influence of air and heat</td>
<td>Can simulate the binders short-term ageing which occurs during mixing and lay-down of asphalt mixtures</td>
<td>Modified binders may have different ageing patterns, so RTFOT may not represent well the plant and field ageing</td>
<td>You et al. (2011), Ezzat et al. (2016), Abdullah, Hainin, et al. (2016), Vargas et al. (2017), Aziz et al. (2015), Santagata, Baglieri, Tsantilis, Chiappinelli, and Aimonetto (2015)</td>
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<tr>
<td>PAV</td>
<td>Pressure ageing vessel</td>
<td>Binders are exposed to heat and pressure to simulate an artificially long-term ageing over a 7- to 10-year period. Simulate binder ageing during the asphalt mixture service life</td>
<td>The use of high pressure increases the diffusion of oxygen into the binder sample, which limits the loss of volatiles compounds while ageing the sample</td>
<td>Modified binders may have different ageing patterns. Consequently, PAV may not represent the field long-term ageing. Discussion about recommended temperatures is still open</td>
<td>Guern et al. (2010), Abdullah, Hainin, et al. (2016), Zhao, Huang, Ye, Shu, and Jia (2014), Aziz et al. (2015)</td>
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<tr>
<td>Iatroscan TLC-FID</td>
<td>Iatroscan chromatography</td>
<td>Used to determine the bitumen chemical fractions, grouped into four classes (SARA fractions)</td>
<td>Offers good accuracy and precision, in addition to low solvent consumption and quick analysis. Organic substances, which show no UV-absorption and no fluorescence, can be analysed</td>
<td>Reproducibility needs to be improved. Variable response factors for the polar fractions</td>
<td>Guern et al. (2010), Ortega et al. (2015), Paliukaitė et al. (2014), Ortega, Navarro, García-Morales, and McNally (2017), Polacco et al. (2015)</td>
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<tr>
<td>Method</td>
<td>Description</td>
<td>Advantages</td>
<td>Limitations</td>
<td>References</td>
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<tr>
<td>FTIR</td>
<td>The chemical bonding and molecular-level interactions of binders can be analysed through the band positions. Extensively used in many industries.</td>
<td>Provides the IR absorbance spectrum of a solid, liquid or gas. It permits quantitative and qualitative analysis of samples. It allows studying ageing effects through monitoring variations in the spectra.</td>
<td>Reduced sensitivity due to fluorescence of certain elements. It has a high initial cost which permits only a spot test.</td>
<td>Guern et al. (2010), Ortega et al. (2015), Zhang et al. (2012), Abdullah, Hainin, et al. (2016), Polacco et al. (2015), Karahancer et al. (2014), Li, Wu et al. (2017), Babagoli et al. (2017).</td>
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<tr>
<td>DSC</td>
<td>Used to observe glass transition, fusion and crystallisation events and temperatures. Can also be used to study oxidation and other chemical reactions. It is possible to make kinetic studies.</td>
<td>Versatile tool which can be operated over a wide range of pressures and temperatures. Provides information on the energetic changes associated with chemical reactions.</td>
<td>Scanning rate and delay times. Low accuracy in results. Difficult to interpret. Requires calibration in temperature range.</td>
<td>Guern et al. (2010), Liu, Shaopeng, van de Ven, Molenaar, and Besamusca (2010), Abdullah, Hainin, et al. (2016), Polacco et al. (2015), Sureshkumar et al. (2010).</td>
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<tr>
<td>HS-SEC</td>
<td>Used to separate and quantify different materials in solution based on their molecular size.</td>
<td>Can be applied to large molecules or macromolecular complexes. Good separation of large from small molecules with a low volume of eluate.</td>
<td>In some conditions, the bands of eluting molecules may be broadened or only approximate measurements can be obtained.</td>
<td>Guern et al. (2010), Weigel and Stephan (2017).</td>
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<th>Test ref.</th>
<th>Test/procedure</th>
<th>Usefulness</th>
<th>Advantages</th>
<th>Drawbacks</th>
<th>Some references</th>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
<td>Used to measure the attractive or repulsive force between a sharp AFM tip and the sample surface. Used to test the binder-aggregate adhesion</td>
<td>No previous preparation of samples. Very high resolution. Imaging almost all types of surfaces. Can analyse the dispersion degree of nano-modified bitumen</td>
<td>Slow scan time. Single scan image size</td>
<td>Ortega et al. (2015), Zhang et al. (2012), Polacco et al. (2015), Li, Wu et al. (2017)</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
<td>Offers imaging characterisation, crystal structure information and chemical composition. Used to observe the morphologies of neat bitumen, nanoclays and modified binders</td>
<td>High resolution. Easy to operate. Permits 3D images. Samples with any thickness. Wide range of magnifications</td>
<td>Big size and expensive equipment. Requires vacuum and pre-preparation of small samples (conductive and solid). Lower resolution than TEM. It is not ideal to analyse bitumen samples</td>
<td>Polacco et al. (2015), Karahancer et al. (2014), Li, Wu et al. (2017), Babagoli et al. (2017)</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
<td>Can be used to characterise the nanoscale structure behaviours of nano-modified binders and their fracture morphologies</td>
<td>Very high resolution, better than SEM. Offer the possibility to investigate different materials. Quantitative identification of structural defects</td>
<td>Big size and expensive equipment. Requires pre-preparation of small samples (conductive and solid). Destructive technique. It is not ideal to analyse bitumen samples</td>
<td>Vargas et al. (2017), Paul and Robeson (2008), Munera and Ossa (2014), Pei et al. (2015)</td>
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</table>
You et al. (2011) used rotational viscosity (RV), dynamic shear rheometry (DSR), rolling thin-film oven tests (RTFOT) and a direct tensile test (DTT) to show that two different nanoclays enhanced the binder complex modulus ($G^*$) and its viscosity. Ezzat et al. (2016) also used an RV and a DSR to demonstrate that the addition of 3 wt.% of nanoclay can enhance the performance of the asphalt binder. However, when bitumen is blended with polymers, the DSR results may have poor correlation with the permanent deformation resistance (Batista et al., 2016).

Rheological measurements (flow curves and temperature sweeps in oscillatory shear), X-ray diffraction (XRD), atomic force microscopy (AFM) and FTIR were used by Ortega et al. (2015) to analyse the individual and joint effects of two modifiers (an OMMT, Cloisite 20A®, and a polymeric MDI, methylene diphenyl diisocyanate). Bonati et al. (2013) also used XRD techniques to measure the distance between layers and this information gives indications for the calculation of the extent and level of exfoliation of the nanoclay in the binder. In addition, Walters et al. (2014) and Vargas et al. (2017) used XRD measurements of nanoclay-modified samples to show also the intercalation and exfoliation of nanoclays in bitumens. The latter researchers also used TEM to evaluate the extent of intercalation and dispersion of MMT in the binder.

Regarding the specimen preparation for tests, Zhang et al. (2012) claimed that MB is a determinant in achieving a good division of the nanoclay in MMT/SBS-modified bitumen. They characterised the microstructures of this blending by XRD, FTIR and AFM. Those researchers also investigated the effect of MMT on ultraviolet (UV) ageing of the PMB with SBS, and used AFM to confirm that a network configuration was formed in this blend, having obtained an intercalated structure.

Galooyak et al. (2010) prepared SBS and OMMT/SBS-modified bitumen by a melt intercalation process and concluded, through XRD analysis, that an exfoliated structure was obtained.

Zhang et al. (2012) concluded that, in the case PMB with SBS, the viscosity ageing index (VAI) and the softening point (R&B) increment decrease when a sodium montmorillonite ($\text{Na}^+$-MMT) is added and can be further reduced if mixed with another montmorillonite (OMMT). The VAI is calculated in function of the viscosity values before and after UV ageing, obtained under the European standard EN 13302. R&B represents the temperature at which material under standardised test conditions attains a specific consistency, determined under the European standard EN 1427.

Guern et al. (2010) tried to understand, through Iatroscan chromatography, how the ageing of the chemical species is processed for different bitumens, confirming that the observed increase in resin or asphaltenes content is due to the aromatics or polar resin association, respectively.

Sultana and Bhasin (2014) investigated the effect of chemical composition on TS and rheology of asphalt binders, testing two different binders that were separated in the four SARA (saturated, asphaltenes, resins and aromatics) fractions, based on their polarity. The results evidenced an increase not only in the TS but also in the stiffness of the binders. Jamshidi et al. (2015) used a Brookfield RV, at elevated temperatures (when the modified asphalt is in the viscous phase), to prove that the activation energy of the binders were lower than when using a DSR at an intermediate temperatures (when the binders are in a visco-elastic phase). They claimed that the energy required by the modified asphalt binders (MAB) depends on the type and content of nanomaterials used, in addition to the physical phase of the sample (which is a function of the temperature). Santagata, Baglieri, Tsantilis, and Chiappinelli (2015) used a DSR to analyse the base bitumen and the additive used, having concluded that the MMT nanoclays can affect the fatigue strength and the recovery of bituminous binders. Yao et al. (2013) used FTIR spectroscopy to show the influence of nano- or micro-materials in asphalt binders, and explained that when they are exposed to sunlight and heat, its oxidation can be decreased.

Jasso et al. (2012) studied the impact of the addition of MMT and OMMT on the high-temperature properties of conventional asphalt modified by linear SBS block copolymer. They
were able to prove the linear visco-elastic (LVE) properties of PMBs through the use of oscillatory shear flows.

Liu et al. (2010) used the X-ray photoelectron spectroscopy to characterise the composition of the organic surfactant cations in the nanoclay in order to evaluate two bitumen nanoclay modifiers (both organic surfactant-modified MMT). They also used differential scanning calorimetry and thermogravimetric analysis (DSC-TG) to obtain the thermal stability of the OMMTs and confirmed that the surfactants in the two nanoclays have different thermal behaviour at temperatures below 200°C, which means that no problems are expected in the use of this modified bitumen (used at temperatures below 180°C).

Golestani et al. (2012) used XRD to show that the linear SBS-nanocomposite-modified bitumens may form an exfoliated configuration. However, modified bitumen with branch SBS-nanocomposite (BSN) may form a different structure (intercalated). The authors also showed that nanoclays can improve the rheological behaviours of those binders as well as their physical properties and the storage stability. The same conclusion was drawn by Farias et al. (2016) with the use of Cloisite.

Ashish et al. (2016) used a linear amplitude sweep (LAS) test to confirm that an increase in the Cloisite 30B® content originates a growth in the number of the load cycle to failure. They were also able to prove that the LVE limit of NMB follows the tendency for growing binder stiffness as the addition of nanoclay increases.

Abdullah, Hainin, et al. (2016) studied short- and long-term artificial ageing of an NMB. They characterised the morphological and chemical changes using field-emission scanning electron microscopy (FE-SEM) and FTIR, and conducted rheological evaluations using DSC. Among other conclusions, they reported that modified binders give an important contribution for adhesion between aggregates, which induces a better moisture resistance.

Yazdani and Pourjafar (2012) applied an orthogonal array (a fractional factorial design which minimises the number of test runs when used to estimate how multiple process variables influence, simultaneously, the performance) of the Taguchi method to optimise a modified bitumen composition. They prepared binder samples with 4.5% of bitumen 60/70 content and tested three control factors (a polypropylene plastomer, an SBS elastomer and an MMT nanoclay) and four levels of concentration contents (from 1% up to 7%). After some software calculations, they found that SBS with 3%, PP with 5% and nanoclay with 1.5% were the optimised concentrations, having noted that a small amount of nanoclay caused enormous changes in results.

Many other tests and methods can be used to study the binder composition and its properties. For example, Guern et al. (2010) used n-heptane precipitation, Iatroscan chromatography (which combines thin-layer liquid chromatography on silica gel, TLC, with flame ionisation detection), Fourier-transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC), to obtain information on bitumen chemistry (related with oxidisation of aromatics or resins, ageing, chemical organisation, etc.). They also used size-exclusion chromatography under high-speed conditions (HS-SEC), which yields information relative to asphaltene associations, allowing the simulation of several years of road ageing through 25 h at 100°C and 2.1 MPa, in a pressure ageing vessel (PAV) test (respecting, in Europe, the Standard EN 14769).

Regarding the study of low-temperature attributes of binders, it is also recommended that RTFOT (short-term ageing) and PAV (long-term ageing) procedures are applied before testing the blends (Mollenhauer et al., 2016).

Usually, when a polymer is also added to the blend, a solution intercalation method is used first. The clay is premixed with the melted polymer in order to get an intercalation of polymer (between the clay layers) (Farias et al., 2016). Then, this polymer/nanoclay composite is blended with bitumen and, finally, this NMB is ready to be mixed with the aggregates and filler to produce asphalt mixtures.
Other procedures have been developed to improve the final quality of the blends, namely *in situ* polymerisation, solvent blending and dry blending methods. Meanwhile, more investigations are still needed mainly on dispersion conditions and their evaluation (Li, Wu et al., 2017).

Regarding common mixing conditions, it seems that there are no consensus opinions since up to now different methods, temperatures, speed and durations were used to produce nanoclay-modified binders and asphalt mixtures. For example, in the cases mentioned in Table 3 authors used sample preparations with temperatures ranging from 130°C to 180°C, mixing speeds from 1550 to 5000 rpm (omitting one outlier) and durations ranging from 15 to 180 min.

### 3.3. Design and characterisation of asphalt mixtures

Recent design methods to prepare HMA or WMA mixtures contemplate different stages in its development: selection of materials (granulometric curve of the aggregates mixture, binder and mixture types and additives); selection of binder content and calculation of the volumetric properties of the mixture; evaluation of parameters such as coating compactability, water sensitivity and workability; and mechanical performance of the final mixture (Capitão et al., 2012).

The use of nanoclays may create supplementary design problems, introducing some difficulties to disperse them homogeneously in the bitumen. Therefore, the design of such asphalt mixtures should take into account the characteristics of all materials and the industrial process followed in the bitumen plant (bitumen supplier) or in the asphalt mixing plant (under the responsibility of the contractor). Recommendations regarding mix design and asphalt properties can be extracted from the available literature, covered in the following sections. The huge differences and uncertainty in the literature, regarding both the used materials and the test procedures, currently preclude any conclusion on the main trends of asphalt mixtures containing nanoclays.

The performance of plasma-modified mineral fillers in HMA might also be estimated by determining the Marshall stability (MS) and the ITS (Karahancer et al., 2014). MS is the maximum resistance to deformation of a moulded asphalt specimen, determined in Europe by the standard EN 12697-34. ITS test yields the maximum tensile stress applied on a cylindrical specimen loaded diametrically until it breaks at the specified test temperature and speed of displacement of the compression testing machine (in Europe, using the standard EN 12697-23).

Ziari et al. (2015) evaluated the fatigue and rutting resistance of HMA mixtures prepared by BT-modified bitumen. They modified bitumen with 10–30 wt.% of BT and the results showed that its physical properties were improved. The same conclusion was taken by Crucho, Neves, Capitão, Picado, and Garcia (2016) when they used only 4 wt.% of BT.

Other results showed an increase in shear strength and rutting resistance and the fatigue life was longer than in conventional HMAs. Walters et al. (2014) studied a naturally occurring nanoclay (an OMMT, *Cloisite 30B®*), blended at 2 and 4 wt.%, with and without a bio-binder (5 wt.% of dry mass). The bio-binder was obtained from swine manure through the use of a thermochemical conversion process. This process was then followed by a filtration to produce the bio-char. The bio-char was ground to nanoscale and mixed with a virgin asphalt binder at 2, 5 and 10 wt.%. Ashish et al. (2016) also used *Cloisite 30B®* in percentages up to 6 wt.% to show that the fatigue life of the mixtures was improved, but only for strain levels that do not exceed 1%. Another strategy was followed by Ortega et al. (2015) by mixing pure bitumen with another OMMT (*Cloisite 20A®*) and a polymeric MDI.

Iskender (2016) evaluated the mechanical properties of asphalt mixtures with an NMB using a modified Lottman test (MLT) and repeated creep tests (RCT) with Nottingham asphalt tester (NAT). He concluded that a 2% nanoclay content optimises the resistance to rutting, stripping and cracking.
To investigate the effects of nano-modification of the asphalt binder (with OMMT) and the influence of the mineral filler composition and the aggregate gradation on the fire-resistance behaviour of different asphalt mixtures, Bonati et al. (2013) used a cone calorimeter test (CCT) with a heat radiation of 70 kW/m². They concluded that the mineral filler composition has a strong influence in the fire reaction and the alkaline filler amount can be reduced if it is coupled with OMMT.

4. Mechanical performance evaluation of binders and asphalt mixtures with nanoclays

4.1. Binder properties

4.1.1. Introduction

The literature shows that nanoclays can improve the behaviour of binders used in asphalt mixtures. In fact, recent reports in the literature confirm that nanoclays can be successfully used as modifiers to change different physical and mechanical properties of asphalt binders, improving the elastic and visco-elastic behaviour of PMBs (Abdullah, Hainin, et al., 2016; Ameri et al., 2016; El-Shafie et al., 2012; Farias et al., 2016; Golestani et al., 2015; Iskender, 2016; Silvestre et al., 2015; Walters et al., 2014; You et al., 2011).

In the following subsections the overall performance trends of bitumens blended with different types of nanoclays are discussed.

4.1.2. Binder stiffness

In the case of nanoclays, their addition to bitumens can increase the binder stiffness, \( G^* \). For some authors, this improvement is due to an increase in the concentration of polar fractions in the binder (Sultana & Bhasin, 2014). This seems to depend on the polarity of the polar fraction and on the frequency of loading (or load time). Some processes (e.g. oxidation or air blowing) may have more impact on the stiffness at high temperature/low rate of loading than at low temperatures/higher rates of loading. Similarly, other processes such as the addition of softer materials or rejuvenators (which restore ductility and adhesion properties of the binders) may result in a decrease in stiffness along the frequency spectrum.

From DSR results, Yao et al. (2013) concluded that the addition of four different modifiers (nanomer I.44P, carbon microfiber, non-modified nanoclay and PMN) can all increase the complex shear modulus of a MAB, especially at high and intermediate temperatures. However, at low temperatures, the recovery ability of these MAB may be reduced (due to its higher stiffness). Golestani et al. (2015) also found enhanced stiffness modulus in modified bitumens, especially at higher temperatures.

Other authors confirmed that nanoclay modifications can not only help increase \( G^* \), but also decrease phase angle (\( \delta \)), when compared to unmodified bitumen (Abdullah, Hainin, et al., 2016; Abdullah, Zamhari, Hainin, Oluwasola, Hassan, et al., 2016; Farias et al., 2016; Golestani et al., 2015; Jahromi & Khodaii, 2009; Melo & Trichès, 2017; Pei et al., 2015; Vargas et al., 2017; You et al., 2011; Zapién-Castillo et al., 2015; Zare-Shahabadi et al., 2010). This means that a lower plastic component is present in \( G^* \). In this respect, Jahromi and Khodaii (2009) confirmed, for an NMB, that \( G^* \) increases by decreasing temperature and/or increasing frequency of loading, whereas \( \delta \) increases as temperature increases and/or frequency of loading decreases.

4.1.3. Resistance to fatigue cracking

Some authors argue that it is always necessary to check the fatigue performance, because the total complex shear modulus, \( G^* \sin \delta \) [fatigue cracking index used by Superpave™ specification (Zhao et al., 2014)], resulting from DSR tests, may or may not be suitable for other materials
than bitumen (Aziz et al., 2015). Superpave™ is an American design method for pavements to replace the Marshall, Hveem or Durier design methods. Moreover, the addition of OMMT can change the fatigue properties of bitumen, due to the type of surfactant used, which determines how the interfacial interaction between bitumen and MMT occurs (Liu et al., 2011).

Santagata, Baglieri, Tsantilis, and Chiappinelli (2015) also concluded that nano-sized additives, such as MMT nanoclays, can influence the fatigue and recovery behaviour of binders. They verified that the fatigue response of base bitumens was always improved by this kind of modification. However, the efficiency of the nanoparticles depends greatly on the physico-chemical properties of the base components, which greatly influence the morphological configuration that the additives take then on the bituminous blend.

4.1.4. Resistance to extreme temperatures

The susceptibility to high and low temperatures and/or the low-temperature cracking resistance of NMB have been studied by different authors (Bonati et al., 2013; Ezzat et al., 2016; Munera & Ossa, 2014; Ortega et al., 2015; Pei et al., 2015; You et al., 2011; Zare-Shahabadi et al., 2010; Zare-Shahabadi et al., 2015). In all cases, the nanoclays were found to enhance the asphalt binders resistance to extreme temperatures, at least, in hot climatic conditions.

Jahromi and Khodaii (2009) confirmed that the temperature susceptibility (defined as the rate at which the consistency of binders changes with a change in temperature, usually characterised by the penetration index, PI, calculated as defined in Europe by the standard EN 12591) is lower for NMB than for unmodified binders. However, Zapién-Castillo et al. (2015) warn that even when the PI points to reducing the bright and rigid appearance of bitumen at low temperatures (which means a lower sensitivity to low temperatures), the results are inconclusive and, therefore, further studies should be carried out.

You et al. (2011) tested two different surfactant-modified nanoclays (intercalated MMT nanoclays), blended in bitumen (at 2 and 4 wt.% nanoclay by weight of bitumen) at high temperature. Through direct tension tests they concluded that a 2 wt.% modified bitumen had better low-temperature cracking resistance.

Nanoclays can also be used in polymer-based flame retardants (FR) for improving asphalt fire resistance. Bonati et al. (2013) showed that, due to a migration mechanism (which leads the clay platelets to the top of the burning sample, when the FR fillers are mixed with OMMT), the performance of the protective layer of coal improves, resulting in a clear decrease of the smoke and heat released.

Ortega et al. (2015, 2017) studied the impact on rheological properties of a combination of MDI (a blend of methylene diphenyl diisocyanate and its higher homologues) with nanoclays. They addressed the improvement in thermoreological behaviour including thermal stability of the different bituminous products, particularly those used for roofing and road applications. These authors claimed that the addition of 2 wt.% MDI and subsequent curing at 150°C, enhanced the composite properties, due to the chemical interactions between the MDI and the bitumen/clay composite.

Crucho et al. (2016) studied the influence of several nanomaterials, one being a nanoclay (BT). They found that an NMB (which included 4 wt.% BT) increased penetration (16%) and viscosity (6%), but the softening point remains without changes. These facts confirm the tendency for higher resistance at high temperatures.

4.1.5. Ageing resistance

Usually, the short-term ageing process of the asphalt binders is simulated using RTFOT (respecting the European standard EN 12607-1) and the long-term ageing process is replicated with PAV
(European standard EN 14769) (Hill & Jennings, 2011; Yao et al., 2013; Zhao et al., 2014). However, Aziz et al. (2015) have pointed out that some alternative binders (for example, made with recycled products, such as waste cooking oil, plastic and tire rubber) may have significantly different ageing characteristics, suggesting that RTFO and PAV tests may not represent well the mixing plant and field ageing.

Walters et al. (2014) reported that the addition of nanoparticles to bio-MAB was very effective to improve its ageing resistance. Guern et al. (2010) studied the impact of ageing on chemical species (saturate, cyclic or aromatic) and changes in the chemical organisation, depending on the type of bitumen. They concluded that the agglomeration during its ageing can be influenced by the lack of crystallised fractions.

Liu et al. (2011) showed that mastics with OMMT revealed better ageing resistance than conventional base bitumens due to its barrier properties and Li, Wu et al. (2017) proved that this effect was also due to its inhibition to VOCs emission. Furthermore, Galooyak et al. (2010) observed that layered silicates can prevent oxygen diffusion into PMB, and thus the OMMT can improve the ageing resistance of PMB. Finally, Zhang et al. (2012) proved that the addition of MMT clay can successfully prevent changes in the micro-morphology of binders and Li, Xiao, Amirkhanian, You, and Huang (2017) also summarised in its review that the oxidation process (which leads to ageing) can be retarded by nanoclays.

4.2. Asphalt mixture properties
4.2.1. Introduction

Usually, the performance of asphalt mixtures is studied by taking into account their main mechanical properties (namely, fatigue life, stiffness, resistance to permanent deformation, low-temperature cracking and ageing). The incorporation of nanomaterials has a strong influence on the structures of the blends and, consequently, on its rheological behaviour, even leading to WMA showing properties comparable to HMA (Abdullah, Hainin, et al., 2016; Abdullah, Zamhari, Hainin, Oluwasola, Hassan, et al., 2016; Abdullah, Zamhari, Hainin, Oluwasola, Yusoff, et al., 2016; Jamshidi et al., 2015).

The mechanical performance of all types of asphalt mixtures, including those containing nanoclays, varies with the type of mixture as well as its composition. Fracture and strength characteristics, which are critical to pavement performance, are determined by aggregate mineralogical composition (Cui, Blackman, Kinloch, & Taylor, 2014; Zhang, Apeagyei, Airey, & Grenfell, 2015), gradation (Aziz et al., 2015), bitumen content (Capitão et al., 2012) and adhesion binder/aggregates (Cui et al., 2014).

Since the specific conditions used in tests (such as load characteristics and temperatures) can significantly influence their results, in the following paragraphs are discussed the overall performance trends of mixtures produced with different types of nanoclays.

4.2.2. MS, TS, water sensitivity and binder/aggregate interaction

The Marshall stability MS, obtained in Marshall tests, was found to be higher in asphalt mixtures prepared with NMB than in control mixtures, produced with bitumen or PMB (Babagoli et al., 2017; Karahancer et al., 2014; Li, Wu et al., 2017; Taherkhani, 2016). However, Ziari et al. (2015) confirmed this tendency only while the percentage of BT was lower than 20% (content by weight of bitumen), a value from which the MS started to decrease. In these tests, the flow of the mixtures did not follow any specific tendency.

Goh et al. (2011) studied the effects on the moisture sensitivity of asphalt mixtures produced with nanoclays and carbon micro-fibers, in terms of TS ratio, calculated as the ratio between
the TS (indirect, by diametral compression) of wet specimens (conditioned in water) and that of dry specimens. The results indicated that, for all mixtures which included nanoclay and carbon micro-fibers, the TS ratio values are higher than those recommended (typically defined with a minimum value of 0.9). In addition, it seems that the incorporation of 1.5% of nanoclay into mixtures increased the TS. Consequently, in regions with severe winters, these mixtures will be able to better withstand the effects of materials applied to promote the thaw. An increase in the polar fractions of the binders also leads to an increase in its TS (Sultana & Bhasin, 2014).

Regarding water sensitivity, or moisture susceptibility, it is well accepted that the aggregate mineralogical composition plays an important rule on aggregate–bitumen bonds. For example, Zhang et al. (2015) tested, through three different methods, four aggregate types (two granites and two limestones) and two types of bitumen (40/60 and 70/100 pen), concluding that the aggregates effect was greater than the bitumen effect. In addition, Ashish et al. (2016) observed that a sandstone aggregate provided the best interaction with bitumen and it was followed by granite, limestone and finally basalt aggregates.

Other authors also have demonstrated that polymer- and nanocomposite-modified asphalts are more resistant to moisture damage than conventional asphalt mixtures mainly due to the reduction of air voids (Ameri et al., 2016; Ashish et al., 2016; Golestani et al., 2015; Iskender, 2016; Karahancer et al., 2014; Taherkhani, 2016). Li, Xiao et al. (2017) and Melo and Trichês (2017) also explained that this higher moisture resistance is due to a lower surface tension and a better chemical affinity binder-aggregate. However, Ashish et al. (2016) noted that the addition of nanoclay increases the adhesion aggregate-binder mainly in dry conditions.

4.2.3. Asphalt mixture stiffness

In general, the results indicate that the binder’s visco-elastic properties of low shear viscosity (LSV), complex modulus and phase angle, have no impact on the air voids content in the asphalt mixture, but their influence in the value of the resilient modulus of elasticity at 20°C is significant (for asphalt mixtures compacted at 125°C) (Nicholls, Valentin, Benešová, & Eberl, 2016).

The addition of NMB to asphalt mixtures can increase the HMA (or WMA) complex stiffness modulus ($E^*$), determined in Europe by the standard EN 12697-26. Several authors confirmed this fact and also a reduction in the phase angle ($\delta$), which means a lower plastic component in $E^*$, when compared to asphalt mixtures with an unmodified binder (Abdullah, Hainin, et al., 2016; Abdullah, Zamhari, Hainin, Oluwasola, Hassan, et al., 2016; Farias et al., 2016; Golestani et al., 2015; Melo & Trichês, 2017).

However, Abdullah, Zamhari, Hainin, Oluwasola, Yusoff, et al. (2016) proved that, for WMA with NMB, the stiffness at 25°C had lower values when compared with HMA (in the same conditions).

4.2.4. Resistance to fatigue cracking

Most studies report an improvement in the resistance to fatigue of asphalt mixtures modified with nanoclays, which leads to a higher fatigue life (determined, in Europe, by the standard EN 12697-24) and longer durability than conventional HMA or WMA. This was confirmed by Ziari et al. (2015) when they tested a BT-modified bitumen. These authors proved that mixtures containing 10% and 15% BT have longer fatigue life than the control mixture; however, they also stated that the modification of the base bitumen with higher percentages of BT did not enhance the fatigue life of the mixtures. Meanwhile, Melo and Trichês (2017) tested a conventional binder with 3 wt.% (by weight of binder) of an organophilic nanoclay and concluded that the asphalt mixture produced with this blend presented greater resistance to fatigue (@ 15°C and 10 Hz).
Ashish et al. (2016) concluded that the use of Cloisite 30B®, in percentages up to 6 wt.% and for strain levels that do not exceed 1%, enhances the mixture fatigue life. This may be related to cluster formation in the asphalt blends, which reduce the propensity for cracking.

Through indirect tensile fatigue tests, Abdullah, Zamhari, Hainin, Oluwasola, Yusoff, et al. (2016) also verified that, for WMA and HMA mixtures, the fatigue life was similar, but that for WMA with nanoclay (compacted at 135°C) it increases considerably.

4.2.5. Resistance to permanent deformation (rutting)

The resistance to permanent deformation (determined, in Europe, under the standard EN 12697-22) is one of the most important parameters to achieve stable and long-lasting pavements, especially when used in the base or binder course layers. Based on rheological results, Golestani et al. (2012) concluded that the highest rutting resistance in their asphalt mixtures was obtained when an SBS polymer was combined with OMMT in the proportion of 100/25 (SBS/OMMT).

In general, bitumen modification with nanoclays improves rutting resistance, especially at elevated temperatures (Abdullah, Hainin, et al., 2016; Abdullah, Zamhari, Hainin, Oluwasola, Hassan, et al., 2016; Ameri et al., 2016; Ameri et al., 2017; Ezzat et al., 2016; Farias et al., 2016; Golestani et al., 2015; Melo & Trichês, 2017; Vargas et al., 2017; Yao et al., 2013). Ziari et al. (2015) also stated that the addition of BT improves not only the physical properties of bitumen, but can also increase the rutting resistance and the shear strength of HMA. They used a dynamic creep test (DCT) to prove that the addition of BT could considerably reduce the permanent deformation which leads to a better rutting resistance of asphalt mixtures at high temperatures. The wheel-tracking tests (WTT) showed that mixtures containing BT gave a better rutting resistance (thus reducing its permanent deformation). Ameri et al. (2016) reported the same conclusion when they tested PMB (where the polymer was an SBS) with and without nanoclay.

Jamshidi et al. (2015) suggested characterising the influence of nanomaterials on asphalt binders using a non-dimensional Superpave™ rutting factor gradient analysis (\(\nabla_{\text{NSRP}}\)) (Hill & Jennings, 2011; Zhao et al., 2014), to compare the resistance to permanent deformation of bituminous mixtures with and without modified binder. In this respect, they also found that the \(\nabla_{\text{NSRP}}\) gradient is influenced by the type and content of the nanomaterial and by the temperatures used in tests.

Iskender (2016) also concluded that binders with (2–5 wt.%) nanoclays have a higher rutting resistance (in average 50% larger than the control mixtures), using an MLT water damage conditioning method, which includes hot water conditioning (respecting the AASHTO T283 standard).

4.2.6. Low-temperature cracking

The low-temperature behaviour of asphalt mixtures is evaluated through the low-temperature cracking resistance. This important parameter can be determined by different test procedures, being the tensile stress restrained specimen test (TSRST), as defined in EN 12697-46, the one which has the largest number of results available (Mollenhauer et al., 2016).

The addition of NMB significantly improved the low-temperature cracking resistance of asphalt mixtures (Li, Wu et al., 2017; Mollenhauer et al., 2016). A similar conclusion was also reached by other authors, for example, Iskender (2016) and Galooyak et al. (2010). However, it was reported by Abdullah, Hainin, et al. (2016) that the usual increase in stiffness of NMBs may lead to a reduction in resistance to low-temperature cracking.
5. Conclusions

Nanoclays have a high potential for application in some types of asphalt mixtures. These additives can improve the binder stiffness and, consequently, the asphalt mix stiffness, fatigue life, permanent deformation resistance of asphalt mixtures and ageing resistance of binders at an acceptable cost. OMMT, in particular, is a promising alternative to improve the lifetime of asphalt pavements. However, before its widespread use some issues still need further investigation, namely the efficient dispersion of the nanoparticles.

Since different sources of binders can be used in the same type of asphalt mixture, the results obtained with its modification can have many variations. For this reason, it is important to assess, for example, the individual properties of each bitumen fraction, the differences in those properties for each crude source and the performance of the final blends, at different rates of loading and temperatures. It is also desirable that the introduction of nanoclays in binders confirms that possible storage stability problems will be minimised and its use in asphalt mixtures consider its long-term performance and recyclability in future.

Regarding the design of new mixtures, further work is needed to find the best procedures to evaluate the uniformity of nanoparticles dispersion. The validation of results by studying a wider array of base materials and their most adequate combinations must be also developed, as well as the influence of the mixing methods used and its correlation with temperature, speed and duration adopted. In this context, from a statistical point of view, the most frequent values mentioned in the reviewed literature were the following: 3 wt.% of bitumen for nanoclay content, 160°C for the temperature used, 4000 rpm for the mixing speed chosen and 120 min for the mixing process duration.

An important and actual driving factor for the use of bitumens modified with nanoclays is related to the contribution that this additive can give to sustainability and reduction of global greenhouse gas emissions (due to performance improvement and reduction of bitumen and fuel consumption), as recommended in the Paris Agreement (December 2015).

At this point it is premature to conclude the life-cycle cost and the cost–benefit analysis of NMB on an industrial scale since no data on their long-term performance are yet available. Nanoclay-modified binders have a promising future in the pavement industry, especially if these materials are combined with WMA approaches, to take the best advantages of both technologies.

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