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Comparative assessment of the effect of micro- and nano- fillers on the microstructure and linear viscoelasticity of polyethylene-bitumen mastics

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HIGHLIGHTS

- Mastics obtained by combination of micro/nano-fillers showed enhanced rheology.
- Polymer dispersion improved with addition of nanoclay.
- Polymer droplets size decreased as the microfiller approached its limiting content.
- Fluorescence Optical Microscopy enabled visualization of polymer-rich domains.
- Atomic Force Microscopy provided information on the filler reinforcement.

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ABSTRACT

In order to minimize permanent deformation in bitumen mastics, the combined addition of traditional mineral filler and an organo-modified nano montmorillonite to different bitumen/polymer matrices was evaluated by dynamic shear/torsional tests and microscopy techniques. Individual addition of microfiller or nanoclay was also studied. The most remarkable result corresponded to a polymer modified mastic containing a mix of 40 wt% microfiller and 5 wt% nanoclay. As compared to a reference mastic with 45 wt% microfiller, the complex modulus at 65 °C increased more than two decades. The nanoclay has thereby shown high reinforcing potential if combined to standard mineral filler in bitumen mastics.

1. Introduction

Mineral fillers with a typical average particle size in the 10–50 μm range have traditionally been used in hot asphalt mixtures for road construction [1]. They provide contact points between larger aggregate particles in order to strengthen the mixture. It is noteworthy to mention that the composite formed when bitumen and filler are mixed, termed mastic, is the actual binder which holds the aggregates together. The rheological characterization of this composite is therefore essential to improve the understanding of the asphalt pavements performance [2,3].

The macro-mechanical behavior of flexible bituminous pavements is conditioned by the morphology and physical properties at the smaller meso- and micro-scales [4]. As the volume, speed and load of traffic have dramatically increased over the last decades, the use of polymer modified bitumens (PMBs) is very often required in order to enhance pavements performance and, so, to prolong their in-service life and reduce maintenance costs [4,5]. Numerous studies [6–10] have reported increased shear complex modulus of bitumen upon addition of polyethylene (PE). Moreover, PE is the most popular commodity plastic and, so, is abundantly available as waste material. Its addition to bitumen represents an environment-friendly alternative approach for the future of waste PE valorization.

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In another order of things, layered silicates (nanoclays) are well-known to form polymer-based nanocomposites when are incorporated to a polymer matrix. In polymer/layered silicates nanocomposites, complete exfoliation of nanoclay tactoids into individual platelets has yielded to materials showing extraordinarily enhanced rheological properties [11–14]. A similar practice involving bitumen is gaining an increasing significance. Nanoclays have emerged as promising bitumen modifiers due to unique features like nano-scale size and high surface to volume ratio, among others [15–22]. The incorporation of nanotechnology into the bitumen field can drive a further step in the search of improved physical properties induced by the formation of assembled particles at the nano-scale. If organo-modified nanoclays are used, the bitumen maltenic components with the lowest molecular weights may diffuse between the nanoclay tactoids, yielding complete exfoliation, under the most favorable scenario. In practice, complete exfoliation is not always reached, but a combination of exfoliation, intercalated structures and small tactoids resulting from a size reduction of the original nanoclay particles. Moreover, the stability of these structures is guaranteed by their interactions with asphaltenic components presenting polar functional groups. Recent literature studies have shown the extraordinary modifying capacity of Cloisite20A, a commercial organo-modified montmorillonite, when added to different asphalt binders [17,20,23]. Hence, the reinforcement of bituminous binders with this type of nanoclays has shown enough potential so as to redefine the field of asphalt mixtures in terms of high efficiency, cost-effectiveness, multi-functionality and long-term pavement performance.

Despite of that, many studies make evident that a deeper knowledge is still needed before nanotechnology can be adopted in asphalt mixes on a large scale [24]. For example, factors like bitumen nature, polymer type, clay type or mixing procedure have been envisaged [19,20]. However, the combined use of traditional microfiller and nanoclay in the formulation of mastics has captured much less attention. Regarding this type of mixes, Santagata et al. [25] studied fatigue and healing properties, and Bonati et al. [26] evaluated the effect of nanoclay in the presence of fire. Even so, a comparative evaluation in terms of end-performance benefits with respect to traditional mastics needs to be addressed.

Based on that, a type of siliceous filler with particle size below 100 μm and the organo-modified montmorillonite Cloisite20A were chosen as representatives of micro and nanofiller, respectively. Hence, this research firstly presents experimental results on the single contribution of microfiller and nanoclay to the linear rheology and morphology of traditional bitumen mastics and bitumen nanocomposites, respectively, so as to establish reference formulations. The effect of polymer modification was also explored by using a polymer modified bitumen with 4 wt% LDPE. Finally, for a traditional mastic with a selected concentration of 45 wt% microfiller, a part of that (5 wt%) was replaced with nanoclay, so as to evaluate the effect of the combined addition. Extraordinary results were achieved, in terms of stiffness and elasticity.

2. Experimental

2.1. Materials

Bitumen with penetration grade within the range 70/100 (referred to as BI), donated by Repsol S.A. (Spain), and recycled low density polyethylene (LDPE) in form of pellets, provided by Cordoplas S.A. (Spain), were used in the preparation of the polymer modified bitumen (PMB), base for the modified mastics. A fixed LDPE concentration of 4 wt% was chosen to modify BI. DSC scans carried out on the polymer revealed two melting peaks located at 110.4 and 124.5 °C, which correspond to LDPE and Linear-LDPE, respectively.

A second neat bitumen with 50/70 penetration (referred to as BII), also kindly supplied by Repsol S.A., was used as an unmodified control sample, with the purpose of using modified/unmodified bitumens with comparable hardness. Bitumen specifications, shown in Table 1, correspond to the values of penetration grade (EN 1426 [27]), softening temperature (EN 1427 [28]) and chemical composition, given in terms of the so-called "SARAs" fractions.

Two different types of fillers, representing the categories of micro and nanofiller, respectively, were used:

(a) Siliceous-type filler (referred to as "microfiller"), with apparent density of 1.32 g/cm^3, obtained by taken the fraction with particle size smaller than 100 μm from a sample of mineral aggregate supplied by Eiffage Infraestructuras S.A. (Spain). Table 2 presents its granulometry, in terms of mass fraction passing each of four standardized sieves according to ISO 3310-1 [29]. This material is largely used in paving in South-West Spain. Its mineral composition is: Quartz (40 wt%), Clay minerals (35 wt%), Opaque minerals (10 wt%), Muscovite (5 wt%), Feldspars (5 wt%) and Carbonates (5 wt%).

(b) Cloisite20A nanoclay (referred to as "C20A nanoclay"), a natural montmorillonite clay which, in order to facilitate its dispersion in bitumen, has been organically modified by replacing the metal cations with N,N-dimethyl di(hydrogenated tallow) quaternary ammonium cations, in a concentration of 92.6 meq/100 g clay. The hydrogenated tallow is composed of a combination of C18 (65 wt%), C16 (30 wt%) and C14 (5 wt%) groups. This layered silicate presents platelets of approximately 1 nm thick (interlayer distance of 2.42 nm according to X-ray diffraction) and average value of 8 μm in their largest dimension.

2.2. Specimens preparation

2.2.1. Bituminous composites processing

The PMB was firstly prepared at 170 °C using a high shear Silverson L5M-A laboratory homogenizer, equipped with a Silverson Square Hole High Shear Screen, specifically suitable for dispersing molten polymers. The base bitumen BI was heated up to the set temperature in a metal container and the required amount of recycled LDPE (4 wt%), in form of pellets, was added gradually and pre-dispersed over the first 15 min, whilst the dispersing tool was rotating at the speed of 3500 rpm. Afterwards, high speed mixing at 5000 rpm for one more hour allowed a fine polymer dispersion to be achieved, due to the combined effect of shear and elongational forces.

In a second stage, the adequate amount of siliceous filler and/or C20A nanoclay was added into the PMB at 175 °C, and dispersed at 3000–3500 rpm for 30 min, aided by the Silverson Ultramix ele-

Table 1
Average values of selected technological tests and "SARAs" fractions (±standard deviation) for the base bitumens BI and BII, and 4 wt% LDPE PMB.

Properties	Results		
Technological tests	BI	BII	PMB
Penetration at 25 °C (1/10-mm), EN-1426	73	50	50
R&B softening point (°C), EN-1427	45	50	61
SARAs fractions			
Saturates (wt%)	6.2 (± 0.8)	6.2 (± 0.6)	–
Aromatics (wt%)	47.3 (± 1.6)	50.3 (±1.8)	–
Resins (wt%)	28.0 (± 2.2)	24.5 ± 1.6	–
Asphaltenes (wt%)	18.5 (± 1.2)	19.0 (± 1.2)	–