Construction and Building Materials 75 (2015) 395–403

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effect of sonication on high temperature properties of bituminous binders reinforced with nano-additives

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HIGHLIGHTS

- Nano-additives improved high temperature properties of bituminous binders.
- Ultrasounds were used to aid dispersion of nano-additives in bitumen.
- Effects of sonication were highly dependent on additive type.
- Results were found to be coherent with nano-scale interaction phenomena.

ARTICLE INFO

Article history:
Received 3 June 2014
Received in revised form 30 September 2014
Accepted 12 November 2014

Keywords:
Carbon nanotubes
Nanoclays
Bituminous binders
Sonication
Rheology
Rutting

ABSTRACT

The study focused on the effect of sonication on high temperature properties of bituminous binders containing carbon nanotubes and nanoclays. Blends at various dosages were prepared in the laboratory according to two techniques, based on sonication and/or shear mixing. Rheological behaviour of binders was investigated, in the unaged and short-term aged state, by means of oscillatory and creep–recovery tests. Experimental results were found to be coherent with interaction phenomena occurring at the nano-scale and indicate that effects caused by sonication on nano-modified blends are not univocal, but are highly dependent on additive type.

1. Introduction

Nanotechnology has aroused, in recent decades, a great deal of interest in a wide variety of scientific disciplines, including biology, physics, chemistry and materials engineering [1–4].

Among the nano-sized additives that have been taken into account in literature, carbon nanotubes and nanoclays currently represent the most promising products. Carbon nanotubes were discovered by Iijima in 1991, as cathode deposit in electrical arc experiments [5]. They basically consist of graphene sheets, made of hexagonal networks of carbon atoms, which are rolled up into cylinders and capped with a half fullerene molecule. Carbon nanotubes can be found in either single-wall or multi-wall configurations, constituting a tubular shell with only one atom in thickness or multiple coaxial tubes of increasing diameter, respectively [6]. Nanoclays are sheet-like structures that are capable of yielding a huge surface area by means of clay platelet separation. The most common nanoclays are obtained from 2:1 phyllosilicates, the crystal lattice of which is made of a central octahedral sheet sandwiched between two external silica tetrahedrons. In order to give a hydrophobic character to phyllosilicates, which are typically hydrophilic, clays can be organically modified by means of specific surfactants, thus obtaining the so-called organoclays [7,8].

In the area of bituminous binders and mixtures employed in road paving applications, use of nano-sized additives is quite new and a relatively limited number of studies have been conducted by researchers worldwide. Some authors have highlighted the capability of nano-sized particles to improve rheological properties of bitumens, especially at high in-service temperatures [9–15]. However, in most cases, the full potential of nano-sized products has been limited by the difficulty of achieving a homogeneous dispersion, which ensures their effectiveness at the nano-level. Consequent performance-related benefits of

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http://dx.doi.org/10.1016/j.conbuildmat.2014.11.021
0950-0618/

modification, even if significant, are far below theoretical expectations.

The unique properties of nano-particles, which are associated to their large surface area to volume ratio, can be fully exploited only if an efficient homogenisation and disaggregation of individual units is obtained within the bituminous matrix. In the case of carbon nanotubes, these phenomena depend upon entanglement, which arises as a consequence of the synthesis process, and agglomeration, due to intermolecular van der Waals forces [16,17]. In the case of organoclays, apart from agglomeration concerns, the degree of penetration of bitumen molecules between silicate layers plays a key role in defining the final properties of the composite binder. A successful bitumen-clay interaction may generate intercalated or exfoliated morphologies. Intercalation occurs when the galleries between the layers are expanded but silicate platelets still retain a well-defined spacing, whereas exfoliation results from complete separation and random dispersion of clay sheets [18,19].

In the effort of maximising interactions between nano-particles and bitumen, encouraging outcomes have been obtained by means of ultrasound energy. Experimental results published by Zare-Shahabadi et al. [20] indicate that the combined use of sonication and shear stresses during mixing may lead to intercalated or exfoliated structures, depending on the type of employed silicate. Khattak et al. [21] showed that preliminary sonication treatment of carbon nano-fibres in a solvent may be beneficial to enhance visco-elastic and fatigue characteristics of bitumen. Santagata et al. [22] demonstrated that an actual reinforcement effect against fatigue cracking can be achieved in binders modified with carbon nanotubes when dispersion is performed by means of ultrasounds.

On the basis of the promising results provided by sonication, the study presented in this paper focused on the effect of ultrasounds on high temperature properties of bituminous binders containing carbon nanotubes and nanoclays. Several blends at various dosages were prepared in the laboratory according to two processing techniques, based on sonication and/or simple shear mixing. Rheological behaviour of binders was investigated by means of tests performed in both the oscillatory and creep–recovery mode. Experimental results were analysed with the specific goal of highlighting the effects of the dispersion technique on high-temperature performance properties of such innovative materials.

2. Experimental investigation

2.1. Base materials

A single base bitumen was employed in the present work. Based on the results of preliminary rheological tests carried out according to AASHTO M 320 (Table 1), it was classified as a PG58-22. Chemical analysis, performed by means of the combined use of Thin Layer Chromatography and Flame Ionization Detection, yielded the relative amounts of Saturates, Aromatics, Resins and Asphaltenes shown in Fig. 1 (where measured electric potential difference ΔV is plotted as a function of time).

Three commercially available nano-sized additives were considered in the investigation: one type of carbon nanotubes (CNT), and two types of nanoclay (NC_A and NC_B). Carbon nanotubes were produced by means of the Catalyzed Chemical Vapour Deposition (CCVD) process in thin multi-wall structures, which have the advantage of guaranteeing a satisfactory aspect ratio (>150) while limiting production costs. The two nanoclays were originated from natural montmorillonites by inserting within clay platelets specific surfactant coatings, constituted by different types of quaternary ammonium salts. This allowed polarity to be altered, thus providing an organophilic character to the silicate surface. Main characteristics of the additives, based on manufacturers' technical specifications, are reported in Tables 2 and 3.

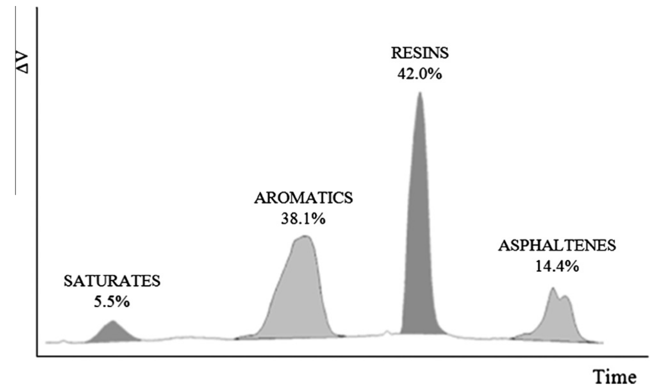

Fig. 1. Chemical analysis of base bitumen.

Table 1
Rheological characterisation of base bitumen.

Ageing condition	Temperature (°C)	Rheological characteristic
Unaged	135.0	η = 0.375 Pa s
	63.2	$G^*/\sin\delta$ = 1 kPa
Short-term aged	64.0	$G^*/\sin\delta$ = 2.2 kPa
	19.9	$G^*\cdot\sin\delta$ = 5000 kPa
Long-term aged	−16.6	m = 0.300
	−17.6	S = 300 MPa

2.2. Preparation of nano-reinforced blends

The base bitumen and additives described in Section 2.1 were employed for the laboratory preparation of several nano-reinforced blends. Experimental factors which were kept variable in the study were additive dosage and mixing technique.

Dosages of the nano-sized additives were defined by taking into account the significant differences in terms of volumetric properties of carbon nanotubes and nanoclays. Thus, percentages by weight of the base bitumen were fixed at 0.5% and 1% for carbon nanotubes and at 3% and 6% for nanoclays. These dosages were selected on the basis of previous investigations [12,13,22] which showed that they are sufficient to affect the rheological response of neat bitumen. Moreover, they are compatible with the needs of limiting costs (of base materials) and of avoiding excessive viscosity of blends at mixing temperatures.

Since mixing operations can influence the rheological behaviour of nano-reinforced materials [16,18], two mixing techniques were compared in the whole study. The first one is based on a simple shear mixing protocol previously developed by the authors [12,13]. The procedure begins with initial hand-mixing of the additive in the preheated binder, followed by a phase during which the blend is mixed with a mechanical stirrer, operated at a speed of 1,550 rpm for a total time of 90 min at a temperature of 150 °C, kept constant by means of a thermostatic oil bath. The second protocol consists in the addition of a sonication phase to the shear mixing procedure described above. This further phase is carried out by employing the ultrasonic homogeneizer UP200S from Hielscher GmbH (200 W and 24 kHz), equipped with a cylindrical titanium sonotrode (7 mm diameter). This element is immersed in the blend which is kept in a fluid state at a constant temperature of 150 °C. Ultrasounds are then generated, propagating within the material in the form of compression attenuated waves. As a consequence, separation of individual nano-particles from existing agglomerates is promoted, thus leading to a more homogeneous dispersion [16].

In order to choose sonication parameters which lead to an adequate dispersion of nano-particles, a preliminary set of tests dedicated to the evaluation of the effect of sonication duration and wave amplitude was performed on a reduced set of nano-reinforced blends. Values of these parameters were respectively fixed at 30 and 60 min and at 87.5 and 157.5 μm. In the case of sonication duration, these values were adapted from those proposed elsewhere for carbon nano-fibres and nanoclays dispersions [20,21,23]. Selected amplitudes correspond to 50% and 90% of the maximum value that can be attained by the equipment. They were chosen in the attempt of maximising the overall efficiency of the system and of limiting wearing phenomena which may occur at the tip of the sonotrode in the case of high viscous media.

The effect of sonication parameters on distribution of nano-particles may be assessed via microscopic inspections or indirect estimative techniques. Even if microscopy represents the only way to obtain direct information on morphology, it requires a stringent protocol for specimen preparation that cannot be easily adopted in the case of bituminous materials. Moreover, microscopy provides information that is limited to the cross-section of the sample, whereas results obtained from the use of indirect rheological methods are related to the bulk properties of considered specimens [17]. In the light of these observations and of the numerous works which have established a correlation between microscopic inspections and dynamic rheological measurements [17,24–27], in this study the efficiency of the sonication protocol on dispersion of nano-sized additives was indirectly assessed