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Fatigue and healing properties of nano-reinforced bituminous binders

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ABSTRACT

The research work focused on fatigue and healing properties of bituminous binders containing carbon nanotubes (CNTs) and nanoclays (NCs) as reinforcing additives. Investigations were carried out by means of a dynamic shear rheometer and by employing specifically devised testing protocols. Experimental results were analysed with the specific goal of highlighting the role played by additive type and base bitumen. Although fatigue response of base bitumens was always improved by nano-modification, effectiveness of nano-particles was found to be highly dependent on the physico-chemical properties of blend components, which strongly influence the morphological configuration assumed by additives within bituminous media. Results obtained in healing tests were processed in order to discern between self-healing of cracks induced by fatigue damage and other artefact phenomena which are related to viscoelastic changes occurring in the bulk of the material. Outcomes of fatigue and healing tests were found to be coherent with interaction mechanisms which take place at the nano-scale.

1. Introduction

Fatigue is one of the most common phenomena which occur in bituminous mixtures subjected to repeated loadings in flexible pavements. Accumulation of fatigue damage in the binder phase of these materials is recognised to be a complex process which evolves from micro-crack initiation to macro-crack growth by means of coalescence and propagation mechanisms [1]. However, bituminous binders are capable of recovering a significant portion of damage during rest periods or in certain environmental conditions [2]. This intrinsic capability, commonly known as self-healing, has been thoroughly investigated in the last decades with the aim of providing an explanation of experimental evidence and of fully exploiting the performance potential of bituminous products [3–10]. It has been postulated that the primary competing and inter-dependent healing mechanisms which take place in the fracture zone are flow and wetting of crack faces, diffusion of molecules from one face to the other, and randomisation of diffused molecules. Extent of flow depends on the combination of viscoelastic properties of the material and thermodynamic conditions of the process. Wetting is governed by surface energy, with a short-term contribution that is inversely proportional to the Lifshitz-van der Waals or non-polar component of surface tension and a long-term contribution that is directly proportional to its acid-base component. Finally, inter-diffusion and randomisation stem from reptation-type interactions which are strongly affected by molecule structure [3,4].

Use of nano-sized materials as reinforcing additives in bituminous binders and mixtures has attracted in recent years an increasing interest by researchers worldwide [11]. Due to their unique mechanical properties and to their large surface area to volume ratio, carbon nanotubes (CNTs) and nanoclays (NCs) are currently considered as the most promising modifiers, capable of greatly improving performance characteristics of bituminous materials. According to preliminary investigations, it is envisioned that their use may open undiscovered scenarios in the development of new classes of smart, multifunctional and high-performance products.

A number of studies have been carried out on the capability of nano-sized particles to improve rheological characteristics of bitumens, with an emphasis placed on high in-service temperatures [12–18]. However, relatively limited works have focused on the effects of fatigue and healing properties. Khattak and co-workers [19–20] demonstrated that carbon nano-fibres can enhance the fatigue resistance of bituminous materials by means of crack bridging and pull-out mechanisms. Santagata et al. [21] showed that an actual reinforcement effect against cracking can be attained in binders modified with carbon nanotubes if a proper dispersion technique is adopted. Experimental results published by Liu et al. [22] and Wu et al. [23] indicated that an adequate interfacial interaction between bitumen and nanoclays particles can be beneficial in improving fatigue resistance. Moreover, extent of improvement was found to be highly influenced by chemical characteristics of the nanoclay surfactant.

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On account of the little evidence that is currently available on this topic, the work presented in this paper focused on fatigue and healing properties of bituminous binders containing CNTs and NCs. Fatigue resistance and healing capability of nano-reinforced binders were assessed via rheological measurements carried out by means of a Dynamic Shear Rheometer (DSR). Experimental results were analysed with the specific goal of highlighting the role played by additive type and base bitumen.

2. Materials

Two standard 70/100 penetration grade bitumens provided by different Italian refineries and two commercially available nano-sized additives were employed in the present work as base materials.

Neat bitumens, marked as A and B, were subjected to a preliminary laboratory characterisation by means of empirical and rheological tests. Empirical tests included those for the determination of penetration at 25 °C (according to EN 1426-07) and of Ring and Ball (R&B) softening point (according to EN1427-07). Rheological measurements were carried out following AASHTO M 320-10 procedures in order to classify both binders in terms of their Performance Grade (PG). Corresponding results are summarised in Tables 1 and 2, which highlight minor differences between the two materials.

Table 1
Empirical characterisation of base bitumens.

Binder code	Penetration at 25 °C (dmm)	R&B Softening Point (°C)
Bitumen A	98.2	45.2
Bitumen B	95.4	44.6

Table 2
Rheological characterisation of base bitumens.

Ageing condition	PG parameter	Measured value	
		Bitumen A	Bitumen B
Original	T = 135 °C	η = 0.375 Pa s	η = 0.347 Pa s
	$\|G^*\|/\sin\delta$ = 1 kPa	T = 63.2 °C	T = 63.3 °C
RTFO	$\|G^*\|/\sin\delta$ = 2.2 kPa	T = 64.0 °C	T = 63.8 °C
	$\|G^*\|\cdot\sin\delta$ = 5000 kPa	T = 19.9 °C	T = 22.0 °C
PAV	m = 0.300	T = −16.6 °C	T = −14.3 °C
	S = 300 MPa	T = −17.6 °C	T = −16.2 °C
Performance grade	PG58-22	PG58-22	

RTFO: Rolling Thin Film Oven (short-term ageing); PAV: Pressure Ageing Vessel (long-term ageing); η: dynamic viscosity (Brookfield viscometer); T: test temperature; $|G^*|$ and δ: norm and phase angle of the complex modulus (Dynamic Shear Rheometer); m and S: creep rate and creep stiffness (Bending Beam Rheometer).

Information on the chemical structure of neat binders was gathered from the combined use of Thin Layer Chromatography (TLC) and Flame Ionization Detection (FID). TLC allowed the separation of saturates, aromatics, resins, and asphaltenes by means of their successive elution in solvents of increasing polarity (n-hexane, toluene, and a solution of toluene and dichloromethane), while FID yielded relative amounts of the four fractions. Obtained results are displayed in Fig. 1, where the electric potential difference ΔV measured during FID analyses is plotted versus time. It can be observed that the two binders are characterised by a significant difference in chemical structure, probably originated by the use in each refinery of different crudes and/or different fractionation and processing schemes [24].

Nano-sized additives used as modifiers in the investigation were one type of CNTs and one type of NC.

CNTs are one-dimensional carbon materials consisting of a rolled-up graphene sheet with hexagonally arranged sp^2-hybridised carbon atoms [25]. The commercial product employed in the present work was produced by means of the Catalysed 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.

NCs are layered mineral particles that are capable of yielding an exceptionally high interfacial surface as a consequence of clay sheet detachment [26]. The NC used in the experimental investigation was originated from a natural montmorillonite by inserting a quaternary ammonium salt within clay platelets. Montmorillonites are a 2:1-type phyllosilicate, the sheets of which are made of a central octahedral layer sandwiched between two silica tetrahedrons. The quaternary ammonium salt, capable of providing an organophilic character to silicate surfaces, was composed by two methyl groups and two alkyl chains bonded to a hydrophilic positively charged nitrogen. The hydrophobic alkyl chains consisted of a mixture of saturated C_{14} to C_{18}, with C_{18} being the most functional and abundant.

Main characteristics of the additives, based on manufacturers' technical specifications, are reported in Tables 3 and 4.

Nano-reinforced blends were prepared in the laboratory by combining neat bitumens and additives according to a previously developed protocol based on the use of shear mixing and sonication [21,27].

Table 3
Main properties of carbon nanotubes.

Average diameter (nm)	Average length (μm)	Surface area (m^2/g)	Carbon purity (%)	Density (g/cm^3)
9.5	1.5	250–300	90	1.72

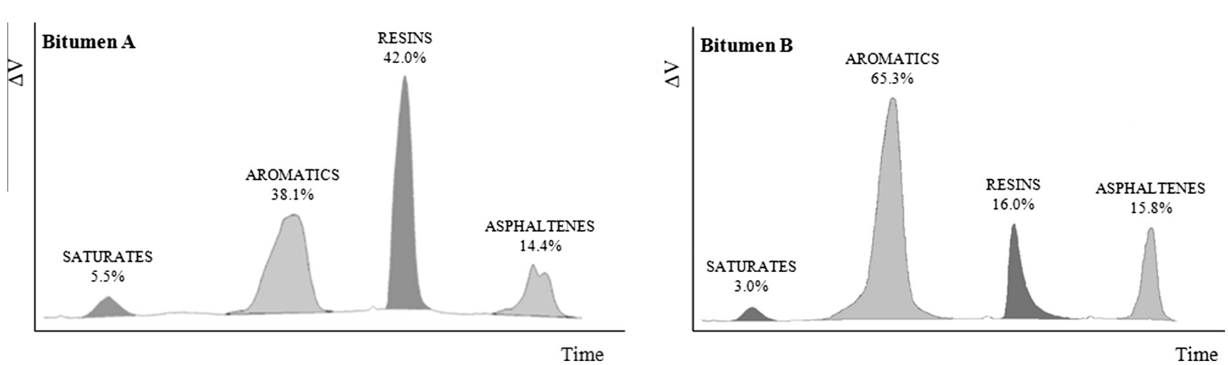

Fig. 1. Chemical analysis of base bitumens.