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Quantitative evaluation of organosilane-based adhesion promoter effect on bitumen-aggregate bond by contact angle test

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ABSTRACT

The performances of a modified bitumen as a function of the concentration of an added organosilane modifier was examined in terms of its consistency, adhesion and rheological properties. In particular, the modifier guarantees excellent performance at 0.01 wt% loading, and almost complete resistance to water at 0.03 wt% loading. A quantitative evaluation of the modified bitumen's performance was carried out by a contact angle test. Moreover, SEM/EDS analysis showed that the organosilane modifier was able to penetrate the surface of the stone, thus aiding anchoring of the binder to the surface.

1. Introduction

Mineral aggregates and bitumen binder are the principal constituents of road surfaces which are subjected to wear. Bitumen from an asphalt pavement typically comprises about 5 to 7 percent of the total asphalt mixture. The bitumen is required to coat and bind the aggregate particles together, whereby its adhesion properties will be of great importance in all asphalt pavement applications. The word 'adhesion' is from the Latin word "adhaerere", which means 'to stick to'. ASTM D907 defines 'adhesion' as a "state in which two surfaces are held together by valence forces or interlocking forces, or both" [1]. Fundamental theory builds the adhesion concept on the forces between atoms at an interface, but, practically, adhesion is evaluated mechanically, performing tests able to control the forces between surfaces. In fact, as reported in the literature [2], it is possible to distinguish between "basic adhesion" and "practical adhesion". The first depends on the interatomic interactions at the interface of a film and substrate, while the second depends on a complex combination of characteristics relating to both the substrate and film. In general, adhesion defines many complex phenomena, which appear in the bitumen-aggregate union. Some are physical or physicochemical (such as aggregate surface texture and porosity, bitumen viscosity, surface tension or film thickness) and others are chemical such as bitumen composition or aggregate nature [3]. Several methods can be used to measure also the practical adhesion for bituminous systems for which the adhesion failure is induced by water entering the bituminous mix, a phenomenon known as stripping [4,5]. Water damage causes a loss of stiffness and structural strength [6].

In order to improve adhesion, bitumen may be modified with antistripping additives. In fact, it is important to improve the capacity of the binder to cover aggregates so as to minimize stripping under water or traffic aggressions. Therefore, we define "adhesion agent" or "antistripping agent" as the product that improves the adhesion of bitumen to a specific aggregate. The quality of the adhesive bond in an asphalt-aggregate mixture is affected by mineralogy (chemical composition), surface texture, absorption surface age, surface coatings, particle shape and binder viscosity [7–10].

The water susceptibility of bituminous mixtures is evaluated by using empirical methods like boiling water tests (Riedel-and-Wieber test), rolling bottle tests, wash test, swell tests, and eventually wet-dry mechanical tests [11]. Willing to obtain a quantitative evaluation, in order to decrease the error limits of these tests, a modern surface analysis technique for investigation of the interactions at the bitumen-aggregate interface was recently used, specifically the contact angle analysis [3]. In this work the performance characteristics of an organosilane antistripping agent were analysed and the good results were observed surfactant.

In the present work, the adhesion performance of the same

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organosilane surfactant (herein referred as **P2KA®**) on the interface bitumen/stone was further investigated and quantitatively evaluated by contact angle test on decreasing concentrations. Organosilane surfactants can be used as adhesion promoters (or antistripping agents), because they may act on surface tension allowing the aggregate to be wetted by the bitumen (active adhesion) and/or can be used as asphaltene dispersant agents [12]. Furthermore, we explored the mechanical properties of the modified bitumen by rheological methods in an effort to understand the effect of these surfactants on the supramolecular structure of the bitumen. Finally, scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDS) measurements were carried out to investigate the stone-bitumen interface when the bitumen was modified by organosilane surfactant.

2. Materials and methods

2.1. Materials

Bitumen was supplied by Total spa (Italy). The bitumen was produced in Saudi Arabia, and was used as fresh standard. The bitumen was modified with pure organosilicon based surfactant (**P2KA®** Kimical SRL, Italy) and with an oil solution of organosilicon surfactant (ratio **P2KA®**:oil=1/9). A soybean oil (**SO**), furnished by Baldini srl (Italy), was used. The **P2KA®** was added in a 0.1 wt% ratio (sample **B_0.1%_P2KA®**) and the organosilane surfactant based oil solution was added in 0.1 wt% and 0.3 wt%, with the final concentrations in surfactant 0.01 wt% (**B_0.01%_ P2KA®/SO**) and 0.03 wt% (**B_0.03%_ P2KA®/SO**). Data not reported in this paper on the bitumen with oil showed that the added small quantity can be considered as not influencing the bitumen properties. Therefore, the modifications observed are only due to the organosilane based surfactant. This is further confirmed by rheological tests presented further.

The stone materials were natural mineral chips and were kindly furnished by the laboratory of civil engineering of Prof. R. Vaiana, University of Calabria.

2.2. Sample preparation

The bitumen was modified using a shear mixing homogenizer (IKA RW20, Germany). First, 200 *g* of bitumen was heated to 150 ± 1 °C until it fully flowed, then a given part of **P2KA®** or **P2KA®_SO** oil solution was added to the melted bitumen under a high-speed shear mixer at 800–1000 rpm. Stirring of the mixture was maintained at 150 °C for a further 10 min to allow homogenisation of the blend. After mixing, the resulting bitumen was poured into a small sealed can and then stored in a dark chamber at 25 °C to retain the desired morphology.

For SEM/EDS analysis, the bituminous samples were prepared according to the ASTM 03625 standard [13]. They were frozen in nitrogen liquid and fractured at low temperature to produce a fragmentation of the rock in order to analyse the interface. This treatment maintains the character of the organic layer thus enabling accurate observation of the bitumen/stone interface by SEM.

2.3. Empirical characterization

According to the standard procedure (ASTM D5) the bitumen consistency was evaluated by measuring the penetration depth (531/2-T101, Tecnotest, Italy) of a stainless steel needle of standard dimensions under determinate charge conditions (100 g), time (5 s) and temperature (25 °C) [14].

The ring and ball test (R & B) was used to determine the bitumen softening temperature (R & B T, ring and ball temperature) according to ASTM Standard D36. The test was performed by means of a ring and ball B530 (Tecnotest, Italy) apparatus [15].

Boil Tests. The boil test procedure used in this study was according to ASTM D3625 [13]. In particular, the sample was placed in boiling water for 10 minutes after which it was cooled to room temperature and the water decanted and the sample spread to dry on a paper towel. A panel of judges subjectively rated the percent of asphalt coating retained. A lighted magnifying glass was used to examine samples. The average of the ratings was rounded to the nearest 5%.

Table 1
Softening temperatures of the pristine bitumen and modified bitumen systems determined with the R & B test.

Sample	R & B T (°C) ± 0.2
Pristine bitumen	50.4
B_0.1%_P2KA®	50.0
B_0.03% _P2KA®/SO	49.6
B_0.01%_P2KA®/SO	50.2

2.4. Rheological characterization

Rheological tests on bitumen samples were carried out using a controlled shear stress rheometer (SR5, Rheometric Scientific, USA) equipped with a parallel plate geometry (gap 2.0 ± 0.1 mm, ϕ=25 mm for the samples analyzed within the temperature range 20-120 °C) and a Peltier system (± 0.1 °C) for temperature control.

Dynamic oscillatory tests, carried out in conditions of linear behaviour previously determined by stress sweep tests, have given information about the structure of material and were adopted for material characterization [16].

Aimed at investigating the material phase transition, temperature sweep tests were performed at 1 Hz at increasing temperature from 20 °C to 120 °C at 1 °C/min and applying the proper stress values to guarantee linear viscoelastic conditions at all tested temperatures. The adopted heating rate represents a suitable compromise between the duration of the experiment and an acceptable accuracy of data.

Small amplitude dynamic tests provided information on the linear viscoelastic behavior of materials through the determination of the complex shear modulus:

$$G^*(\omega) = G'(\omega) + iG''(\omega)$$

where tanδ is given by:

$$tan\delta = G''(\omega)/G'(\omega)$$

where G'(ω) is the in phase component, G''(ω) is the out-of-phase component, and *i* is the imaginary unit of the complex number. G'(ω) is a measure of the reversible, elastic energy, while G''(ω) represents the irreversible viscous dissipation of the mechanical energy [17].

The dependence of these quantities on the temperature gives rise to the so-called time cures.

2.5. Chemical and morphological analysis

The bitumen surface, the interface between the bitumen and aggregate and the aggregate surface were observed by an enviromental scanning electron microscope equipped with an energy dispersive X-Ray spectrometer (ESEM/EDS) (QUANTA 200F – FEI COMPANY, USA – GENESIS 4000, EDAX Inc. USA). Sample specimens were cryogenically fractured in liquid nitrogen to guarantee a sharp brittle fracture, and were successively sputter coated with a thin gold film prior to SEM observation. The dimensions of the observed peculiarities on the surface were directly read from the SEM image.

2.6. Contact angle measurements

Contact angle measurements were performed using an automated pendant drop tensiometer (FTA200, First Ten Angstroms, USA) equipped with the *fta32 v2.0* software. Contact angles were measured