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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, ~~the~~ 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.

Keywords: Modified bitumen, adhesion promoter, contact angle measurements, SEM-EDS.

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 pavements 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 three different types of antistripping agents added to bitumen at 0.1 wt% were analysed, and the best results showed a bitumen modified with an organosilane surfactant.

In the present work, the adhesion performance of the same 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 asphaltenes 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®**) 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 ~~of~~ at 800 to 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 25ºC 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 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%.

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 ±0.1mm, 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:

$$G^*(\omega) = G'(\omega) + i\,G''(\omega)$$

where $\tan\delta$ is given by:

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

where $G'(\omega)$ is the in phase component, $G''(\omega)$ is the out-of-phase component, and *i* is the imaginary unit of the complex number. $G'(\omega)$ is a measure of the reversible, elastic energy, while $G''(\omega)$ 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 by fitting a mathematical expression to the shape of the drop and then calculating the slope of the tangent to the drop at the liquid-solid-vapor (LSV) interface line. The instrument comprises an automated pump that can be fitted with various sizes of syringes and needles to allow for software control of pendant drop formation and of sinusoidal variations in the drop volume or surface area. All experiments were carried out at room temperature (22 ± 1 ºC), and two trials on each samples were performed. The contact angle was measured in triplicate and a mean value with a standard deviation was obtained for each sample.

3. Results and discussion

The SARA content of the bitumen and the performance of the organosilane-based antistripping agent (**P2KA®)** added in 0.1% to the bitumen were reported previously [10]. Herein, the effects on the properties of the bitumen-(**P2KA®)** system on decreasing concentration of the organosilane surfactant (0.03% wt and 0.01% wt) is investigated, in an attempt to obtain best performances at lower quantity of surfactant added.

In order to have a clearer view, data for the pristine bitumen and bitumen-**P2KA®** at 0.1% surfactant concentration reported previously [3] will be also presented herein. The concentration of 0.1 % wt was obtained by adding the required quantity of pure organosilane-based surfactant to the bitumen (sample **B_0.1%_P2KA®**). Decreasing concentration, the ratio surfactant/bitumen does not fulfil anymore the requirements for technological transfer due to the difficulty of obtaining a homogeneous system in an industrial plant. Therefore, lower concentrations of surfactant were obtained by diluting it with soybean oil (**SO**), in a weight ratio **SO**:**P2KA®** of 9:1. Thus, modified bitumen with 0.03 wt% of surfactant (**B_0.03%_P2KA®/SO**) and respectively with 0.01 wt% of surfactant (**B_0.01%_ P2KA®/SO**) were obtained.

Initially, the modified bitumen were characterized and compared with the pristine bitumen to investigate the influence of the surfactant on the physical and mechanical properties of the resulting systems. The bitumens' softening temperatures were determined with the ring and ball temperature test (R&B T) and the results are presented in Table 1.

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

All samples show similar softening temperatures suggesting that the additive does not affect the material's consistency.

Dynamic rheological measurements were performed in order to better understand the mechanical properties of the investigated bitumens'. The rheological behaviour of bitumen binder is currently described by a colloidal model with a composite internal structure of asphaltene micelles dispersed into a maltene phase [18]. This model, describes bitumen as a weak gel. Hence, the mechanical and rheological properties should depend on the asphaltene content and particle-particle connections. In Figure 1 the time cure tests of the samples are shown.

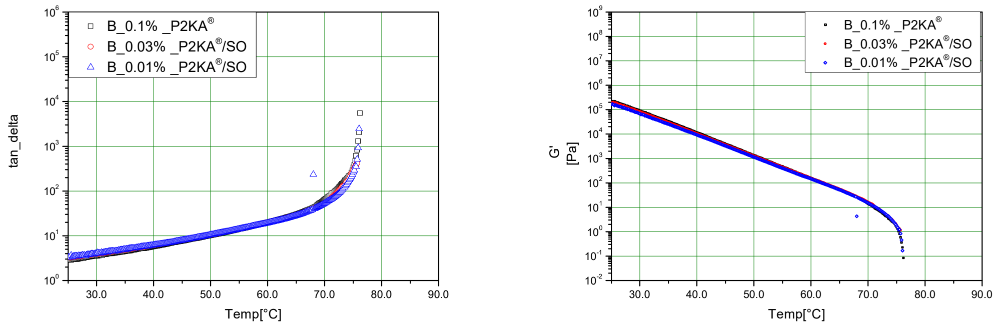

Figure 1. Temperature ramp test (1 Hz) for the modified bitumens'.

The transition temperature (TR) from a viscoelastic to a viscous behaviour could be assumed as the value at which loss tangent diverges, even though it could be difficult to estimate exactly this asymptotic value. All samples presented similar values of tanδ over the temperature range investigated and the viscoelastic-liquid transition temperatures remained constant following modification. This "mechanical spectrum" can be considered as a finger print of the morphological structure of the material. The almost overlapped trends of loss tangent for neat and doped bitumen indicate no structural changes induced by the adhesion promoter. This is an important experimental result because it demonstrates that the adhesion promoter (organosilane based surfactant **P2KA®)** does not affect the mechanical properties of the bitumen as desiderate and required.

Furthermore, the interaction between inert stone and bitumen was investigated. Images showing coverage of the inert stone with pristine bitumen and respectively modified bitumen with the organosilicon-based surfactant **P2KA®,** are reported in Figure 2.

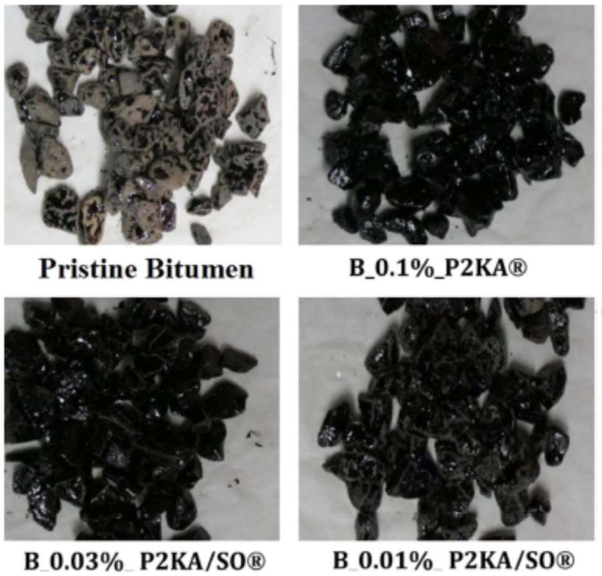

Figure 2. Visual estimation of aggregate surface area covered with bitumen. The images of pristine bitumen and **B_0.1%_P2KA®** were taken from reference [3].

The modification of the bitumen with the organosilane surfactant visibly increases the adhesion properties of the bitumen. Moreover, contact angle tests were carried out and the results were compared with those obtained with the Boiling Test method (Table 2).

Table 2. Boiling test and contact angle measurements.

Sample	**Boiling test (%) ± 5**	**Contact angle[a] (°)**		**Increment of the contact angle**
		S1[b]	**S2[c]**	
Pristine bitumen[d]	25	29.04 ± 0.05	37.30 ± 0.07	8.26 ± **0.02**
B_0.1%_P2KA®3[d]	100	27.40 ± 0.03	27.81 ± 0.05	0.41 ± **0.02**
B_0.03% _P2KA®/SO	95	23.23 ± 0.07	24.72 ± 0.04	1.49 ± **0.03**
B_0.01%_P2KA®/SO	60	27.51 ± 0.03	30.93 ± 0.06	3.42 ± **0.03**

[a]average value with standard deviation; [b]samples before exposure to water; [c]samples after exposure to water; [d]data taken from reference [3].

The detailed descriptions of sample preparation and contact angle measurement were described in detail previously [3]. In particular, the inert stone was suitably cut to obtain a smooth surface, washed with water and left to dry at room temperature for 24 hours. Subsequently, hot bitumen (150°C) with and without adhesion promoters, were applied to the stone surface at a temperature of 25°C with the help of a needle. The samples were kept for 10 min at a temperature 25-30°C higher than the R&B of the bitumen and the contact angle was measured (**S1**). In order to measure the effect of water on contact angle, samples were subsequently kept in distilled water for 2 hours at a temperature 5°C less than the R&B of the bitumen (**S2**) and the contact angle was measured again. The increment of the contact angle can be quantitatively related to water damage.

The contact angle values reported in Table 2 are in agreement with those obtained from the boiling tests and confirm the visual estimation of the stones coverage. In particular, the use of the **P2KA®** additive guarantees excellent performance when dosed at 0.01%. Moreover, it can be observed that increasing the concentration up to 0.03% results in an almost complete resistance to water, therefore an improvement of the wettability.

In order to obtain a greater insight into the interaction/adhesion mechanism between bitumen and aggregate resulting from the incorporation of surfactant, SEM-EDS analysis was carried out. Initially, the inert stone was analysed where it was observed that rock fragments existed with an acid silica phase (quartzite, darker area in Figure 3) and a basic limestone phase (dolomite, clearer area in Figure 3).

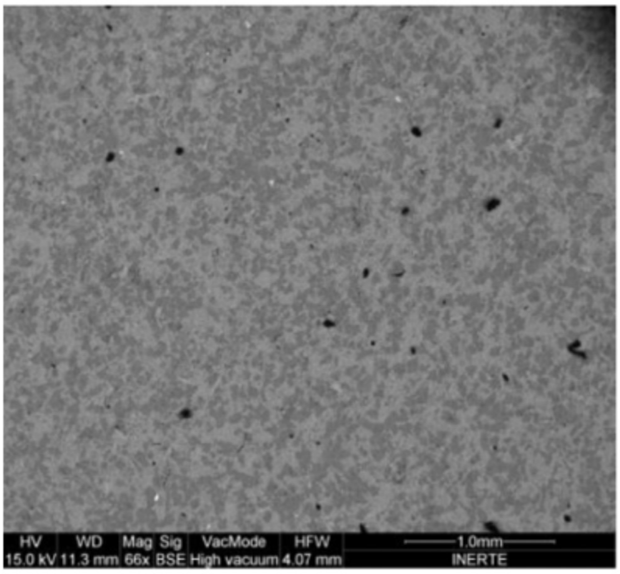

Figure 3. SEM image of the inert stone with darker acid silica regions and light basic limestone regions.

Next, the bitumen surface, the interface between bitumen and aggregate and the aggregate surfaces were observed by SEM/EDS. Samples of **B_0.1%_P2KA®** were obtained by cooling with liquid nitrogen followed by breaking of the covered stone.

As shown in Figure 4, there are no observable differences between the SEM images of the interface between pristine bitumen and stone (Figure 4a) and modified bitumen (**B_0.1%_P2KA®**) and stone (Figures 4b), evidencing no structural change and confirming the rheological data.

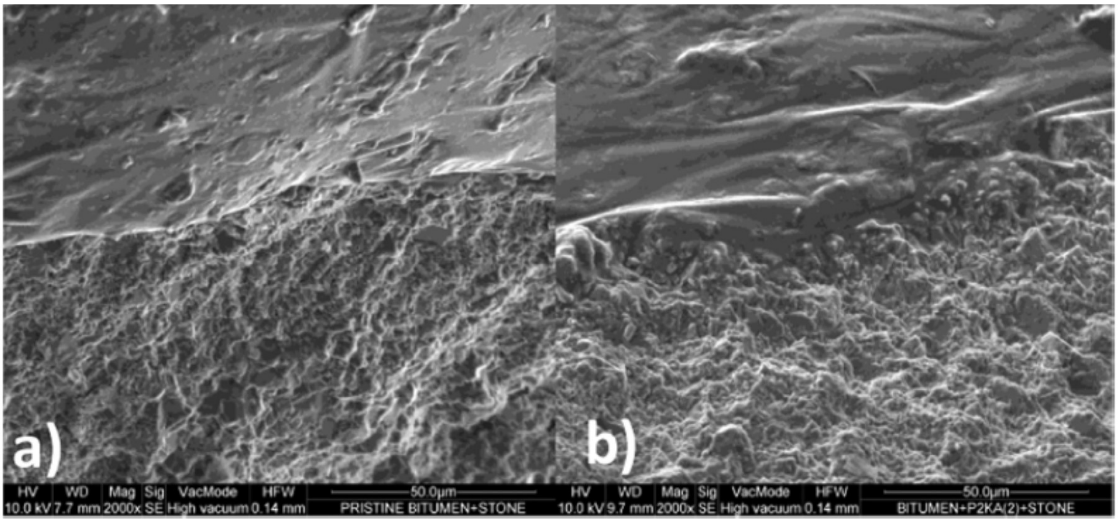

Figure 4. SEM images showing a) the interface between pristine bitumen and stone and b) modified bitumen (**B_0.1%_ P2KA®**) and stone.

Results from the EDS analysis of both pristine and modified bitumen surfaces are presented in Table 3, whilst data for the inert limestone regions of the stone material from interfacial regions involving both types of bitumen are presented in Table 4.

Table 3. EDS analysis for pristine and modified bitumen surfaces

	Pristine bitumen		**B_0.1%_P2KA®**	
	Weight %	Moles %	Weight %	Moles %
CO_2	97.76	98.75	97.44	98.56
SO_3	2.24	1.25	2.48	1.38
SiO_2	--	--	0.08	0.06

Table 4. EDS analysis for the inert stone (light basic limestone region), and stone-bitumen and modified bitumen interfaces

	Inert limestone region		**Interface pristine bitume**		**Interface B_0.1%_P2KA®**	
	Weight %	Moles %	Weight %	Moles %	Weight %	Moles %
CO_2	60.62	68.11	83.45	86.89	75.16	79.72
MgO	7.32	8.98	0.18	0.20	0.39	0.45
MnO	0.76	0.76	0.04	0.02	0.37	0.24
Fe_2O_3	9.12	2.82	0.55	0.16	0.47	0.14
SO_3	0	0	0.69	0.40	0.74	0.43
CaO	22.17	19.55	14.92	12.19	22.43	18.67
SiO_2	0	0	0.18	0.14	0.44	0.35

As indicated in Table 4, the percentage of SiO_2 is doubled with the interface stone-modified bitumen in relation to the stone-pristine bitumen interface, confirming that the nanometer part of the additive (Si) is absorbed by the inert bitumen, creating a physical interaction between the latter and the inert stone.

4. Conclusions.

Previous workers have reported on the performance of organosilane surfactants as anti-stripping agents for improving the quality of asphalt materials. Herein, the adhesion properties between bitumen and stone was studied as a function of the concentration of the organosilane surfactant added. It was demonstrated that this surfactant guarantees excellent performance at concentrations as low as 0.01% wt (**B_0.01%_ P2KA®/SO**). Moreover, on increasing the concentration up to 0.03% wt (**B_0.03%_ P2KA®/SO**), a significant improvement in wettability was obtained.

The performance of the bitumen modification was quantitatively determined by contact angle testing, a method previously reported by our group. The results were confronted with the conventional empirical boiling test in an additional attempt to verify the correctness of the quantitative test. The results obtained by the two methods are in perfect agreement.

More insights on the interaction between modified-bitumen and stone was made by SEM/EDS analysis. We may conclude, based on these results, that this surfactant behaves as a strongly efficient adhesion promoter. This can reasonably be attributed to the polar head (Si, nanoscale) being able to penetrate the surface of the stone, anchoring the binder to it. Moreover, as desired, it does not affect the chemical structure of the bitumen, as showed by rheology tests, acting only at the interface between the bitumen and the stone.

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