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Effects of adhesion promoters on the contact angle of bitumen-aggregate interface

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ABSTRACT

Herein, the evaluation of the effectiveness of several adhesion promoters for asphalt according to the chemical and mineralogical nature of the stone was investigated. From research in the road construction sector, the most common types of activators present on the market are classified according to the chemical nature of their active ingredient: amides, polyphosphoric acid (PPA) esters and organosilanes. Therefore, for each of these families, the adhesive properties of the corresponding modified bitumen loaded with a fixed amount of active agent, were tested on four types of stone materials. X-Ray Powder Diffractometry (XRPD), X-Ray Fluorescence (XRF) and Environmental Scanning Electron Microscope Energy Dispersive Spectroscopy (ESEM–EDS) were carried out in order to establish the chemical and mineralogical nature and identify the agglomerate structures of the selected inert rocks. Among various screened products, the organosilane-based additive showed excellent adhesive performances, independently of the chemical composition of inorganic interfaces, as confirmed by both contact angle and boil test measurements. Conversely, basic nature activators such as amides and those with an acidic nature, such as the esters of PPA, were greatly affected by the type of mineral substrate. Finally, the effect of added adhesive agents on the viscoelasticity of modified bitumen was checked in the linear regime by oscillatory rheology. Differences in the adhesive properties observed among the tested classes of amphiphilic binders were discussed in terms of difference in the sizes of their respective head groups.

1. Introduction

Bitumen is a complex solid or semisolid colloidal suspension of asphaltenes in a continuous phase of saturated paraffins, aromatic oils and resins [1,2]. Nowadays bitumen makes up 4–7% of the road pavement and acts as a binder in-between the aggregate skeleton, giving sufficient internal cohesion to the asphalt. Strong adhesion is of great importance in all asphalt pavements to ensure good roadway performance and durability. Unfortunately, moisture damage, sometimes called stripping [3], is a major cause of pavement failure, owing to a loss of adhesion occurring at the microscale of the bitumen-aggregate interface. At a macroscale level, the adhesive failure induced by water entering the bituminous mix is responsible for rough surfaces, potholes, structural weakness, susceptibility to freeze-thaw damage and cracking [4]. Other serious drawbacks deriving from adhesive failure consist with rutting and shoving, deformation, loss of chippings from surface dressings (chip seals), raveling of surface layers and cohesive failure of the binder mastic structure. [5,6].

Stripping depends on many variables, such as the type and use of a mix, asphalt and aggregate characteristics, environment, traffic, construction practice, and the use of anti-strip additives [7]. The asphalt viscosity plays also a key role in the stripping phenomenon [7,8]. Indeed, although low viscous asphalts allow for better coating, high viscous ones exhibit great resistance to stripping [9,10]. The significance of determining factors such as asphalt composition and physico-chemical compatibility between bitumen and aggregate in the stripping process was investigated by several researchers [9,11]. It has also been ascertained that the efficiency of an adhesive bond in an asphalt-aggregate mixture can be affected by mineralogy (rock chemical composition) [12,13],

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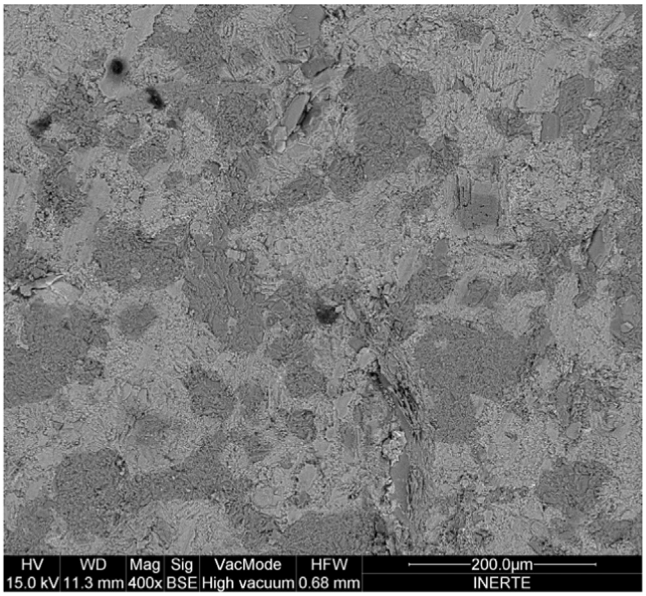

Fig. 1. SEM image of the inert stone with darker acid silica regions and light basic limestone regions.

Table 1
Group composition of the pristine bitumen.

Sample	Area % (±0.01)
Saturated	4.52
Aromatics	68.71
Resins	20.47
Asphaltenes	6.30

Table 2
Softening temperatures (R&B test) and % of bitumen coating retained (boil test) for both pristine and modified bitumen (mixture of aggregates: 50 wt% acid based- and 50 wt% basic based-stones).

Sample	R&B T (°C) ± 0.2	% Covering after boiling ± 5
Pristine bitumen	49.8	25
Bitumen + 0.1% Organosilane	49.4	100
Bitumen + 0.1% Amide	49.6	65
Bitumen + 0.1% EsterPPA	50.0	90

surface texture, absorption [7], surface ageing [14,15], surface coatings and particle shape [7,15]. However, there are still no definitive studies that demonstrate the nature or the magnitude of these effects, although the role played by the presence of water in the failure of the bitumen-aggregate interface has been well established in the comprehension of the stripping phenomenon [16]. In order to assess the water susceptibility of bituminous mixtures, pavement engineers evaluated it by using different empirical methods, such as boiling water tests (Riedel-and-Wieber test), rolling bottle tests, the wash test, swell tests, and also wet-dry mechanical tests [15].

In the present contribution, we illustrate and discuss experimental results based on the determination of the contact angle to investigate interactions at the bitumen-aggregate interface when different adhesion promoters are added to the bitumen. Previous investigations demonstrated the feasibility of the contact angle method to test the bitumen adhesion capacity and provided results in agreement with usual empirical standard methods [17]. In particular, the effect of addition of an organosilane-based adhesion promoter to bitumen was monitored through measurements of contact angle of the bitumen-aggregate interface. A decrease of the contact angle of the bitumen on dried aggregate interfaces (better wettability) was effectively detected in the presence of the adhesion promoter, which in turn minimized the increase of contact angle with water. In the present work, we explored the physico-chemical activity of different types of adhesion promoters on the contact interface bitumen/stone. Parallel Environmental Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (ESEM–EDS) measurements were carried out in order to characterize the chemical composition of the tested aggregates (four stones materials), which were made up of both acidic silica and basic limestone regions, in particular two are mainly acid and two are mainly basic stones. The quantification of the adhesion activity of the surfactants modified bitumen was performed by using a pendant drop tensiometer and the contact angle analysis. Finally, we exploited the mechanical properties of the modified bitumen by rheological methods in order to understand the effect of these surfactants on the supramolecular structure of the bitumen.

2. Materials and methods

2.1. Materials

The bitumen was kindly supplied by Total spa (Italy) and was used as fresh standard. It was produced in Italy and the crude oil was from Saudi Arabia. Its penetration grade (70/100) was measured by the usual standardized procedure [18] in which a standard needle is loaded with a weight of 100 g and the length traveled into the bitumen specimen is measured in tenths of a millimeter for a known time, at fixed temperature. The bitumen was modified by adding the following types of active ingredients: a) an amide based surfactant, b) a polyphosphoric acid ester provided by Aldrich SRL (MIlano, Italy) and c) an organosilane surfactant provided by Kimical SRL (rende, Italy). All detailed information on those compounds were proprietary and unavailable to the investigators.

The additives were added in a 0.1 wt % ratio on bitumen [19]. The stone materials (sample I: Quartz monzogabbro; sample II: White marble; sample III: Metamorphite with anisotropic texture; sample IV: Limestone) were kindly furnished by the laboratory of civil engineering of Prof. R. Vaiana. The term “asphalt” denotes a semi-solid mixture of crushed stone materials, sand, filler and bitumen, which is commonly used as a road paving material [20]. The asphalt mixture contains approximately 5% wt bitumen.

2.2. Sample preparation

The bitumen was modified by using a high shear mixing homogenizer (IKA RW20, Germany). Firstly, 200 g of bitumen was heated up to 150 ± 1 °C until it flowed fully, then a given part of adhesion promoter was added to the melted bitumen under a high-speed shear mixer of 800–1000 r/min. Furthermore, the mixture was stirred again at 150 °C for 10 min until the blends became essentially homogenous. After mixing, the resulting bitumen was poured into a small sealed can and then stored in a dark chamber thermostated at 25 °C to retain the obtained morphology.

2.3. S.A.R.A. determination

The Iatroscan MK 5 Thin Layer Chromatography (TLC) was used for the chemical characterization of bitumen by separating it into four fractions: Saturates, Aromatics, Resins and Asphaltenes (S.A.R.A) [21]. During the measurement, the separation took place on the