Construction and Building Materials 71 (2014) 618–627

Contents lists available at ScienceDirect

Construction and Building Materials

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

Newly observed effects of water on the microstructures of bitumen surface

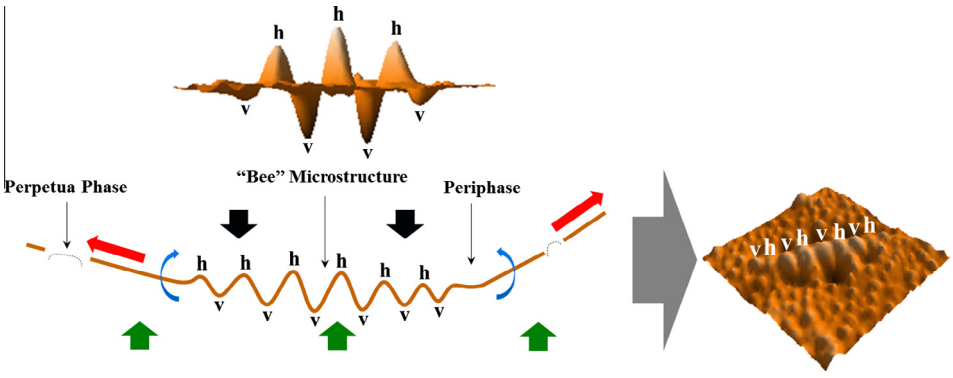
Salomé dos Santos *, Manfred N. Partl, Lily D. Poulikakos

EMPA, Swiss Federal Laboratories for Material Testing and Research, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

HIGHLIGHTS

- Exposure to water changes the surface properties of bitumen films.
- Weaker points of the microstructure are revealed due to forces applied on the film.
- Periphase, perpetua phase and underneath material have distinct properties.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 May 2014
Received in revised form 15 August 2014
Accepted 24 August 2014
Available online 26 September 2014

Keywords:
Bitumen
Wax crystallite
Water
Topography
Phase image
AFM

ABSTRACT

Bitumen films with a thickness of 350–400 μm were prepared on glass microscope slides and studied using atomic force microscopy (AFM) in tapping mode. Upon heating and cooling, elliptical microstructures appeared on the bitumen film surface as expected for bitumen containing wax. These microstructures had different sizes and orientations, and depending on the bitumen type either covered the whole surface of the bitumen film or not. In cases where the surface was not completely covered, both the periphase (elliptical microstructure), considered here to be a wax crystallite, and the perpetua phase (matrix around the periphase) were observed. Typically, at the center of the crystallite, the so-called "bee" microstructure was found, consisting of observed hills and valleys. The bitumen films were submerged in water at ~23 °C, under different experimental conditions, and experienced deformations as a response to forces exerted due to the presence of water. As a result, new topographic features were observed on the bitumen film surfaces, e.g. the microstructures were strongly affected. The valleys of the "bee" microstructure as well as the interfaces between the periphase and the perpetua phase contained material with different mechanical properties from the surrounding surface. The increase in the exposure time to water or larger deformation resulted in the spreading of the material which filled the valleys on the original surface. It is proposed that tension, bending and pressure as a result of water exposure, resulted in cracking of the weakest points of the surface structure. After cracking the material situated underneath the cracked surface seeped up through the cracks, for instance due to upward and downward pressures exerted on the film. From these results, it was concluded that the valleys of the "bee" microstructure and the interfaces between the periphase and the perpetua phase were the weakest points on the bitumen surface microstructure and, therefore, were the first to crack. Furthermore, the appearance of nano-bumps on the surface of the wax crystallites was detected, but neither on the perpetua phase nor on the "new" material which seeped through the possible cracks. This observation suggests that the chemical and mechanical

* Corresponding author. Tel.: +41 58 465 4801; fax: +41 58 765 1122.
E-mail address: salome.dossantos@empa.ch (S. dos Santos).

http://dx.doi.org/10.1016/j.conbuildmat.2014.08.076
0950-0618/

nature of the wax crystallites is different from that of the perpetua phase and of the "new" material which filled the valleys.

1. Introduction

Bitumen comprises a complex mixture of different dissimilar hydrocarbon molecules amongst which waxes may be found. Due to thermodynamic incompatibility between wax molecules and bitumen, segregative phase separation generally occurs. Wax molecules self-assemble for instance into crystallites. It is reasonable to assume that these wax crystallites, which have lower density (0.8–0.9 g/cm^3 at 20 °C) [1] than bitumen (~1 g/cm^3 at 20 °C) [2], move to the surface. However, diffusion may be hindered by many factors such as high viscosity of bitumen or interactions between the wax crystallites and other bitumen components. Consequently, a suspension is obtained instead of the macroscopic segregative phase separation (two phases completely separated). The suspended wax crystallites may form interlocking networks which influence the mechanical properties of bitumen both at low temperatures [2–8] and high temperatures [2,4,5,9]. Additionally, it has been hypothesized that the crystallite suspension may be responsible for non-uniform stress distributions upon loading, due to the presence of interfaces between the different phases and distinct differences in the stiffness of the individual phases [10,11]. The presence of wax may also play an important role in preventing water diffusion or sorption in bitumen [12,13]. To this end, the understanding of the properties and organization of the waxes is very important because they strongly affect the macroscopic properties of bitumen.

Recently, considerable research has been dedicated to the microstructure observed on the bitumen surface after heating and cooling cycles [14–21]. For instance, in some bitumen surfaces, three phases appear, the so-called perpetua phase, periphase and catana phase (e.g. [11,15,22–24]), while in other bitumen surfaces only the elliptical and undulated "bee" microstructure (catana phase) and a surrounding continuous surface are observed [20,25]. Moreover, it has been shown that the catana phase is not different from the periphase regarding mechanical properties (e.g. elastic modulus, adhesion, deformation and dissipation). However, the perpetua phase has generally lower modulus and higher adhesion compared to the periphase and catana phase [11,26–29]. The formation of the "bee" microstructure, with hills and valleys, has been attributed to complex stress distribution on the bitumen surface during cooling. Additionally, it has been proposed that the undulated structure originates from wrinkling of the wax crystallites under compressive loading during cooling due to differences in stiffness and thermal contraction properties between the wax crystallites and the underlying continuous matrix [11,17].

In general, the understanding of the microstructure properties from the physicochemical and mechanical points of view is important for the understanding of the macroscopic properties of bitumen. This is particularly true regarding the effect of water on bitumen [30–37]. Hence, in this work, the effect of water on the surface properties of bitumen, and in particular on its microstructure, was studied using AFM in tapping mode.

Table 1
Bitumen properties. G^* and η^* are the complex modulus and complex viscosity, respectively.

Bitumen	V70/100	Bit C
Penetration (×0.1 mm)	76	82[a]
Softening point (°C)	46.8	45.8[a]
G^* at 20 °C, 10 rad/s (MPa)	2.04 ± 0.008	2.02 ± 0.008
η^* at 20 °C, 10 rad/s (kPa s)	204 ± 0.8	202 ± 0.8
Phase angle at 20 °C, 10 rad/s (°)	59.3 ± 0.18	66.2 ± 0.08

[a] According to Ref. [25].

2. Materials and methods

2.1. Materials

The bitumen used in this study is referred to as V70/100 (V stands for virgin). It was supplied by Berag AG Rubigen Switzerland (RP-Bit 2 206834 PEN 70/100). Five years had passed since it was taken from the mixing plant. The second type of bitumen, Bit C, was used less extensively in this study. Bit C was supplied by Kuwait Petroleum Research & Technology B.V and it was roughly 2 years old. Complex modulus, complex viscosity and phase angle were determined within the linear viscoelastic regime at constant strain amplitude of 0.01 %, constant angular frequency of 10 rad/s and 20 °C. The bitumen properties are presented in Table 1.

Deionized and "ultrapure" water with pH value of around 6 and electrical resistivity value of 18 Ωcm was used throughout the experiments.

2.2. Methods

2.2.1. Sample preparation

In order to prepare the bitumen films, ca. 150 mg of bitumen were removed from the supplier's bucket using a spatula at room temperature (~23 °C), avoiding the bitumen at the surface of the bucket. The bitumen was thereafter spread by a buttering action over a ca. 20 × 20 mm^2 area on a 25 × 25 mm^2 clean and flat microscope glass slide. To obtain the effect of heating and cooling, the bitumen films were first annealed by placing them in the oven at 110 ± 2 °C for 18–20 min and, thereafter, allowed to cool down in air, as shown in Fig. 1(a).

Upon removal from the oven, the films were placed in a Petri glass dish and covered with a second Petri glass dish to prevent dust deposition. The annealing temperature of 110 °C was chosen to be just above the melting temperature of the wax components, which was measured using differential scanning calorimetry (DSC). The annealing procedure resulted in smooth and glossy film surfaces and the final film thickness was 350–400 μm, calculated assuming bitumen density equal to

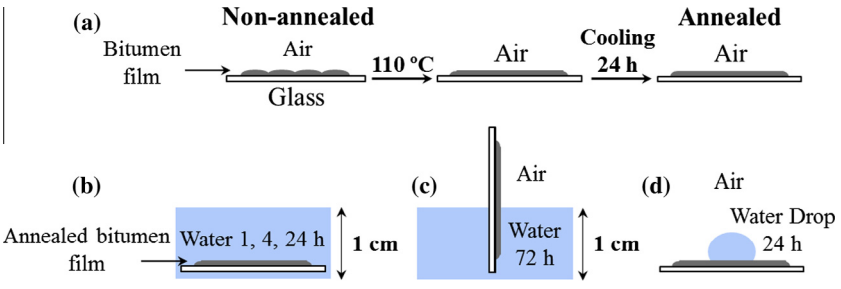


Fig. 1. (a) Bitumen film preparation; bitumen was buttered on a microscope glass slide with a spatula at room temperature (~23 °C) and, subsequently, annealed and left to cool down in air. For the water exposure measurements, the annealed bitumen films were (b) fully immersed in water for 1, 4 or 24 h, (c) partially immersed in water for 72 h or (d) a drop of water was placed on the film for 24 h.