Construction and Building Materials 117 (2016) 1–7

Contents lists available at ScienceDirect

Construction and Building Materials

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

A study of the influence of the microstructure of one type of bitumen grade on the performance as a binder

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HIGHLIGHTS

- New designed micro-direct tensile test for quantitative determination of adhesive forces.
- Relationship between microstructures of 6 different bitumina and their performance as binder.
- Bitumina with developed microstructures show better adhesion.

ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form 13 April 2016
Accepted 26 April 2016
Available online 7 May 2016

Keywords:
Bitumen
Microstructure
Mechanical testing
Adhesion

ABSTRACT

Six different bitumina of comparable PEN grade were investigated to gain a relation between the composition and the development of microstructures and their performance as binder material e.g. for road constructions. It was shown, that especially bitumina with explicit microstructures show an intense interaction between the asphaltene nucleated crystals (peri/catana phase) and solid (aggregate and/or filler) surfaces. Consequently, the developed adhesive/cohesive interaction is also stronger in case of such bitumina than in case of bitumina with extended continuous liquid phases (perpetua phase) and such bitumina seem to be well suited for an application as binder material. This was possible by employing a new designed micro-direct tensile test for quantitative determination of adhesive forces including the possibility to study the nature of the failure upon testing.

The obtained data were correlated with AFM data from surface structure analysis and verified by other data from literature and other experiments regarding the adhesive interaction of parts of the bitumen with solid surfaces.

1. Introduction

Natural bitumen has been used already for a very long time (for about 180,000 years) as an adhesive or glue while sticking flint implements to the handles of various tools.

The first reports concerning the use of bitumen in road construction date back to Nabopolassar, King of Babylon (625–604 BC) where a bitumen-containing mortar was used to cement the foundation made of layers of fired bricks and the stone slabs as top layer together [1,2]. Asphalt based pavements based on natural bitumen were explored in the 19th century in major European towns (Paris 1838, London 1869) and since then extensively adopted [3]. Today, the majority of the highways is paved with asphalt concrete derived from artificial bitumen obtained as the vacuum residue of Petroleum distillation and this will be also remaining the materials of choice for the near future.

The primary function of bitumen in pavements is to act as adhesive with the purpose to provide a bond between different particles. Although it has been discussed for a long time that the (chemical) nature of the aggregate (stones) determines the strength of the adhesive bond between the aggregate/filler particles and the bitumen, recent investigations on a micro or molecular scale show that especially asphaltenes preferentially wet the aggregate surfaces [4–6] and that waxes have a slightly negative effect on adhesion to aggregates depending on type of aggregate and type of wax [7]. The studies of Letoffe, Van Lent and Fischer [4–6] using three different experimental methods show clearly, that the interaction of the asphaltenes with the aggregate surfaces is independent from the chemical nature of the aggregate. Letoffe could measure an increase of the interaction enthalpies with the content of asphaltenes in the samples investigated, Van Lent could determine an increase in concentration of asphaltenes at the

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http://dx.doi.org/10.1016/j.conbuildmat.2016.04.129
0950-0618/

interface to glass compared to the surface asphaltene concentration of different samples and Fischer has measured contact angles of the wetting phases of the microstructures and found a preferential wetting of the asphaltene rich peri-phase to all investigated solids. Another study by Ese et al. [8] describes the investigation of monolayers of asphaltene and resins transferred from a water surface onto mica substrates using the Langmuir-Blodgett technique. The topography of the monolayers was inspected by atomic force microscopy (AFM). Mono layers consisting of pure asphaltene fractions provide a rigid film with a close-packed structure, while the resins build up a continuous open network. Mixed films of these two fractions show that a gradual increase in resin concentration leads to an opening of the rigid asphaltene structure towards a more resin like configuration.

The most probable reason for the preferential wetting of interfaces by asphaltenes is that the amount of adhesion between bitumen and the aggregate surface is possibly not *entirely* enthalpy determined and related due to the suspected polarity but also entropy related. It is certainly entropically more favorable for the whole thermodynamic system bitumen-aggregate surface to adhere a small number of large, flat molecules than a large number of small molecules. In summary, the overall free energy of the system is governing asphaltene molecules towards the solid surface.

The loss of adhesion between binder and filler/aggregates represents one of the main causes of distress and finally failure in asphalt pavements. However, mostly cohesive fracture of the binder is observed in mechanical testing, at least at temperatures above 0 °C. A study of flexural cracking in asphalt beam specimens by Genin and Cebon (2000) revealed that cracks in a typical asphalt composite often run through the binder rather than through the aggregate particles or the aggregate/binder interface [9].

The properties of bitumen as a viscoelastic material are very sensitive to the ambient temperature and the rate of load application. As such, bitumen displays both glassy elastic behavior and viscous behavior, depending on the combination of temperature and strain rate [10]. Various modes of failure have been observed, ranging from brittle cracking through tearing to viscous flow [11–14].

The films of bitumen between aggregate particles in an asphalt mixture are generally thin; the average *thickness* of the films is not more than a couple of tenths of micrometers at the most depending on the asphalt composition. (An estimate of the average thickness is given in Ref. [15]).

An understanding of the behavior of the material as thin films is essential in understanding its fundamental properties of asphalt. During a crack opening process, the bitumen film between aggregates is loaded in tension, and the bitumen–aggregate contact can be idealized as an adhesive joint between two stiff adherents.

Several groups focused on a better understanding and quantification of the tensile strength of the asphalt binder under a state of stress that is similar to what the binder experiences in an asphalt concrete mixture while choosing an experimental set-up which represents the confined geometry of binder films just like in the pavement application (poker chip configuration, PATTI test) [11–14]. The confined asphalt binder experiences high localized stresses when the composite is subjected to external loads. It has been found, that the stress distribution is more uniform for higher aspect ratios [11,12,14]. Tensile failure in confined films under such a state of stress is likely to occur in the form of cavitation. However, as the aspect ratio is decreased the stresses become non-uniform across the cross-section of the specimen and consequently, tensile failure due to cavitation only occurs in these parts of the specimen. As the film gets thinner, there is a stiffening effect, giving rise to an effective Young's modulus, E_e. For a thin axisymmetric, incompressible film, with an assumed parabolic stress distribution, Nadai [16] showed that

$$E_e\Im \leftarrow A^2E/8 \tag{1}$$

where E is the Young's modulus of the film material and A is the aspect ratio (diameter/thickness) of the film. This stiffening effect is most pronounced for incompressible films.

Harvey and Cebon [12] presented a systematic study of the failure of bitumen films and the regimes of temperature and strain rate in which brittle fracture and ductile failure occur. They found, that the toughness in ductile regime shows a strain rate and thickness dependency. Normalization via the thickness is possible as long as the aspect ratio is still large and a transition from ductile to brittle failure occurs only at very high strain rates (>100 s^{-1} at room temperature).

Ductile failure in butt joints is either defined at the point of void nucleation, the point of peak stress, or the point of final rupture.

A miniaturization of these adhesion tests based on AFM technology was recently introduced by Pauli et al. [17]. Also in such tests, rupture occurred in the bitumen film where the material deforms as an elongated neck prior to loss of contact and not at the bitumen-glass interface. Bond strength increases with increasing temperature, the binder exhibits more plastic flow and consequently stretches more prior cohesive rupture occurring.

In this short study, the effects of the formation of microstructure, the appearance and surface coverage of the different microphases are evaluated on the mechanical behavior of a number of bituminous binders by analyzing the development of microstructures and testing the binder quality in a new miniaturized setup. All investigated binders have the same PEN grade, the main criteria for selection of binders for pavement applications.

2. Experimental

The materials under investigation were a number of bituminous binders with a PEN grade of 70–100 (×0.1 mm) received through Latexfalt BV, The Netherlands, and originated from different producers/manufacturers. The SARA fractions of the binders were analyzed using an IATROSCAN procedure and the relative fractions of their constituents are given in Table 1.

Bitumen films were prepared by the application of a bead of bitumen onto a steel disk, followed by a heating stage at 120 °C for 1–2 min in an oven to ensure a low viscosity of the binder.

All samples were prepared in thin films of 25–35 μm thickness close to the thickness as used in the pavement application by casting the hot binders (110 °C) using a 50 μm thick Kapton® film mask with circular hole as spacer onto glass plates. Their thickness was verified by confocal microscopy. The preparation of thinner samples turned out to be more difficult and also to be impractical given the experimental protocol of the micro-tensile testing. The test includes the establishment of contact with the test-counter surface as explained below resulting in a penetration of the half-sphere by some microns. Thinner sample thickness could and has resulted in a direct contact of the two solid surfaces, hence not representative and reproducible for the determination of adhesion forces.

The samples were cooled down to room temperature which resulted in a smooth and glossy finish of the bitumen film. The films were subsequently covered to prevent contamination by dust. Prior to imaging, the samples were annealed at room temperature for at least 24 h.

Atomic force microscopy (AFM) structural investigations were performed as earlier described [18]. Here a brief description of the applied procedure is given.

Table 1
Bitumen samples investigated in this study with a PEN of 70–100 (×0.1 mm) and SARA fractions of the samples.

Sample	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)
Kuwait Petroleum Research & Development (Q8)	4.6	41.9	27.4	26.1
Esso	6.1	23.2	49.7	21
Nynas	8.7	34.2	35.6	21.5
Shell	7	33.4	34	25.6
Total	5.9	29.5	47.0	17.6
Venezuela	8.7	28.2	44.5	18.6