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Effect of annealing conditions on the molecular properties and wetting of viscoelastic bitumen substrates by liquids

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Abstract

Typically, in the production of asphalt concrete, bitumen and mineral aggregates are heated and mixed at temperatures above 100 °C. After the mixing process bitumen ideally coats the mineral aggregates and remains in the form of thin films. Because bitumen is highly temperature sensitive, the study of its properties in terms of chemistry, microstructure and rheology as a function of different annealing conditions is very relevant. The resultant molecular properties have a direct correlation to bitumen macroscopic response to liquids such as water, which is of extreme relevance to the understanding of the detrimental effect of water on asphalt pavements. The wetting characteristics play a crucial role on the extension of detachment of bitumen from the mineral aggregates when asphalt is exposed to wet conditions. Therefore, in this work, the effect of the annealing temperature and cooling history on the chemistry, microstructure and wetting of bitumen films was studied. Crystalline microstructures were identified in bulk and on the surface of the bitumen films. Larger crystals presenting higher crystallinity degree were identified when the annealed bitumen films were cooled slowly. Moreover, higher annealing temperatures increased the oxidation level. The change of the rheological properties due to the alterations of the annealing conditions produced changes in the wetting characteristics. For instance, the advancing motion of a liquid drop on the viscoelastic bitumen substrate presented an intermittent behaviour due to the deformation of bitumen at the liquid-bitumen-air contact line. Consequently, changes in the contact angles were also observed.

Keywords: Bitumen; Crystallization; Oxidation; Advancing contact angle; Wetting

1. Introduction

The wetting behaviour of viscoelastic surfaces is a very active research topic due to its relevance in a range of materials from natural to synthetic [1–5]. In the case of bituminous materials, the wetting by water is of extreme relevance in particular for asphalt concrete where bitumen films, used to glue the mineral aggregates, are displaced or detached from the mineral surface in the presence of water. The amount of bitumen in asphalt concrete is generally 4–10 wt% and, therefore, it coats the mineral aggregates forming relatively thin films (<50 μm) [6]. Typically, asphalt concrete is prepared by mixing heated bitumen and heated mineral aggregates at temperatures higher than 100 °C. High temperature is required to decrease the viscosity of bitumen to facilitate the mixing and to increase the coating of the mineral aggregates with bitumen as well as adhesion between those two components. In the presence of water, the adhesion between bitumen with hydrophobic characteristics and the mineral surface with hydrophilic character is compromised.

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The mixing temperature and the cooling history of the thin bitumen films have a significant impact on the cohesive and adhesive properties of bitumen. Temperature variations result in the alteration of chemical, microstructural and rheological properties of bitumen. For instance, high temperatures accelerate the ageing of bitumen, eventually leading to failure of asphalt pavements. However, the ageing mechanism is complex and includes different molecular processes such as oxidation and molecular aggregation [7–9]. Typically, these processes result in the embrittlement of bitumen.

Molecular assemblies that are influenced by the thermal history of bitumen are for instance wax crystals, present in some bitumen types. At low temperatures, wax components are insoluble in bitumen and segregate as crystals which remain dispersed in bitumen and influence its rheological properties. For instance, the dispersion of the crystals in the form of networks has been correlated with the increase in viscosity of petroleum-related materials [8,10–13]. Additionally, the cooling conditions influence the degree of crystallinity and size of wax crystals [11,14]. One way of detecting the wax crystals in the bulk of bitumen is by using wide angle X-ray scattering (WAXS) measurements. Presumably, the wax crystals present low adhesion to mineral aggregates [15,16].

In this work, a systematic alteration of the annealing temperatures and cooling conditions of bitumen films was conducted in order to gain understanding on the relations between the chemical, microstructural and wetting properties of the films as a function of annealing and cooling history. Bitumen films were subjected to different annealing temperatures selected from the temperature range used in practice for the preparation of asphalt concrete, and different cooling processes. For instance, the location of the bitumen films in the asphalt mixture will affect the cooling process; if the films are exposed readily to cold air they will cool down faster as compared to inners layers. The bitumen films were characterized using atomic force microscopy (AFM), attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and advancing contact angle measurements. The advancing contact angle measurements were used to study the wetting behaviour of the bitumen films when a sessile drop of water and ethylene glycol was dispensed on the bitumen surface. When a sessile drop is deposited on viscoelastic substrates, the substrate is pulled at the three phase contact line due to the contribution of different forces such as the normal component of the liquid–air surface tension and the Laplace capillary pressure that pushes on the entire substrate-liquid interface. These phenomena lead to the formation of a wetting ridge on soft viscoelastic substrates [17–20]. The wetting ridge and advancing contact angle characteristics depend on the rheological characteristics of the substrate i.e. stiffness, which in turn depend on the molecular properties. In the present work, the molecular properties of the bitumen substrates were strongly influenced by the annealing conditions.

2. Materials and methods

2.1. Materials

The types of virgin straight run bitumen used in this study had the standard penetration 70/100 and 160/220. Different properties of the bitumens are presented in Table 1.

Generally, for penetration lower than 30 the bitumen is considered hard and values higher than 100 correspond to soft bitumens. Usually, the softening point range for paving bitumen goes from 35 to 65 °C. Above 60 °C bitumen is generally considered hard, while below 40 °C it is classified as soft bitumen. Hence, the bitumen 70/100 is between hard and soft and bitumen 160/220 is considered soft.

The wetting liquids used for the measurements of the advancing contact angle were deionized water and ethylene glycol. Table 2 presents the surface tension of the liquids σ_l, as reported by Ström et al. [21], density ρ, and dynamic viscosity η, at 20 °C.

2.2. Methods

2.2.1. Sample preparation

For the investigations using wide angle X-ray scattering (WAXS), atomic force microscopy (AFM), attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and advancing contact angle measurements the samples were prepared as follows. A certain amount of bitumen was removed with a spatula from the supplier's bucket at room temperature, avoiding the bitumen at the surface of the bucket as this layer could be already oxidized, and, subsequently, buttered over a glass slide. The amount of bitumen used depended on the test method and was calculated to achieve a final film thickness of around 400 μm assuming the bitumen density equal to 1 g/cm^3. The bitumen films covered approximately 20×20 mm^2 for WAXS, 8×8 mm^2 for AFM, 3×3 mm^2 for ATR-FTIR and 70×20 mm^2 for advancing contact angle measurements. For annealing, the bitumen films were placed in a ventilated oven for 20 min. Three dif-

Table 1
Penetration value, softening point and complex shear modulus $|G^*|$, complex viscosity η^* and phase angle δ, for bitumens 70/100 and 160/220 at 20 °C and angular frequency of 10 rad/s.

Bitumen	Penetration (×0.1 mm)	Softening point (°C)	$\|G^*\|$ (MPa)	η^*(kPa)	δ (°)
70/100	76	46.8	2.04	204	59.3
160/220	184	39.8	0.451	45.1	70.3

Table 2
Surface tension σ_l, density ρ, and viscosity η at 20 °C of deionized water and ethylene glycol.

Liquid (l)	σ_l (mN/m)	ρ (g/cm^3)	η (mPas)
Deionized water	72.75	1.00	1.00
Ethylene glycol	47.70	1.11	16.1