A predictive and experimental method to assess bitumen emulsion wetting on mineral substrates

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HIGHLIGHTS

- Assessment of theoretical bitumen emulsion/mineral substrate work of adhesion.
- Study of wetting kinetics of bitumen emulsions onto mineral substrates.
- Influence of various parameters on bitumen emulsion wetting.
- Determination of experimental bitumen emulsion/mineral substrate work of adhesion.

GRAPHICAL ABSTRACT
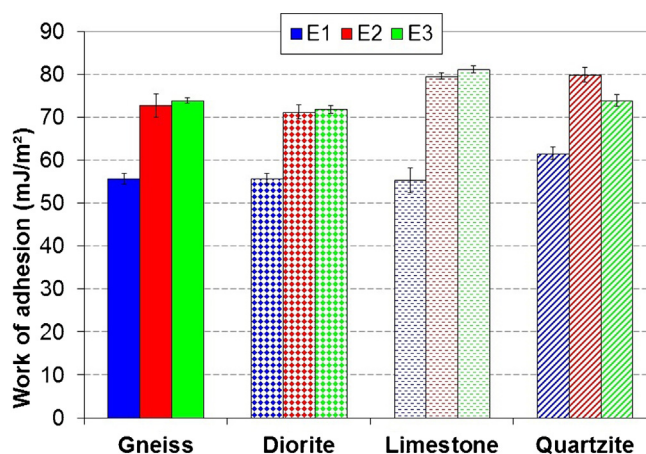
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ABSTRACT

This paper deals with wetting kinetics and adhesion of bitumen emulsions on mineral surfaces. To this purpose, four mineral substrates: gneiss, diorite, limestone and quartzite and three emulsions were tested. First, surface properties of the materials were determined and theoretical bitumen emulsion/mineral substrate work of adhesion was calculated. Second, bitumen emulsion/mineral substrate contact angles were measured as a function of time and images of emulsion droplets were taken to highlight drop shape evolution and water evaporation. Experimental bitumen emulsion/mineral work of adhesion was assessed using contact angle values and Young-Dupré equation usually employed for pure liquids. It was proved that quartzite has the highest surface energy, and gneiss has the lowest. The highest theoretical work of adhesion was noted with one of the emulsions studied and quartzite. However, error bars found for all the values were important. The calculation of experimental work of adhesion showed the same tendency as for theoretical work and error bars were lower. Consequently, Young-Dupré equation is valid for emulsion/substrate systems at short times.

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1. Introduction

The technique of hot mixtures is traditionally used for manufacturing road materials and pavements. It consists of introducing in a mixer 5% wt. bitumen and 95% wt. aggregates at high temperature

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(160 °C for both components). Aggregates present different sizes (from <63 μm to 14 mm in diameter) and mineralogies (siliceous, calcareous or silico-calcareous). Bitumen, which plays the role of binder in the mixture, is the heaviest fraction obtained after vacuum distillation of crude oil. Its chemical composition is generally separated into two groups: the asphaltenes, which are the insoluble part in n-heptane, and the maltenes, the soluble part [1]. Bitumen is also classified as a function of the chemical nature of crude oil: paraffinic, naphthenic or aromatic, which respectively refers to saturate, cyclic and aromatic groups contained within [1]. Bitumen is composed of natural surfactants having interfacial properties, such as naphthenic acids [1,2]. It shows a thermo-susceptible behaviour: viscous at ambient temperature, it becomes fluid at high temperature. The technique of hot mixtures presents many advantages: high resistance to traffic-loadings, high rigidity and easy application. However, preparation of the materials (bitumen, aggregates) requires too much energy. Moreover, bitumen heating generates fumes.

Since decades, the technique of bitumen emulsion cold mixture is developed. Cold mixtures are composed of aggregates (90–95% wt.) and bitumen emulsion (5–10% wt.), which itself contains bitumen, water and a cationic emulsifier (generally a surfactant) used for solubilising both phases. An acid is often added to protonate the emulsifier in solution. The technique of cold mixture allows the reduction of energy consumption and emission of greenhouses gases. Nevertheless, mechanical properties of bitumen emulsion cold mixtures are lower than those of hot mixtures. This is the reason why they are applied in low and medium-traffic pavements, in wearing courses as well as in base courses.

Adhesion of a bituminous binder (bitumen or bitumen emulsion) onto aggregates is a quality criterion for the mixture performance and durability [3,4]. In particular, loss of adhesion can occur when water enters through bitumen/mineral substrate interface [5]. As the substrate has more affinity for water, bitumen is withdrawn and the mixture resistance decreases [6].

Adhesion is described following several mechanisms [7,8]:

- Mechanical adhesion, which stresses strong bonding when the binder recovers the asperities and fills the voids of the substrate;
- Chemical adhesion, which relates the high affinity between the acid compounds of bitumen and the basic species from the aggregates;
- Surface free energy theory, which describes the surface energy evolution of the mineral when the binder wets the surface;
- Molecular orientation, which is explained by the orientation adsorption of polar molecules onto bitumen and substrate surfaces;
- Electrostatic adsorption, which indicates the affinity for two materials having opposite charges.

Adhesion strength depends on substrate mineralogy. It is known in road engineering that bitumen/limestone couple shows a strong adhesion, although it displays defects in adherence because of a poor resistance to wear. On the contrary, siliceous aggregates are subjected to stripping [9]. Surface structure of the aggregate (roughness, porosity) plays an important role in adhesion [10]. Binder properties (composition, viscosity) and operating conditions (temperature, aggregate treatment, introduction of additives,...) may also affect adhesion [8].

In the case of bitumen emulsions, adhesion is favoured by the emulsifier. The charge located at the hydrophilic head of the amine-based emulsifier reacts with the ionic species from the substrate, thus creating ammonium carbonates (calcareous aggregates) or ammonium silicates (siliceous aggregates). These new products are responsible for the emulsion adhesion [11]. Adhesion can also occur after electrostatic adsorption between bitumen and the mineral substrate and rise in pH of the emulsion [12]. Adhesion is effective after evaporation of water from the emulsion.

Anyway, bitumen/substrate and bitumen emulsion/substrate adhesion is strongly dependent on the surface properties of the materials. In particular, it is reported that surface energy contributes more to the total adhesion than mechanical and chemical adhesion [13]. Adhesion is also correlated to bitumen and bitumen emulsion wetting on substrates.

2. Theory

2.1. Surface properties of materials

Surface tension is the energy per unit area necessary to expand the surface of a material. In terms of vocabulary, surface tension refers to the liquid/vapour interface. For the solid/vapour interface, "surface energy" is rather used. The energy required to separate two immiscible media is called "interfacial tension".

Liquid surface tension and substrate surface energy can be divided into a polar γ^P and a dispersion component γ^D. This dispersion component corresponds to Van der Waals interactions (Keesom, Debye and London forces) and is present in every molecule [14]. According to Good-Van Oss theory, the polar component can be separated into electron donor γ^+ (Lewis acid) and electron acceptor γ^- (Lewis base) component [14]. The overall surface energy or surface tension is:

$$\gamma = \gamma^D + \gamma^P = \gamma^D + 2\sqrt{\gamma^+\gamma^-} \qquad (1)$$

Liquid/substrate work of adhesion W_{adh} can be expressed as a function of the substrate surface energy γ_S, the liquid surface tension γ_L and the liquid/substrate interfacial tension γ_{SL}:

$$W_{adh} = \gamma_S + \gamma_L - \gamma_{SL} \qquad (2)$$

W_{adh} can also be divided into two components to traduce the polar and non-polar interactions occurring at the interface:

$$W_{adh} = W_{adh}^P + W_{adh}^D \qquad (3)$$

W_{adh}^P and W_{adh}^D are respectively the polar and the dispersion components of work of adhesion. In a scientific point of view, polar interactions are responsible for adhesion. Nevertheless, it was noticed in a paper that Van der Waals interactions can also favour adhesion [15].

Surface energy of substrates and binder/substrate interfacial tension are strongly correlated to binder wetting. The following section gives theoretical aspects about wetting and the factors affecting it.

2.2. Wetting theory

At a liquid drop deposition onto a solid surface, several wetting regimes can be observed:

- The liquid spreads completely;
- The liquid partially wets the surface. At equilibrium, the liquid presents a spherical calotte shape and forms a contact angle θ with the surface;
- The liquid does not wet the solid. In this case, the contact angle is close to 180°.

These wetting regimes are characterised using the spreading coefficient S. This latter is calculated as a function of γ_S, γ_L and γ_{SL}:

$$S = \gamma_S - (\gamma_L + \gamma_{SL}) \qquad (4)$$

$S > 0$ indicates a complete wetting; $S < 0$ indicates a partial wetting [16].