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Study of the mechanical properties and self-healing ability of asphalt mixture containing calcium-alginate capsules

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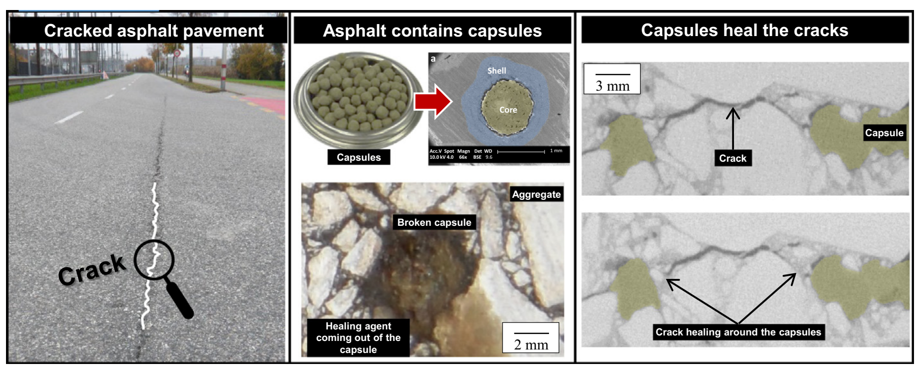
HIGHLIGHTS

- Calcium-alginate capsules with a maximum payload of 75% were produced.
- Capsules without hard shell resist mixing and compaction.
- Capsules deformed and broke with loading.
- Oil diffused in the bitumen in less than 24 h.
- Large reduction of cracks around the capsules after resting 4 days at 20 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

The natural self-healing ability of asphalt mixtures can be enhanced with encapsulated rejuvenators: when crack damage appears the capsules release healing agents, which dissolve bitumen and drain into the cracks. In this study, the effect of a new type of capsules in the mechanical properties and the self-healing ability of asphalt mixtures is investigated. Sunflower oil was encapsulated in calcium-alginate, and protected with a hard shell made of epoxy-cement composite. Results show that the hard shell was not required for these capsules to resist mixing and compaction procedures. Capsules deformed and broke with loading, releasing oil that diffused in the bitumen in less than 24 h. Healing of cracks in asphalt mixture led to an increase of stiffness. However, asphalt specimens with capsules had lower deformation resistance. Computer tomography scanning of specimens showed large reductions in cracks around the capsules, after resting 4 days at 20 °C.

1. Introduction

Asphalt mixtures are the most worldwide used material to build roads. Although pavement structures with asphalt layers are designed for a 10–30 years of service life, replacing the top layer with new asphalt materials is required about every eight years [1]. Damage in asphalt mixture starts at the micro-structure level and evolves continuously up to the macro-level that is seen by road drivers and causes disturbances in comfort and safety of driving. Ultraviolet radiation, temperature and moisture contribute altogether to the binder's ageing [2,3], which becomes stiffer with time, and loses flexibility and adhesion. Hence, the binder is not able to support temperature and/or

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traffic induced stresses anymore, and microcracks occur in the material [4,5].

However, bitumen is a self-healing material [6]. When a crack occurs in an asphalt road, bitumen tends to drain into the crack and, if adequate time and temperature conditions are given, the crack may be fully closed. This process takes a very long time at normal temperatures, making it extremely ineffective [7]. In addition, asphalt self-healing is highly influenced by the viscosity and surface energy of bitumen [8–11].

In most countries a large portion of the asphalt materials reclaimed from old pavements are recycled and incorporated into new pavement layers [12]. Moreover, virgin binder, additives and aggregates are added to recycled mixtures in order to achieve minimum quality for using recycled asphalt materials in roads. Additives are softening agents or rejuvenators that modify the chemical composition of the old binder, rebalancing the proportion of light and heavy elements, and also lowering the viscosity [13,14].

Ideally, asphalt layers should be rehabilitated *in situ* without milling or scarifying interventions. One technique that has been proven in the laboratory is to heat asphalt mixture using induction energy to promote the flow of bitumen into the cracks [15]. A different approach to accelerate self-healing is the incorporation of capsules containing rejuvenators which break and release their content when damage occurs in their vicinity [16]. Then, the rejuvenators diffuse into bitumen reducing its viscosity and it can easily drain into the cracks [17].

Up to now, two different methods for the fabrication of capsules for asphalt self-healing have been proposed: (1) saturating porous aggregates with rejuvenators and sealing them with a shell made of epoxy resin and cement [17]; (2) microencapsulation of the rejuvenator by *in situ* polymerization of urea-formaldehyde [18], methanol-melamine-formaldehyde [19] or phenol–formaldehyde [20]. The first type of capsules resist mixing and compaction operations [17] and release the rejuvenator in asphalt specimens due to loading [21]. In addition, microcapsules release their content in presence of cracks [22,23] but have not been yet tested in asphalt mixture. Moreover, crack healing induced by capsules has been shown in bitumen [24], but never before in asphalt mixture.

This paper describes an experimental study aimed at investigating the ability of a new type of capsules containing rejuvenators to induce self-healing in asphalt. The rejuvenator, sunflower oil, was encapsulated in a polymeric structure created by the ionotropic gelation of sodium alginate in the presence of calcium ions. Moreover, certain batches of capsules were additionally coated with a hard shell made of epoxy resin and cement. The research analysed the effect of (1) capsules on the mechanical behaviour of asphalt specimens subjected to cyclic loading and (2) introducing rest periods on the self-healing properties of asphalt mixture containing capsules. Finally, asphalt self-healing was visualised using computer tomography scans.

2. Materials and experiments

2.1. Materials

To fabricate the capsules the following materials were used: (1) sodium alginate ($C_6H_7O_6Na$) (Sigma-Aldrich), which is an anionic polysaccharide widely distributed in the cell walls of brown algae; (2) calcium chloride ($CaCl_2$), provided by Sigma-Aldrich as anhydrous, granular pellets of 7 mm diameter and 93% purity; (3) epoxy resin (Araldite® 506 epoxy resin, Sigma-Aldrich), obtained by combining the epoxy resin with a fast hardener; (4) micro-cement (MICROCEM 550®, Tarmac), with average particle size ranged from 5 to 10 μm, provided by; (5) sunflower oil (East End, UK).

Limestone aggregates (Tunstead quarry, Derbyshire, UK) and paving grade bitumen 40/60 were used to fabricate asphalt mixture.

2.2. Capsules

The core of the capsules was composed by a polymeric structure made of calcium-alginate that encapsulates the rejuvenator. Moreover, in some batches the core was coated with a shell made of epoxy-cement. The polymeric core results from the reaction of alginate with calcium ions, creating a porous structure, often named as "egg-box" [25]. The fluid (rejuvenator) is entrapped in the structure during the reaction.

The rejuvenator was a commercial sunflower oil, selected because it does not require special health and safety measures at the lab and is thermally stable. Vegetable oils can be used as bitumen rejuvenators [26,27], and they have also been encapsulated with self-healing purposes before [21,28].

The fabrication procedure is illustrated in Fig. 1. The left-hand side flowchart shows the procedure to fabricate the polymeric capsules, defined in [29], and the right-hand side flowchart shows the procedure to fabricate the hard-shell, defined from [17]. All tasks were performed at room temperature. First, 600 ml of deionized water and oil were introduced in 1 L glass container. Two types of emulsions were built with oil/water (o/w) ratio 1.0 (300 g of oil and 300 g of water) and 0.5 (200 g of oil and 400 g of water), respectively. Oil and water were homogenised using a laboratory gear drive mixer at 400 rpm during 1 min. Then, 15 g of sodium alginate were added and stirred until complete solution at 400 rpm, for 10 min. The alginate acted as an emulsifier, stabilizing the emulsion. Simultaneously, a calcium chloride solution was prepared by mixing 600 ml of water with 12 g of calcium chloride in 1 L glass water container. Capsules were formed by letting the oil-in-water emulsion drop into the calcium chloride emulsion from a 1000 ml pressure-equalizing dropping funnel with 3 mm socket size. During the capsule formation process, the calcium solution was gently agitated using a magnetic stirrer. Capsules were allowed to stay in the solution until the end of the encapsulation process, which lasted for approximately 4 h. Finally, capsules were decanted and washed with deionized water. They were dried during 12 h under the constant movement of air produced by a fan.

Then, selected batches of dry capsules were covered with an outer shell made of epoxy-cement to increase their strength. The process of making the shell started by covering the calcium-alginate capsules with epoxy in a mass ratio of 14% (14 g of epoxy for each 100 g of capsules). Later, seven steel balls of 20 mm diameter were placed in a plastic container, together with approximately 1 kg of cement. After, 250 g of capsules and epoxy were added, the container was closed, and shaken vigorously by hand for 15 s. After this, capsules, cement, and steel balls were separated in a 2 mm sieve, and let to rest for 12 h. The epoxy-cement coating process could be repeated various times for each batch of capsules to improve their strength.

Three types of capsules were used in this study: (I) *o/w* 1.0, with three epoxy-cement coatings; (II) *o/w* 0.5, with two epoxy-cement coatings; (III) *o/w* 0.5, with no epoxy-cement coatings. Fig. 2 displays these capsules, which were selected because of the different morphology, size and strength characteristics.

2.3. Asphalt mixture

Asphalt mixture for base courses, AC 20 base 40/60 (EN 13108-1), was used. Table 1 describes the composition of the mixture. Furthermore, asphalt mixture was pre-fabricated and aged in the laboratory before adding the capsules to simulate the natural