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Calcium alginate capsules encapsulating rejuvenator as healing system for asphalt mastic

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HIGHLIGHTS

- Calcium alginate capsules with rejuvenator are proposed for self-healing asphalt.
- Individual rejuvenator droplets are stored in porous media inside the capsule.
- The capsules are able to survive the asphalt mixing and compaction period.
- Calcium alginate capsules are capable of local crack healing in asphalt mix.

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ABSTRACT

Researchers have demonstrated that the rejuvenator encapsulation method is a promising autonomic self-healing approach for asphalt pavements, where by the self-healing system improves the healing capacity of an asphalt pavement mix. However, potentially high environmental risk via leaching of hazardous chemicals such as melamine formaldehyde renders the technology unsuitable for widespread use in road design. This paper explores the potential for the use of more environmentally friendly and economically viable rejuvenator encapsulation method, where the calcium alginate is used as rejuvenator encapsulation material. The capsule morphology and microstructure were studied using the Microscopy and X-ray tomography. Capsules thermal resistance and mechanical strength were investigated using the Thermogravimetric analysis (TGA) and micro-compressive tests. The results demonstrated that the capsules have sufficient thermal and mechanical strength to survive the asphalt production process. The healing efficiency of the system was evaluated by embedment of calcium-alginate capsules encapsulating rejuvenator in an asphalt mastic beams and subjected to monotonic three-point bend (3PB) loading and healing programme. The results illustrated that the calcium-alginate capsules encapsulating rejuvenator can significantly improve healing performance of the asphalt mastic mix.

1. Introduction

Asphalt mixture have intrinsic healing potential to repair the damage (close cracks), restore its stiffness and strength when subjected to rest periods. Although the self-healing of asphalt has been proven in bitumen, asphalt mortar, asphalt mastic and asphalt concrete, this self-healing capacity is deteriorated by ageing of the bitumen and low ambient temperatures [1,2]. Thus, it is a challenge for asphalt pavement engineers to improve asphalt pavement design to increase the self-healing capacity of asphalt pavement.

With the objective of increasing the self-healing capacity in asphalt, extrinsic healing methods [3] have been investigated, which can be concluded into two ways: induction healing and embedded capsules encapsulating asphalt binder rejuvenator. The concept of induction healing is to mix conductive particles inside the asphalt mixture and generate induction heating from outer alternating electromagnetic fields [4–7]. Using the induction healing, the temperature of asphalt mixture can be increased to soften the bitumen within asphalt mix allowing it to flow, close the cracks and repair the damage. Induction heating proved to be a very effective method for asphalt crack healing, but the increasing of temperature also accelerates ageing of the asphalt binder.

In order to address the issues of the asphalt ageing presented by induction healing approach, researchers studied different methods of encapsulation of the bitumen rejuvenator self-healing system. The concept of embedding the capsules which contain binder rejuvenator is to deliver healing agent (rejuvenator) to the damage site

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and rejuvenate the aged binder, by allowing the rejuvenator to diffuse into the aged binder and soften it, allowing it to flow and in turn close the crack and repair the damage. The healing agents used for asphalt healing includes vegetable oil, waste cooking oil and bitumen rejuvenator [8–10].

There are various rejuvenator encapsulation methods, such as:

1. Melamine-formaldehyde (MMF) modified capsules, Su [11] used MMF modified by methanol to encapsulate rejuvenator. Controlled by stirring rates, the prepared capsules have the mean size from 100.5 to 2.0 μm. The microcapsules had survived in bitumen under temperature of 200 °C, which indicates that these microcapsules can resist the thermal effect of bitumen in application. Microcapsules had the elastic-plastic deformation ability resisting the temperature changes and mixing stress. However, this encapsulation technology presents a potential environmental problem, where material used in production of the capsules: 'formaldehyde' in high concentration can be dangerous for human health.
2. Epoxy capsules, a series of capsules were successfully prepared by García et al. [12]. These capsules comprise a porous sand which absorbs the rejuvenator, the sand granules are bound together and coated by a hard shell made of an epoxy-cement matrix with a volume percentage of 20.9, 13.1, 24.9 and 13.0% of rejuvenator, porous sand, cement and epoxy, respectively. The capsules obtained have a mean size of 1.60 mm. The capsules are embedded into the asphalt mix by substituting a part of the aggregates in asphalt concrete by the capsules. The working principle of the system is, when the stress in capsules embedded in the asphalt reaches a certain threshold value, the capsules break and rejuvenator is released. These capsules are strong enough to survive the mixing and compaction, but the breaking mechanism is not clear and difficult to control.
3. Xue et al. [13] prepared microcapsules by in-situ polymerization method with water, urea, formaldehyde, asphalt rejuvenator, emulsifier and modifier. The morphology, particle size, coating rate, thermal stability and molecular structure of the microcapsules were investigated. The healing capacity of these microcapsules were evaluated by ductility test and asphalt fatigue test.
   Results indicate that the microcapsules could survive during the asphalt melting process and showed good healing performance under conditions of low-temperature and fatigue load. While low temperature behavior and fatigue behavior on asphalt binder are not sufficient to evaluate the healing effect of these microcapsules, more evidences are needed.
4. Compartmented Alginate Fibres, Except capsules, compartmented fibres could also be used to encapsulate healing agent for self-healing purpose. This concept was first proposed to provide local healing with liquid healing agents in fibre reinforced polymer composites [14]. Followed this concept, Tabaković et al. [15] used alginate as a rejuvenator encapsulating material and successfully prepared compartmented fibres to encapsulate rejuvenator. The prepared fibres were tested in both thermal and mechanical properties, and the results turned out to prove that the compartmented fibres could survive from the mixing and compaction process of asphalt. Tabakovic et al. [15] also showed that the inclusion of the fibres into asphalt mastic mix increased the strength of the asphalt mastic mixture, and these alginate fibres were capable of healing local micro cracks when the asphalt mastic mixtures sustained low level of damage. However, the research showed that this self-healing system can only repair small micro-cracks and the content of rejuvenator is very limited. However, alginate proves to be a very positive material for rejuvenator encapsulation.

Alginate is a long, negatively charged molecule. Positively charged sodium ions (Na^+) dissociate from the alginate when dissolved in liquid solution. Doubly charged calcium ions (Ca^{2+}) can bind two different alginate strands simultaneously, thereby crosslinking and solidifying the solution [16]. Fig. 1 shows the reaction between sodium alginate and calcium to encapsulate rejuvenator.

Alginates can be found in brown algae and also in metabolic products of bacteria, e.g. pseudomonas and azotobacter. Nowadays, alginate hydrogels have been particularly attractive in wound healing, drug delivery, and tissue engineering applications to date, as these gels retain structural similarity to the extracellular matrices in tissues and can be manipulated to play several critical roles [17–19].

With the advantages of low cost and environmental friendly, alginate also has the ability of self-degrading when exposed to ambient conditions (air), this property serves as secondary self healing triggering mechanism, i.e. if capsule is not opened by the propagating crack, the self deterioration will open the capsule and release encapsulated rejuvenator. As such the key objective of this research is to investigate the potential use of calcium alginate capsule as rejuvenator encapsulating and delivery mechanism for asphalt pavement materials. In this research, the calcium alginate capsules encapsulating bitumen rejuvenator have been produced. Thermal stability and mechanical property of the capsules are investigated employing the thermogravimetric analysis (TGA) and micro compression testing. The healing performance of the calcium-alginate capsules encapsulating rejuvenator self healing concept was further tested by embedding the capsuled in asphalt mastic mix. Photography and tomography are used for the structural and volumetric study of the capsules.

2. Experimental method

2.1. Materials and preparation

2.1.1. Preparation of calcium-alginate capsules

The calcium alginate capsules, were produced from an emulsion of rejuvenator suspended solution of sodium alginate. To this aim, 6 wt% sodium alginate in de-ionized was prepared. At the same time a 2.5 wt% solution of poly(ethylene-alt-maleic-anhydride) (PEMA) was mixed with the rejuvenator with ratio of 40% PEMA and 60% healing agent, forming a healing agent solution. After that, the sodium alginate solution and healing agent solution was mixed by the alginate/rejuvenator ration of 30/70 for 30 s at the stirring rate of 100 rpm. To remove air bubbles, the blend was processed in an vacuum environment for 30 min. Subsequently, the blend was pumped through a needle and the capsule beads were dropped into the $CaCl_2$ solution. Finally, the calcium alginate capsules can be acquired after drying in oven. Fig. 2a illustrates the chemical structures of PEMA, the average molecular weight of PEMA is 100,000 to 500,000. Fig. 2b illustrates the schemes of the encapsulation process with alginate and PEMA.

Industrial rejuvenator R20 supplied by Latexfalt, The Netherlands was used as healing agent in this research. Other chemicals used in the process were purchased from Sigma Aldrich, The Netherlands.

2.1.2. Asphalt mastic mix design and mixing procedure

Asphalt mastic beams were prepared in order to evaluate the healing efficiency of calcium alginate capsules. These mastic beams were prepared containing three different proportions of the calcium alginate capsules (Table 1), including: control beams (without capsules), beams with 2 wt% capsules and beams with 4 wt%