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Doctoral thesis

NTNU
Norwegian University of Science and Technology
Thesis for the Degree of
Philosophiae Doctor
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Department of Civil and Environmental
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Laboratory investigation of the rejuvenating and self-healing properties of aged asphalt containing Ca-alginate capsules

Preface

This PhD dissertation is being submitted to the Norwegian University of Science and Technology (NTNU) in partial fulfilment of the requirements for the degree of Doctor of Philosophy (PhD).

The project was carried out between September 2019 and September 2023 through the Department of Civil and Environmental Engineering at NTNU, Trondheim.

Professor Inge Hoff, NTNU, has been the main supervisor. Professor Shaopeng Wu, Wuhan University of Technology (WUT), and Dr Xuemei Zhang, NTNU and WUT, has been the co-supervisors.

Lei Zhang

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I have been living and studying in Norway for four years while working on my dissertation. During the past four years, I've gone through both difficult and rewarding times. Consequently, I’ve gained valuable experience from having had them.

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Lei Zhang

Trondheim, Norway

Abstract

The aging and cracking of asphalt pavement seriously affect the service life of asphalt pavement. Calcium alginate capsules have been shown to release a rejuvenator to repair cracks inside asphalt concrete under traffic loading conditions. Previous studies have primarily focused on Ca-alginate capsule design and its influence on asphalt mixtures' early performance. However, rejuvenating and self-healing of asphalt concrete by capsules mainly occur after asphalt aging, the performances during this period have rarely been investigated. Thus, the objectives of the research were to assess the effect of capsules on the mechanical properties and the self-healing ability of laboratory-accelerated aged asphalt mixture and asphalt mixture containing RAP and investigate the improvement mechanism of Ca-alginate capsules.

In this dissertation, the volume performances, rutting resistance, moisture stability, crack resistance and self-healing performance of different prepared asphalt mixtures were measured by standard tests. The aged bitumen and extracted RAP binder with and without capsules were used to investigate the mechanism of rejuvenating and self-healing by diffusion, DSR, BBR and chemical component tests.

The Ca-alginate capsules and laboratory aging had minimal impact on the volumetric properties of asphalt mixtures. The capsules reduce water stability and resistance to permanent deformation of asphalt mixtures, primarily due to the capsules' substantial release of oil, which softens bitumen during incidents of rutting. Additionally, the crack resistance of asphalt mixtures at low temperatures was enhanced by the addition of capsules. After aging, the resistance to permanent deformation increased, while water stability and low-temperature crack resistance declined in all asphalt concrete samples. In cases where aged asphalt mixtures contained capsules, the anti-rutting performance decreased to the level of normal virgin asphalt mixtures; consequently, both water stability and low-temperature crack resistance were reduced. The presence of a small quantity (0.5wt%) of capsules was likely responsible for the observed effects. The Ca-capsules can effectively improve the strength healing rate and fracture energy healing rate of asphalt mixtures before and after ageing, which is mainly caused by the diffusion of the capsules' oil into the asphalt which softens it. The self-healing rates of the aged asphalt mixtures containing capsules can also reach the level of ordinary virgin asphalt concrete without capsules.

After applying Ca-alginate capsules and RAP (40%-70%) to asphalt mixtures, no effect on the asphalt mixtures' volume performance was found. Replacement of RAP and Ca-capsules decreased the Marshall stability and residual Marshall stability of asphalt mixtures, and its negative effect became more pronounced as the amount of replacement of RAP increased. Moreover, Marshall stability has become the most important mechanical index of RAP replacement quantity in asphalt mixtures containing Ca-alginate capsules. Indeed, the presence of capsules decreases the rutting resistance and increases the crack resistance of asphalt mixtures, while RAP has the opposite effect. The comprehensive utilization of RAP and capsules can effectively prevent their respective shortcomings; in addition, a combination may be found that produces the same performance as that of the reference samples. The self-healing ability of asphalt mixtures containing RAP is lower than that of the virgin samples, while Ca-alginate capsules have significantly improved mixtures' self-healing ability. The comprehensive utilization of capsules and RAP can therefore better make the asphalt mixtures containing RAP maintain their excellent self-healing ability for a long time, ultimately compensating for the shortcomings of using RAP.

The bitumen tests showed that the reaction between the sunflower oil in the capsules and aged bitumen replenish the saturates and aromatics components, which can perfectly explain the improved performance of aged asphalt mixture. Additionally, based on DSR results, it can be demonstrated that the rheological properties and flow behavior index of aged bitumen that has been rejuvenated by the capsules can be restored to the level of virgin asphalt. This achievement serves the purpose of rejuvenating aged asphalt concrete and enhancing its self-healing capabilities.

This thesis reveals in detail the influence of Ca-alginate capsules on the mechanical and self-healing properties of aged asphalt mixture and RAP asphalt mixture. It provides effective guidance and reference for the full-cycle application of Ca-alginate capsules in asphalt concrete pavement to effectively extend the life of asphalt pavement.

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Publications

Paper I

Lei Zhang, Inge Hoff, Xuemei Zhang, Jianan Liu, Chao Yang, Fusong Wang.

A Methodological Review on Development of Crack Healing Technologies of Asphalt Pavement[J].

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Contributions:

Lei Zhang: Conceptualization, Data Curation, Formal Analysis, Investigation, Methodology, Writing – Original Draft, Writing – Review & Editing. **Inge Hoff**: Conceptualization, Supervision, Writing – Review & Editing. **Xuemei Zhang**: Conceptualization, Supervision, Writing – Original Draft. **Jianan Liu**: Conceptualization, Writing – Review & Editing. **Chao Yang**: Conceptualization, Writing – Review & Editing. **Fusong Wang**: Conceptualization, Writing – Review & Editing.

Paper II

Fusong Wang, **Lei Zhang**, Boxiang Yan, Dezhi Kong, Yuanyuan Li, Shaopeng Wu.

Diffusion mechanism of rejuvenator and its effects on the physical and rheological performance of aged asphalt binder. [J]

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Paper III

Lei Zhang, Inge Hoff, Xuemei Zhang, Chao Yang.

Investigation of the self-healing and rejuvenating properties of aged asphalt mixture containing multi-cavity Ca-alginate capsules. [J]

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Paper IV

Lei Zhang; Chao Yang; Inge Hoff; Xuemei Zhang; Hao Chen; Fusong Wang;

A self-healing asphalt pavement with both RAP and Ca-alginate capsules.[J]

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Additional publications (not included in the dissertation)

Paper V

Fusong Wang, **Lei Zhang**, Xiaoshan Zhang , Hechuan Li, Shaopeng Wu.

Ageing mechanism and rejuvenating possibility of SBS copolymers in asphalt binders[J].

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Fusong Wang: Data Curation, Investigation, Methodology, Writing—Review & Editing. **Lei Zhang:** Data Curation, Writing—Review & Editing. **Xiaoshan Zhang**: Data Curation. **Hechuan Li**: Formal Analysis, Investigation, Writing—Review & Editing. **Shaopeng Wu**: Methodology, Project Administration, Supervision.

Paper VI

Chao Yang, Shaopeng Wu, Peide Cui, Serji Amirkhanian, Zenggang Zhao, Fusong Wang, **Lei Zhang**, Minghua Wei, Xinxing Zhou, Jun Xie

Performance characterization and enhancement mechanism of recycled asphalt mixtures involving high RAP content and steel slag[J].

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Paper VII

Chao Yang, Shaopeng Wu, Jun Xie, Serji Amirkhanian, Zenggang Zhao, Haiqin Xu, Fusong Wang, **Lei Zhang**

Development of blending model for RAP and virgin asphalt in recycled asphalt mixtures via a micron-Fe3O4 tracer[J].

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1. Introduction

1.1 Background

Over the course of thousands of years of development, roads have been made out of dirt, flagstone, gravel, cement and asphalt. Today, asphalt pavement is the most common road surface; this is especially true in high-grade roads where using asphalt gives drivers a smoother, quieter and safer ride. Asphalt pavement normally consists of 1) an asphalt surface layer, 2) base layer and 3) subbase layer. The asphalt surface layer itself is formed by mixing and compacting bitumen, aggregates, filler and other additives at high temperatures[1].

However, asphalt pavement is inevitably prone to ageing and cracking. There are three main ways that asphalt ages: 1) the volatilization of light bitumen components, 2) oxidation reaction and 3) steric hardening[2,3]. The chemical composition of aged bitumen shows a decrease in saturates and resins and an increase in aromatics and asphaltenes[4]; and all of these molecular-scale changes increase pavement stiffness[5]. In terms of rheological properties, aged bitumen leads to a decrease in complex modulus and sensitivity to temperature and an increase in phase angle[6,7]. Ageing makes bitumen harder and more prone to distress during fatigue loading and moisture erosion, resulting in cracks, unraveling, potholes etc[8]. Water can also enter through cracks and further damage the pavement's base layer. Continual road maintenance is therefore required to ensure its performance; yet this need has become a burden in terms of cost, ecology, energy use and worker health. Indeed, infrastructure related to road construction has become the largest expenditure and source of energy consumption in a majority of countries around the world. There is a need for more research that focuses on finding technological solutions to promote the durability and sustainability of pavement materials[9].

Asphalt is a kind of self-healing material which can heal its cracks spontaneously under certain conditions. However, it is difficult for common asphalt pavement to ensure a healing rate that is faster than a crack rate with respect to certain factors, including ageing, temperature, traffic load and moisture. This is mainly because it is difficult for asphalt molecules to achieve the speed or time needed to heal cracks in accordance with a series of healing theories (molecular diffusion healing model, phase field healing theory, surface energy healing theory, capillary flow healing theory and so on). Various self-healing technologies and aided rejuvenation systems have been studied to delay the ageing process and extend the life span of asphalt roads[10,11].

The term ‘rejuvenator encapsulated technology’ refers to encapsulating the agents in the capsules or fibers, where they are subsequently combined into bitumen or asphalt mixtures. These agents are then released and flow into the crack to soften the bitumen and promote the crack’s healing, a process that results in smaller or fixed cracks; this is because the crack induces the capsules to break. This process solves the shortcomings of difficult penetration compared with spraying rejuvenators on the surface[12]. The better solution for rejuvenating aged asphalt pavement is to release the rejuvenator evenly and in a timely fashion in the materials as soon as ageing starts. This solution helps prolong a road’s lifetime considerably. It is important to prevent the release of the rejuvenator too early (before the asphalt starts ageing) since this could result in the asphalt becoming less resistant to permanent deformation. A very promising method appears to be getting capsules to start breaking when the asphalt material starts to age and crack. The rejuvenating agents are encapsulated and combined with an asphalt binder or mixture when the asphalt pavement is being paved. As ageing progresses, the cracks induce the capsules to rupture, which not only heals the cracks but also rejuvenates the surrounding ageing asphalt binder to recover most of its initial performance[13,14]. So agent-encapsulated technology both heals asphalt cracks and effectively rejuvenates aged adhesives, it requires no additional energy application. Other self-healing technologies (electromagnetic induction and microwave heating, etc.) need to increase temperatures through external energy transfer, excessive healing time and cost[15,16].

The multi-cavity Ca-alginate capsules have been proven to survive when added to asphalt mixtures after mixing and compaction due to their thermal stability and strength[17]. The capsules, having diameters ranging from 2-7 mm, were developed by Micaelo, Al-Mansoori, Norambuena-Contrerats, Xu and Zhang et al[13,18-22]. The capsules have the advantage of containing both saturated porous aggregates and core-shell polymeric microcapsules; they have little effect on asphalt concrete’s initial road performance when directly incorporated into asphalt concrete[21]. Moreover, multi-cavity structural oil has many advantages: firstly, it provides a structural reinforcement for surviving during asphalt mixing and compression; secondly, it does not release all the oil at once, thus providing long-term, multiple crack healing. During the compression process, the capsules can withstand both high temperatures of 180℃ and stress; indeed, the strength and fracture energy recovery rate of asphalt mixtures that contain capsules can reach 92.7% and 180.2%, respectively [22]. The capsules can also be applied to different mixtures like Stone Matrix Asphalt (SMA) and Open-Graded Friction Course (OGFC) Pavement[23,24]. They are added to an asphalt mixture when asphalt concrete is first made; at the same time, their primary function is to release internal oil to repair cracks after asphalt has aged over several years and cracked (in other words, the asphalt mixture has gotten old). At present, the research on this kind of capsule is mainly aimed at its design and influence on the early performance of asphalt mixtures. There is a time lag from when the capsules actually start working.

At the same time, during the maintenance and demolition of asphalt pavement, a large amount of waste and aged asphalt mixture is regenerated, which further aggravates the impact of road construction on the environment. In today's global shortage of natural aggregates, effectively using reclaimed asphalt pavement (RAP) can solve environmental deterioration to a certain degree[25]. The utilization of RAP has been accepted for extensive research and application in the laboratory and field due to its environmentally friendly composition and ease of quality control – without requiring construction equipment to be renewed or improved.

In addition, many researchers have reported that RAP has the potential of being reclaimed without functional degradation[26,27]. The high dosage of RAP's utilization and its effect on the mechanical properties of concrete have been extensively studied. For instance, Zhang et al. reported that using amounts of 40% and 60% RAP can also fulfill the technological requirements of pavement design. Also, using RAP improved the overall rutting resistance and dynamic stability of asphalt pavement [28]. For example, when 10%-50% RAP was added to asphalt mixtures, the moisture susceptibility decreased by increasing the amount of RAP; however, in a study by Wang et al,[29]the Residual Marshall Stability (RMS) and Tensile Strength Ratio (TSR) of mixtures containing 50% RAP also remained at a high level, reaching 90.5% and 80.3%, respectively. Yang et al. also added 50%, 60% and 70% RAP to asphalt mixtures and verified that involving steel slag in RAM with 70% RAP content satisfies design requirements of asphalt pavement's upper surface [30].

Asphalt mixtures that contain a high level of RAP can easily meet the pavement design requirements of mechanical performance design after the structure has been redesigned; this is because the aggregate's firmness has no performance degradation. Further, the binder can be rejuvenated or modified appropriately, which eliminates any barriers to applying the RAP materials[31]. Due to ageing bitumen, the stiffness/brittleness caused by high percentages of RAP can be too high, leading to early fatigue problems and cracking[32]. Interestingly, the effect is partly complementary to Ca-alginate capsules on asphalt mixtures. The rejuvenating of RAP binder is also time-dependent, and the rejuvenator slowly penetrates from its initial position into the contact surface that contains the aggregates[33]. It can overcome its shortcomings and enhance the advantages of asphalt mixtures when combining comprehensive applications of capsules and RAP.

The micro-mechanism associated with asphalt self-healing has been studied for several decades; research has been inspired by the theory of healing in polymers, a process comprised of five stages: 1) surface rearrangement, 2) surface approach, 3) wetting, 4) diffusion and 5) randomization[34,35]. On a macro level, a certain number of researchers believe that asphalt's self-healing ability is mainly manifested in flow capability and the recovery of viscoelastic properties[36,37]. While bitumen like a Newtonian fluid can flow into cracks through capillarity and heal them, the flow capability of bitumen becomes weaker with ageing[38]. In order to reveal improvement in the rejuvenating and self-healing ability of Ca-alginate capsules on aged asphalt mixtures and asphalt mixtures containing RAP; diffusion, rheological changes and creep aged bitumen in laboratory and RAP bitumen should also be studied.

1.2 Problem statement

Ca-alginate capsules can improve the self-healing properties of asphalt concrete. However, there are still some unanswered questions to allow the capsules to be applied to asphalt concrete pavement and play their effective role throughout the service life of the road, especially aged asphalt concrete. Previous studies have primarily focused on the extent to which muti-cavity Ca-alginate capsules influence asphalt mixtures' early performance.

However, the self-healing aspect and long-term durability of aged asphalt mixtures containing the capsules have been less investigated. Rejuvenating and self-healing of asphalt concrete by capsules mainly occur with asphalt aging. There is currently little research on the mechanical properties and self-healing properties of aged asphalt concrete containing capsules. This is detrimental to further practical applications of the capsule. It is also not conducive to the maintenance and application of capsule-containing asphalt concrete pavements.

Besides, RAP can better reflect the actual aging of asphalt concrete. It is unclear for the effect of self-heal capsules on RAP asphalt mixture performance, which hinders the comprehensive utilization of RAP and capsules.

1.3 Research objective and content

The main aim of the research is to design a long-life asphalt concrete pavement using Ca-alginate capsules, by clarifying the influence of the capsules on the performance of aged asphalt. This provides guidance for the maintenance of asphalt concrete pavements containing capsules and extends the service life of asphalt pavements. The following objectives are introduced:

(1) Assess the effect of capsules on the mechanical properties and the self-healing ability of unaged and laboratory-accelerated ageing asphalt mixture.

(2) Explore the possibilities of using capsules and RAP together. Determine the influence of RAP usage on mechanical properties and self-healing ability of asphalt concretes containing both capsules and RAP.

(3) Unraveling the mechanism of rejuvenating and self-healing of capsules on laboratory aged asphalt concrete and asphalt concrete containing RAP.

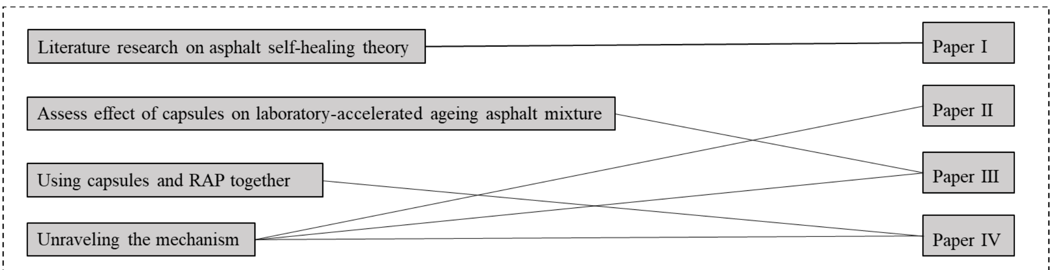


Figure 1 The relationship between research objectives and Papers

In order to reach the objectives, the following research was performed:

(1) Literature research on asphalt self-healing theory, challenges and opportunities of different types of self-healing technologies, including heating technology, agent-encapsulated technology and other technologies;

(2) Research on mechanical performance (volume performances, rutting resistance, moisture stability and crack resistance) and self-healing performance of aged asphalt mixtures containing Ca-alginate capsules under laboratory-accelerated ageing conditions;

(3) Incorporate simultaneously different contents of RAP and capsules into asphalt concrete and testing the mechanical (volume performances, rutting resistance, moisture stability and crack resistance) and self-healing performance of asphalt mixtures with both RAP and Ca-alginate capsules;

(4) Reveal the self-healing and rejuvenating mechanism of Ca-capsules on aged asphalt binder by testing bitumen's diffusion, rheology and creep.

1.4 Thesis structure

This dissertation is divided into five main chapters:

Chapter 1 Introduction of the research background and scope

Chapter 2 Literature review of the self-healing technologies of asphalt pavement

Chapter 3 Illustration of the source and properties of raw materials, test methodologies and research processes

Chapter 4 Discussion of the mechanical and self-healing performances of aged asphalt pavement that contains capsules, including laboratory-accelerated ageing and utilization of RAP. Additionally, analysis and discussion of diffusion, regeneration and self-healing mechanisms in capsules' self-healing properties

Chapter 5 Summary of conclusions and recommendations for future work

Chapter 6 References list

2. Literature review for self-healing of asphalt pavement

2.1. Self-healing theories and evaluation methods

The macroscopic manifestation of crack healing is that the generated crack gradually disappears; as a result, the interfaces on both sides of the crack become integrated until the interface itself disappears. During this process, a series of physicochemical reactions occur inside the material, accompanied by the migration of substances and change of energy[39]. Researchers have described the crack healing process in asphalt materials from different perspectives and developed some asphalt crack healing theories and evaluation methods based on asphalt's own properties.

The *Molecular Diffusion Healing Model* presents the mutual diffusion process of asphalt molecules on both sides of the interface until the interface itself disappears, which is a phenomenon based on polymer chain dynamics[40,41]. Bitumen is a kind of liquid material composed of polymer molecules of different sizes, and its viscosity is sensitive to temperature. Wool et al. [40,42] have proposed that the crack-healing process of polymers from the perspective of molecular diffusion consists of five consecutive stages: 1) surface rearrangement, 2) surface approach, 3) wetting, 4) diffusion, and 5) randomization. During this process, the mechanical force is rebuilt due to molecules' or microstructural components' secondary bonds being restored by Rouse diffusion or reptation [43]. In addition to the chemical molecular composition of the asphalt material itself, the two most important factors that determine crack healing are temperature and time. In brief, a higher temperature response leads to a shorter healing time. Sun et al. [44] have proposed a recovery function of asphalt binder based on molecular diffusion by administering a fatigue-rest-fatigue test, which considers the effect of healing time and temperature, as shown in Equation (1).

$$HL(t,T) = HI_0(T) + D_0 \exp\left(-\frac{E_h}{RT}\right).t^{0.25} \quad (1)$$

where HL(t, T) is the crack-healing ratio of bitumen. HL_0(T) is instant-healing ratio of bitumen. D_0 is a diffusion parameter, R is the universal gas constant (8.314 J/mol/K), and E_h is the activation energy. T is the temperature.

The function adds the material parameter, activation energy, which is determined by the chemical composition of the material itself. It also defines the self-healing potential of bitumen. Zhang et al. [38]have tested different aged levels of bitumen's self-healing capability and calculated its activation energy; the results show that self-healing capability and activation energy both decrease as ageing increases.

Next, *phase field healing theory* describes the process when separate phases are reconfigured after having shown a tendency to be isotropic during the heating process. The phases on both sides of the crack are unevenly distributed. The reason for this uneven distribution is that when fluid substances are mixed together, their minimum level of entropy tends to change. Yet the mechanical properties of asphalt can be restored when the temperature is reduced[45]. Small molecules and long-chain polymeric molecules are not commonly found in asphalt, and the diffusion model does not describe the crack- healing behavior completely. Kringos et al. [46] developed this phase field healing theory by observing the phase movement of asphalt surfaces using AFM (atomic force microscopy) investigations. Other researchers have also observed the two phases first separating and then reaching equilibrium by examining AFM images [47]. Microcracks usually occur at the interfaces between the phases due to stress concentrations. The phases reconfigure to a new homogeneous mix once the thermodynamic conditions change due to energy application.

Next, *surface energy healing theory* explains the decrease of crack surface energy during asphalt's crack-healing process. Simply put, it calculates the energy required to heal cracks when surface area is reduced. Lytton et al. [48] derived the energy balance of the crack interface while undergoing the disappearance process from fracture mechanics and during the fatigue process of viscoelastic materials, as shown in the equations below.

$$2\mathrm{E}_f = E_R D_h(t_a) H_v \tag{2}$$

$$D_h(t) = D_{0h} + D_{1h} t^{mh} \tag{3}$$

$$2E_f = E_R D_f(t_a) J_v \tag{4}$$

where E_f is the fracture surface energy density, E_h is the healing surface energy density of a crack surface, E_R is the reference modulus, $D_f(t\alpha)$ is the tensile creep compliance, $D_h(t\alpha)$ is compressive creep compliance, Jv is the integral of J, and Hv is the integral of H. mh is the slope of concrete's creep compliance over a long period of time.

Through the derivation of the above equations, Si et al. [49,50] defined two healing rates (h1, h2) by applying different mechanisms and fatigue cracking processes for the viscoelastic medium derived by Schapery. h1 is the short-term healing rate determined by non-polarity; it usually occurs quickly. h2 is the long-term healing rate determined by polarity; it is time-dependent. The total healing h is shown in the equations below:

$$h = h_2 + \frac{h_1 - h_2}{1 + \frac{h_1 - h_2}{h_\beta}(\triangle t)_h} \tag{5}$$

$$h_2 = [\frac{2r_m E_R^2 D_{1h} \Gamma^{AB}}{(1 - v^2) C_m^{1/mh} H_v}]\beta \tag{6}$$

$$h_1 = [\frac{K_h E_R D_{1h} H_v}{2\Gamma^{LW}}]^{\frac{1}{mh}}\beta \tag{7}$$

where $(\Delta t)h$ is the rest period, and $h\beta$ is the maximum healing ratio of bitumen

Si et al. [50]investigated the healing rates of 12 kinds of asphalt concrete: it was found that the short-term healing rate (h1) showed a significant difference while the long-term healing rate (h2) was relatively the same.

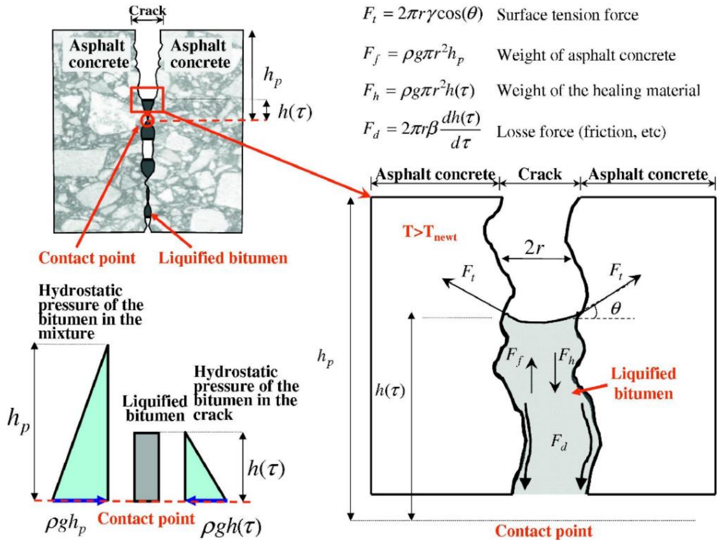


Figure 2 The capillary flow healing model and mechanical analysis

Next, *the capillary flow healing theory* states that the asphalt binder can flow and fill an open crack automatically due to capillary force, which is based on the fact that asphalt is a kind of liquid material. When the crack growth reaches a certain size, molecular diffusion cannot occur through such a large gap. The cracks' healing process can also be observed at this time, mainly because the liquid bitumen fills the cracks under capillary pressure. The capillary flow healing theory can present healing efficiency through a modification of the Lucas-Washburn equation[51]. It has been found that increasing the surface tension force of asphalt can effectively promote its flow into cracks. As the temperature increases, the asphalt's viscosity decreases; subsequently, its surface tension also increases. This healing therefore occurs either at relatively high temperatures or when the viscosity of the asphalt interface decreases due to infiltration by the rejuvenator.

Based on the above self-healing theories and existing testing standards with respect to the rheological and mechanical properties of bitumen and asphalt mixtures, several evaluation methods have been used to quantify asphalt's self-healing level (SHL) by measuring its performance before and after the healing process. Table 1 summarizes the evaluation methods for asphalt binders and mixtures. It has been found that the healing evaluation of bitumen is based on its own performance recovery rate that is due material properties, including complex modulus, dissipated energy, fatigue life, etc. These are mainly due to changes in the bitumen's microstructure and uneven phase distribution under loading conditions. After a period of rest, bitumen becomes a homogeneous mix again through molecular diffusion and phase field reconfiguration, resulting in performance recovery. As for the mixture itself, a crack's healing level (HL) is based on mechanical property recovery, mainly because this meets the pavement design theories of mechanical property attenuation and distress

Table 1 Self-healing evaluation methods on asphalt binders and mixtures

Materials Types	Test Method	Healing Parameter	Healing Level	Notes	Ref.
Binders	Ductility	Ductility value	HL = $\frac{L_{healed}}{L_{original}}$	L_{healed} and $L_{original}$ are ductility test result before and after break-healing	Qiu, J. et al. [52]
	DSR sweep test	Complex modulus and number of cycles	HL = 100· $\frac{G*_{Terminal}}{G*_{initial}} \frac{N_{after}-N_{before}}{N_{before}}$	$G_{initial}$ and $G_{terminal}$ are the dynamic modulus before and after loading test; N_{before} and N_{after} are the numbers of cycles before and after rest period;	Tan, Y. et al.[53]
	Fatigue-rest-fatigue test using DSR sweep test	Area under the curve	HL = $\frac{A_d}{A_{before}}$	A_{before} and A_d is the area between the curves of the modulus versus the number of load cycles and the line of ½ modulus before and after rest;	Shan, L. et al. [54]
	Fatigue-rest-fatigue test	Complex shear modulus	HL = $100 \cdot \frac{G*_{h0}}{G*_0}$	G*0 and G*h0 are the complex shear modulus before and after healing;	Qiu, X. et al.[55]
	Fatigue-rest-fatigue test	Dissipated energy	HL = $100 \cdot \frac{E_{after}}{E_{before}} \frac{N_{after}}{Nbefore}$	E_{before} and E_{after} are the initial dissipative energy before and after healing	Qiu, X. et al.[55]
	Fatigue-rest-fatigue test	Fatigue life	HL = $\frac{\sum N_{fo}}{\sum N_{f1}}$	$\sum N_{fo}$ and $\sum N_{f1}$ are the fatigue life before and after rest	Liu, G. et al. [56]
Asphalt mixture	IDT	Resilient modulus	HL = $\frac{MR(t)-MR0}{MR_{undamaged}-MR0}$	MR(t) is the normalized resilient modulus at time t; MR0 is the normalized resilient modulus at t = 0; and $MR_{undamaged}$ is the undamaged normalized resilient modulus	Chen, Y. et al. [57]
	SCB test or 3-point bending test	Strength	HL = $\frac{F_{after}}{F_{before}}$	F_{after} and F_{before} are fracture peak load before and after healing	Riara, M. et al.[58]
	SCB test or 3-point bending test	Stiffness	HL = $\frac{S_{after}}{S_{before}}$	S_{after} and S_{before} are stiffness before and after healing	Riara, M.et al.[58]
	SCB test or 3-point bending test	Fracture energy	HL = $\frac{E_{after}}{E_{before}}$	E_{after} and E_{before} are fracture energy before and after healing	Riara,M. et al.[58]
	Four-point bending test	Stiffness modulus	HL = $\frac{S2-SS}{S1-SS}$	S1 and S2 are the initial stiffness modulus before and after rest; SS is stiffness modulus when beam reaches fatigue condition	Xiang, H. et al. [59]
	Four-point bending fatigue-healing-fatigue test	Fatigue life	HL = $\frac{N_{f-after}}{N_{f-initial}}$	$N_{f-after}$ and $N_{f-initial}$ are fatigue life before and after resting	Liu, Q. et al.[60]

2.2. Heating technologies

While bituminous material itself is a self-healing material capable of repairing cracks, it must have sufficient temperature and time in order to do so. This is mainly because the viscosity of bitumen is temperature-sensitive; the higher the temperature, the lower the viscosity[61]. Heating bitumen can reduce the asphalt's viscosity , which not only reduces the surface energy of the crack but also causes the bitumen to have the fluidity needed to flow into the crack and heal it[62]. Moreover, high temperatures help improve bitumen molecular diffusion to heal the cracks. Based on the theories, heating asphalt concrete technologies were proposed to heal the crack that occurred in the service process due to ageing, traffic loading or fatigue. For example, induction heating and microwave heating are efficient and non-contact heating methods that are suitable for heating asphalt pavement[63]; indeed, these take only seconds to reach asphalt's self-healing temperature.

2.2.1. Induction heating

The basic principles of induction heating technology are electromagnetic induction and joule heating. In accordance with Faraday's law, during the testing process, when the material is placed in the induced magnetic field, its interior experiences an electro-motive force. Next, the eddy currents are generated to heat the materials in accordance with Joule's law. Additionally, magnetic domain rotation also produces hysteresis heating when applied to magnetic materials. Bituminous materials themselves cannot be heated directly by induction; some electrically conductive materials (like steel fibers, steel wool, steel slag, etc.) may be added to asphalt mixtures [64,65]. After the conductive material heats up under an induction field, it can be conducted to the bitumen in order to heat up and heal the cracks[66]. The basic principle is shown in Figure 3.

In Garcia et al.'s study[67], steel wool fibers were added to dense asphalt mixtures. The results show that a higher volume of steel wool fibers in the mixture may increase the air void content of asphalt-concrete and affect its thermal conductivity. When Liu et al. [68] incorporated steel fibers, steel wool, and steel slag into porous asphalt concrete, it was found that the conductivity of samples with longer fibers and a smaller diameter was better than that of samples with shorter fibers and a larger diameter. Further, the steel fibers and steel wool were more beneficial for increasing temperature than steel slag; they also improved the flexural strength of asphalt concrete[69,70]. For instance, 8% steel wool is considered the optimal content and increases the indirect tensile strength, resilient stiffness and fatigue resistance of porous asphalt concrete [70]. An appropriate amount of steel fibers can increase the basic mechanical properties of asphalt concrete while also increasing its thermal properties.

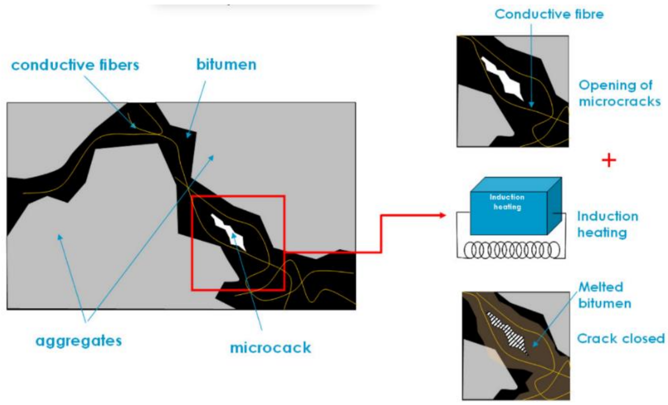


Figure 3 Induction heating scheme.

Induction crack healing technology is primarily used to increase the temperature of asphalt concrete and reduce its viscosity in order to promote crack healing. Temperature is the main index used to determine the crack healing rate. Liu et al. [71] believed that 85 °C was the optimal surface temperature for crack healing as demonstrated by a three-point blending test; they also believed that the optimal strength recovery rate could reach 78.8%. Liu et al. then designed a four-point blending test to investigate the fatigue life extension of asphalt concrete that contained steel fibers. Micro-strain amplitudes would affect the size of cracks between test samples. Higher micro-strain amplitudes and larger cracks were generated from the fatigue testing; all of these showed insufficient healing. Liu et al. [72] found that the fatigue life extension ratio during different micro-strains and temperatures for hot mix asphalt and warm asphalt shows that when induction heating technology heals a crack, this can extend asphalt's lifetime by over 70%.

Another advantage of induction heating technology is that the asphalt pavement can be heated multiple times during its service life. The strength recovery rate and fatigue life extension of asphalt concrete containing steel fibers remain unchanged after 5 cycles of induction heating[73,74]. Yang et al. [75,76]also studied the induction heating crack-healing level of asphalt concrete containing reclaimed asphalt pavement (RAP) and steel slag. The strength healing rate of RAP containing 40% can still reach 57.9%. At the same time, the crack-healing rate decreases by 10% after four cycles.

In December 2010 , the first induction-heating asphalt pavement was laid in the Netherlands [11], where it has remained in good condition until the present time. In June 2014, this same pavement received the first induction heating treatment ever tried, after which it has shown high levels of healing ratios and raveling resistance [77]. In 2018, in the Guangdong Province of China, a 400-meter induction healing pavement test section was also laid [78]. According to estimates, if all roads in the Netherlands were replaced with induction-heated pavements, it could save approximately EUR 90 million annually, and the life span of roads would also be extended by 50%. By the same calculation, China would save a maintenance expense of RMB 1000 billion if only 10% of the roads were replaced by induction healing pavement[70].

However, induction heating technology cannot prevent the ageing of asphalt pavement; more significantly, the pavement becomes increasingly prone to cracks, and the healing temperature reaches an extremely high level during the service process. The total mixing time should be five minutes in order to get a homogeneous mix with a minimum number of steel wool clusters. This is six times more than when normal asphalt pavement is applied[70]. Heating efficiency is also limited; one hour can only heat 5 km since it takes 26.4 s for the temperature of the road surface to increase from 5°C to 85 °C[77]. This is why large-scale induction equipment also requires further study in order to guarantee heating rates and maintenance times.

2.2.2. Microwave heating

Microwave heating is also an effective non-contact heating method used in road surface heating. The basic principle is that the direction of the electric polarity molecules in the object will vibrate concurrently with the oscillating electric field; the inherent electromagnetic field of a molecule is then changed, affecting the adjacent molecules. Thus, a molecule’s vibration passes from one molecule to another when the electromagnetic field is oscillated by microwaves’ high frequency levels. Molecular vibration is internal energy, and increasing internal energy is similar to heating an object[79].

Microwaves cannot heat non-polar molecules. Bitumen contains a large number of polar molecules. Lou et al. have reported that microwave heating rarely affects aged asphalt, a fact that refers back to the ageing index[80]. The mechanism of crack healing is the same as induction heating after the mixture has been heated [81]. Researchers have found that the integration of certain additives can improve microwave heating effectiveness. Gallego et al. have reported that 0.2% steel wool can significantly improve microwave heating potential, whereas only a 1/10 dosage for induction heating can reach the same heat rate [82]. Li et al. [83,84] found that nanometer microwave-absorber materials (like SiC, CNTs, and graphene) can also improve asphalt's microwave heating rate and healing properties. Sun et al. [85] studied the heating and healing properties of a mixture combining steel slag and steel fibers using both induction and microwave technologies. Lou et al. [16] used three kinds of steel slag (hot braised, hot pour, and iron slag) to replace the coarse aggregates in the asphalt mixture and found that the microwave heating rate had improved. A 60% replacement is the most effective dosage. Lou et al. [86] also used ferrite fillers to replace limestone fillers in a mixture that incorporated steel slag; consequently, the microwave heating rate was further improved. Metallic powder and fly ash can also improve asphalt's microwave heating potential[87,88]. In the Jahanbakhsh et al. [89] study, carbon black increased the heating rate of asphalt pavement made of limestone and siliceous types of aggregate by 47% and 25%, respectively. Wang et al. [90] also found that pyrolysis carbon black (PCB) produced an effective microwave-absorbing performance for asphalt pavement. Further, the addition of 15% PCB increased the self-healing rate of bitumen by 3.59 times.

At present, the microwave heating and cracking technology in the laboratory mainly relies on microwave ovens. Heating time and temperature are the biggest factors affecting the crack healing rate of asphalt concrete. For example, Jose et al. comparatively studied microwave and induction heating; the microwave healing rate of dense asphalt mixtures was superior to the induction healing rate as shown in a three-point bending test, where the strength recovery rate reached 93% for microwave healing, while the rate was 75% for induction heating. This is mainly because microwave heating is holistic heating, while induction heating has a temperature gradient from top to bottom, and the bottom crack does not reach the optimal level of healing [91]. Zhu et al. [92]investigated the healing level of asphalt-concrete containing base bitumen and SBS-modified bitumen at different temperatures in a semicircular bending test; it was found that the strength recovery ratio could reach 85% at 80 °C. The microwave heating-healing ratios of asphalt mixtures with different structures (semi-dense, porous, and gap-graded) were investigated in a study by Franesqui et al. [87] It was found that top-down cracks (<4–5 mm)can be completely healed by microwave heating.

The crack healing level of asphalt concrete containing RAP was also investigated by microwave heating, where it was shown that the RAP content adversely affected the microwave heating[93]. Nevertheless, there are obvious disadvantages to microwave heating technology. Trying to control the microwave's reflection from flat surfaces is challenging. The human body can also absorb microwave energy, which can heat exposed tissue and cause thermal damage[94]. Therefore, further extensive research needs to be conducted to enhance the efficiency of microwave heating on asphalt pavements while ensuring that safety is not compromised.

2.3. Agent-encapsulated technology

The agent-encapsulated technology solves the shortcomings of the spraying rejuvenator, including difficult penetration and uneven distribution. Rejuvenating aged asphalt pavement as soon as cracking has started is the optimal solution, as this is the most effective way of prolonging the life of the road. It is crucial to avoid prematurely releasing the rejuvenator before the bitumen has aged, because doing so reduces the road’s permanent deformation resistance [95].

2.3.1. Saturated porous aggregates encapsulate rejuvenators

Figure 4 Characterization and healing process of saturated porous aggregates encapsulate rejuvenators[17]

Garcia et al. [96] first proposed the asphalt self-healing technology with capsules by applying self-healing capsules to cementitious materials. The porous sand is first used as the core material, and its internal porous structure can effectively store the rejuvenator. Then, the surface is coated with epoxy resin and cement, which form a shell. The capsules of various sizes (with diameters ranging from 1.6 to 7.1 mm and shell thicknesses ranging from 0.1 to 0.35 mm) are produced through the same procedure. It has been found that larger capsule cores contain more oil, and their force resistance is over 10 N in capsule compression tests[97,98].

The saturated porous aggregate capsules were added to porous asphalt-concrete and could resist high temperatures (up to 180 °C) and tension during the mixing and compaction of the asphalt mixture[98]. It was found after running the indirect tensile test that the capsules inside the porous concrete could break, causing the oil to flow out and diffuse into bitumen. The crack could then be effectively healed, as shown in Figure 4 [17]. However, the capsules were unevenly distributed in the asphalt mixture. Similarly, they tended to accumulate at a certain depth in the test sample. The capsules decrease the indirect tensile strength of asphalt-concrete because its strength is lower than normal aggregates[17]. Oil in the capsule is also extremely limited owing to the fact that most holes in the porous aggregates are closed. This kind of capsule is not particularly suitable to improve asphalt-concrete's self-healing ability.

2.3.2. Core-shell polymeric microcapsules

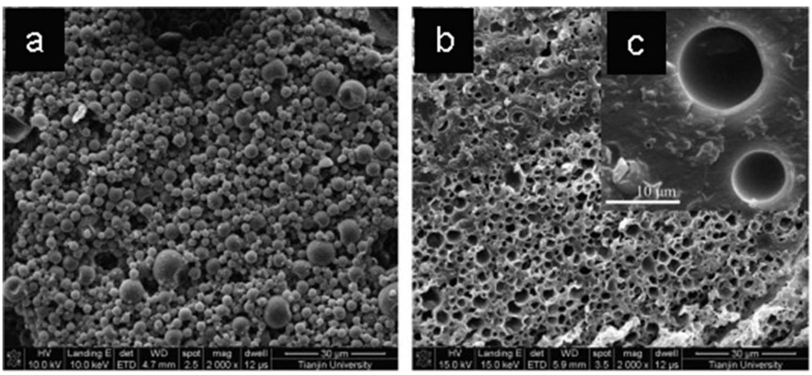


Figure 5 SEM images of core–shell microcapsules: (a) external aspect, and (b,c) cross-section of the microcapsules[99]

Core-shell polymeric microcapsules involve two primary components: the core material (rejuvenators) and the shell materials[100]. These capsules are categorized according to size as nano-capsules (<1 mm), micro-capsules (1mm < D < 1000 mm), and macro-capsules (>1000 mm) [101]. This section focuses mainly on the application of microcapsules in asphalt crack healing. The core material may be surrounded by one or two layers of shell materials. There are two types of core-shell capsules: (1) single-shell capsules [10] and (2) double-shell capsules[99]. Through *in-situ* polymerization and two-step coacervation processes, a type of core-shell microcapsule was created, which significantly reduced the size of encapsulated rejuvenators and improved their integration with bituminous materials[14].

These microcapsules consist of a rejuvenator core surrounded by a protective shell, which can be ruptured by propagating crack fronts, allowing for the release of the healing agent through capillary action. TGA tests have indicated that these microcapsules can withstand the storage and mixing temperatures of bitumen[102] . Sun et al. [102]have demonstrated that they can resist mechanical agitation at high temperatures while still being able to release the rejuvenator during loading, thereby enhancing the healing capacity of aged bitumen . Furthermore, fatigue-rest-fatigue tests have shown that the inclusion of microcapsules containing rejuvenator can enhance the fatigue resistance of aged asphalt binder, with a 1 wt% concentration resulting in a 45.68% increase in fatigue life compared to non-aged neat bitumen[10]. At the same time, a commercial prepolymer of mela-mine-formaldehyde modified by methanol (MMF) was also developed as the shell material of microcapsules [14,99,103,104] . Its SEM images are shown in Figure 5. Thermal tests showed that the microcapsules survived at 200 °C bitumen and could improve the self-healing ability of bitumen with the capsules [105]. Moreover, nano-CaCO3 powder was added to MMF as the shell to enhance adhesion with bitumen and thermal stability; these nano-CaCO3/polymer microcapsules survived in bitumen for a long service time under radical conditions without becoming damaged because of their high level of thermal stability[104].

However, the capsule does have its limitations. For example, its preparation efficiency in the laboratory is relatively low, and the quantity of each preparation is limited, making it challenging to use on a large scale in road engineering. Additionally, there have been no experiments conducted on adding it to the asphalt mixtures; it has only been added to binders. It is difficult to prove that it can stay in one piece without breaking apart during mixing and compression. As the capsule has a single core, once it ruptures, all the rejuvenators inside are released at once, which could potentially reduce the asphalt concrete's resistance to permanent deformation.

2.3.3. Ca-alginate capsules

Calcium alginate capsules are prepared by dripping the emulsion containing sodium alginate, surfactant, and regenerant into a calcium chloride solution. The shell material of the capsule is intended to place the chain alginate ions into a three-dimensional network of calcium alginate material through the method of ion replacement, thereby allowing the rejuvenator to be stored in the gaps of the network structure[22]. Rao et al. also innovated the experimental apparatus and successfully made the capsules using industrial raw materials on a large scale in the laboratory [106]. The size of capsules is typically 1.5–3 mm, and the capsule is incorporated into the asphalt-concrete as an aggregate. Its internal structure is a multi-chamber structure[21], which enables multiple releases of the internal rejuvenator for long-term crack healing, as shown in Figure 5.

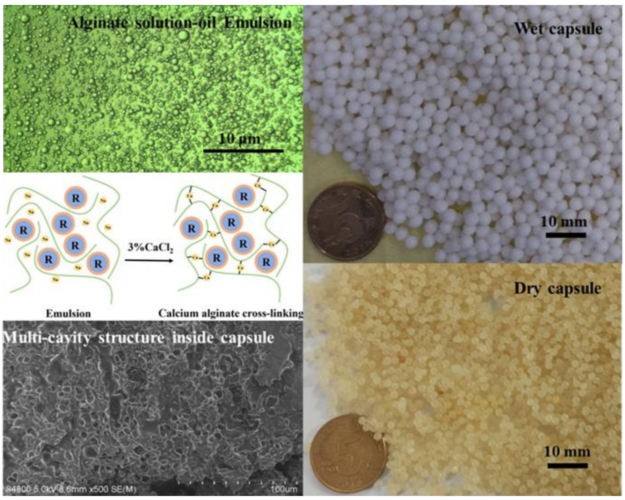


Figure 6 Morphological characterization of calcium alginate capsules

This capsule-healing technology uses an internal rejuvenator to soften the asphalt on the crack interface, reducing its surface energy and increasing its flow activation energy, thereby promoting crack healing. It is generally believed that there are two release mechanisms for the rejuvenator inside the calcium alginate capsule. The first mechanism is the same as the core-shell capsule. The crack, or loading, induces the capsule to rupture and releases the rejuvenator inside, which can then effectively heal the crack. Any damaged capsules embedded in asphalt mixtures can be found by using a CT scan[13,18], as shown in Figure 6. The second mechanism is elastic contraction and expansion. Since not all the chambers inside the capsule are closed, when capsules are loading, they become deformed by pressure; the internal rejuvenator then flows out, yet the capsule does not rupture. The release method can rejuvenate aged bitumen and improve its own self-healing capability[107].

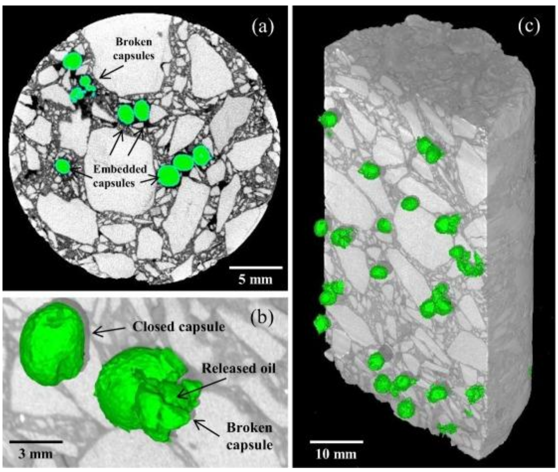


Figure 7 CT-Scans reconstructions of the asphalt mixture containing capsules, (a) sectional view, (b) broken capsules in mixtures, (c) 3D image[20]

Researchers have studied the mechanical and thermal properties of the capsule itself. The uniaxial compression test, which makes capsules break, is usually used to measure capsules' mechanical strength. It was proved that the capsules could resist the pressure during mixing and compressive forces when the strength was higher than 10 N[20,96]. Zhang et al. [25], Wan et al.[27], Xu et al. [24], Al-Mansoori et al. [109], and Norambuena-Contreras et al[111]. tested the strength of this capsule at different temperatures; the results ranged from 12–33 N. By using thermal gravimetric analysis (TGA), the capsules had a mass loss of 2.9–4% at 200 °C and 3.8–5.5% at 160 °C. The rejuvenator content of the capsule weight could also be calculated by the thermogravimetric curve; it ranged from 52–80%. Thus, it may be observed that the capsule can fully survive the mixing and compression of asphalt concrete.

Next, Norambuena-Contreras et al. incorporated 0.25–1% capsules into dense asphalt concrete (AC 13); 0.5% capsule content had basically no effect on the basic road performance (scattering, indirect tensile strength, Marshall stability, and freeze-thaw cycles) of asphalt-concrete and only slightly reduced its resistance to permanent deformation [21]. Al-Mansoori et al. [108] added the capsules to AC20 asphalt concrete and got similar results. When the capsules were added to SMA asphalt-concrete, its stiffness and deformation resistance decreased to such a low level that it had no influence on fatigue resistance. Xu et al.[24]found the capsules could reinforce the stiffness modulus of porous asphalt concrete.

More importantly, this capsule can effectively increase the crack-healing ability of asphalt concrete at low temperatures. Al-Mansoori et al. [109] found that the capsules affected the healing levels of samples when the healing temperature was below 40 °C. Similarly, asphalt samples both with and without capsules reached the same healing levels when the temperature was over 40 °C through the fracture- rest-healing-refracture test. Zhang et al. found that the strength recovery ratio and fracture energy recovery ratio of asphalt with capsules reached 92.7% and 180.2%, respectively, while the reference samples are 61% and 31.5%, as shown in Figure 8. The capsule's presence also significantly improves the healing capability of porous asphalt-concrete, which has been shown in the semi-circular bending (SCB) test conducted by Xu et al. [24]. The self-healing property of reflective crack in asphalt mixtures that contain capsules was investigated in the Garcia-Hernández et al. [110] study. It was found that the capsules had the best self-healing efficiency in porous asphalt-concrete, followed by stone mastic asphalt mixture and dense asphalt mixture. Jose et al. [111]also used leftover cooking oil as the rejuvenator to synthesize the alginate capsules; it was found that leftover cooking oil capsules were useful for self-healing applications because of their mechanical and thermal stability and physical-chemical properties. The capsules can diffuse in the aged bitumen, reducing its viscosity and promoting the self-healing of microcracks. This type of capsule is the focus material of this study.

2.3.4. Hollow fibers

Hollow fibers are used to provide a healing mechanism similar to that of encapsulated rejuvenators, which are encapsulated in the connected hollow pipe. This method also offers an advantage over capsule-based systems because the fibers increase the probability that rejuvenator will be released into cracks, which are more likely to pass through the fiber network[112]. Furthermore, the continuous pipe structure of the hollow system allows for the continuous supply of large volumes of rejuvenators, and the diameter of the fibers is usually 0.5–1.5 mm [113].

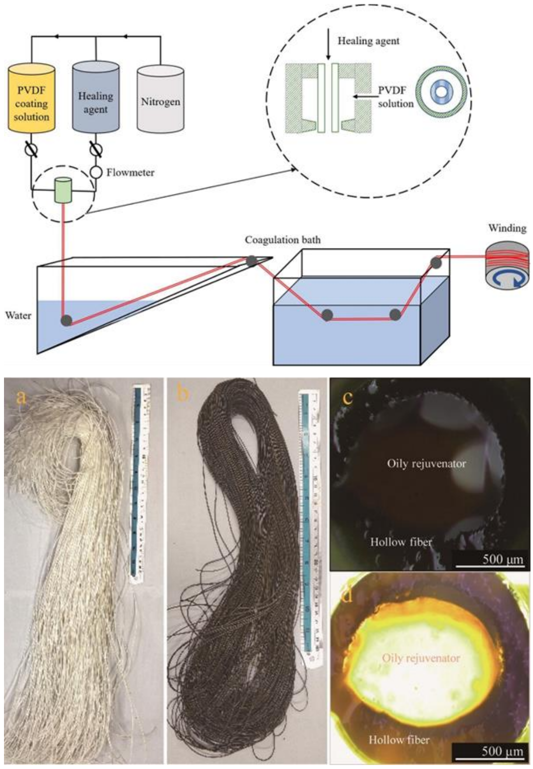


Figure 8 Schematic representation of the preparation of vascular hollow fibers and finished product: (a) fiber without rejuvenator, (b) fiber with rejuvenator, (c,d) cross-sectional of fiber with and without rejuvenator[113]

Zhang et al. prepared polyvinylidene fluoride resin (PVDF) hollow fibers by a one-step, wet-spinning technology; the process is shown in Figure 7. They are distributed evenly in the bitumen base material and aim to reverse bitumen's ageing and improve its crack repair capability [114]. The fibers were added to aged bitumen; they kept their integrality state (as shown in the XCT test), proving they can resist the thermal actions of temperature changes in bitumen. Hollow fibers can survive in bitumen safely without debonding[113]. For example, Guo et al. [115] tested the self-healing ability and efficiency of bitumen ductility specimens containing fibers and found that the self-healing rate reached 64% in the sample, which was larger than the pure bitumen sample. However, an intersection angle between the tensile direction and the fiber hinders the flow of rejuvenator into the crack, which results in a poor self-healing effect.

2.3.5. Compartment fibers

Compartment fibers have their own advantages over hollow fibers. This is because they do not allow the full release of the internal rejuvenator at one point of fracture, which causes excessive local softening. Because the internal rejuvenator is separated into small droplets in the fiber, its self-healing mechanism can be viewed as a merger of capsules and fibers. Tabakovi et al. [116]used the physic-mechanical technique of wet-spinning to prepare the calcium alginate compartment fibers. The fibers had good thermal and mechanical properties because they maintained their integrity even after being heated and mixed with bitumen.

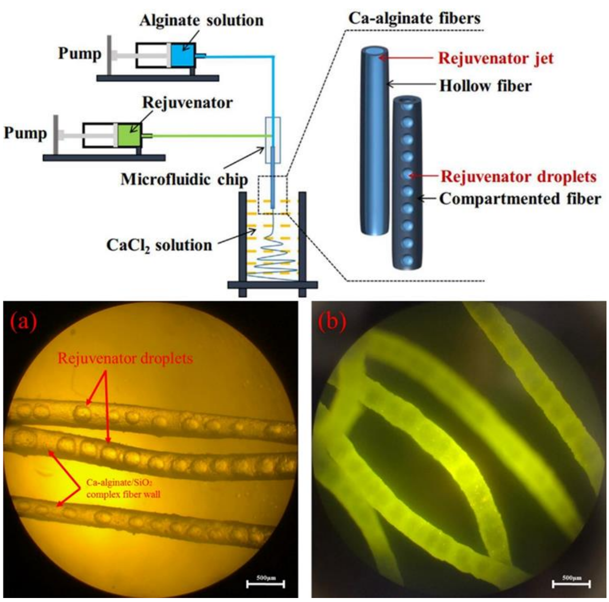


Figure 9 Microfluid synthetics compartment fibers and its morphology image, (a) optical microscope, (b) fluorescence microscope[117]

These fibers show the rejuvenator distributed as individual droplets along their axis. The results demonstrated that the mechanical strength of mastic asphalt containing fibers increases by 36%, and the local micro-crack healing ability of samples containing fiber also increases. Afterwards, Shu et al. used a microfluidic device to produce compartmented fibers using a commercial rejuvenator as a core and a sodium-alginate solution as a shell; the process is shown in Figure 10. The shell of fibers has excellent thermal stability and mechanical properties. The fibers themselves were still intact after mixing and compacting with asphalt. The self-healing ratio of asphalt mix containing fibers increased by nearly 32% compared to asphalt mix without fibers. The system worked and enhanced the self-healing properties of the asphalt mixture[117,118]. In agent-encapsulated technologies, although the shell materials (epoxy resin, MF, MMF, Ca-alginate, and PVDF) used are all organic matter, they are basically non-toxic; further, they do not flow into the environment and cause pollution when mixed into the asphalt. The core materials (commercial rejuvenator, sunflower oil, and waste oil) used are non-toxic and environmentally friendly; they are also a part of bitumen, which can be reclaimed. This combination further advances the sustainability of asphalt pavement.

2.4. Other technologies

There are also other technologies currently being studied to help repair cracks in asphalt pavement.

For instance, the comprehensive application of heating technology and rejuvenator supply technology is being considered to overcome the shortcomings of their separate use. Xu et al. have added both steel fibers and calcium alginate capsules to porous asphalt mixtures. The induction heating not only repairs cracks but also accelerates the outflow of the rejuvenators in the capsule and the diffusion in the bitumen[119]. Wan et al. have designed novel Ca-alginate capsules containing Fe3O4 powder, which can be induced to be heated in order to damage the shell of the capsules, leading to the rejuvenator's release by the low-frequency (2.45 GHz) microwave. So capsules can achieve an artificially controlled release time[120-122].

Electrically conductive asphalt pavements have also been designed to heal cracks in asphalt pavements by adding nanostructured conductive polymers, although asphalt is not electrically conductive [123]. According to Joule’s law, as the resistance of the conductive asphalt increases at a crack’s location, the temperature also increases in order to heal this crack[124].

Three-dimensional printing technologies can also be applied for the maintenance of asphalt pavement cracks. Firstly, building 3D digital models of cracks using an advanced pavement distress detection system, then printing the crack directly *in situ* with prepared printing materials and equipment, and finally, checking printing quality through ultrasonic testing[125]. Jackson et al. have found that bitumen can be used as a printing material to print into the cracks in the road surface in order to repair cracks at high temperatures and prolong the life of asphalt pavement[126].

Bitumen modified by polymer (SBS, Gilsonite, HDPE and crumb rubber in Lv et al. [127], SBS, HDPE and crumb rubber in Zhou et al. [128] crumb rubber, PPA, PE and gilsonite in Huang et al.[129]), nanomaterials (organoclay in Tabatabaee et al.[130], nano-silica in Ganjei et al.[131]), ionomers[132] and shape memory materials[133] increase the self-healing properties of bitumen itself and thus improve the asphalt pavement's own crack-healing ability.

3. Raw materials and Research methodology

3.1 Raw materials

3.1.1 Bitumen

Bitumen with a 60/80 penetration grade was selected to prepare the asphalt mixtures and conduct different ageing processes; bitumen's technical information is shown in Table 2.

Table 2 Technical information of bitumen binder

Technical information	Results	Methods
Penetration (25℃, 100g, 5s)/0.1mm	77.5	EN 1426:2015
Softening point/℃	48.6	EN 1427:2015

3.1.2. Aggregates

The applied aggregates are crushed rocks taken from the Vassfjell area and supplied by Franzefoss (a company located in Heimdal, Norway). The rocks have a high level of mechanical properties and are largely used for pavement bases and surface layers in the central part of Norway [134]. The resistance to wear (abrasion value and Micro-Deval coefficient) and fragmentation (Los Angeles value) of the aggregates are specified in Table 3. In addition, limestone fillers have been used. The aggregates obtained from the quarry were divided into various sizes (16-22.4mm, 11.2-16mm, 8-11.2mm, 4-8mm, 2-4mm, 1-2mm, 0.25-1 mm, 0.063-0.25mm and < 0.063mm) in order to design and manufacture asphalt mixtures.

Table 3 Resistance to wear and fragmentation of rock aggregates

Abrasion value EN 10097-9	Micro-Deval coefficient EN 1097-1	Los Angeles value EN 1097-2
7.8	14.2	18.2

3.1.3. RAP and rejuvenator

The reclaimed asphalt pavement mixture (RAP) used in this research came from a quarry located outside of Heimdal, Norway and was a combination of different roads located throughout central Norway. To quantitatively analyze the bitumen content in the reclaimed asphalt mixture, confirm the aged depth, and evaluate the physical properties and gradation of the reclaimed aggregates, the bitumen was extracted from reclaimed asphalt mixture using a dichloromethane dissolving method. The bitumen content of RAP is 4.1%. The aggregate gradation of RAP is shown in Table 4 through sieving; this process supplies both the base data for asphalt mixture design and usage of fresh rocks and bitumen.

Table 4 The graduation of RAP mixtures

Sieve (mm)	RAP gradation (%)
11.2 - 16	3.64
8 - 11.2	22.71
4 - 8	21.24
2 - 4	16.48
1 - 2	9.21
0.25 - 1	13.24
0.063 - 0.25	6.32
< 0.063	7.16

The rejuvenator comes from Norwegian supplier Kraton AS, which is one of the most commonly used in Norway; its FTIR spectra is shown in Figure 10. The typical functions of rejuvenator contain -CH2(2920cm^{-1}), -CH3(2850cm^{-1}), -C=O(748-1120cm^{-1}) and so on.

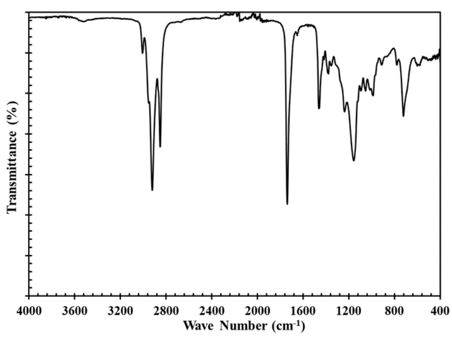


Figure 10 The FTIR spectra of rejuvenator

3.1.4. Ca-alginate capsules

Ca-alginate capsules were synthesized with sodium alginate, sunflower oil, Tween80, deionized water and calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$) by ion exchange. Sunflower oil was selected among several commonly used rejuvenators as a core material because of its positive effect on asphalt rejuvenator, low cost and lack of need for extra treatment [135]. The synthesis process of capsules has been introduced in Figure 11. Multi-cavity Ca-alginate capsules were added to asphalt mixtures as automatic *in-situ* rejuvenation systems and a supplier of self-healing capability, whose physical properties are shown in Table 5. The capsules containing alginate solution (2.5wt%)-oil ratio of 10/1 has a similar density (1.056 g/cm^3) to asphalt binder and high oil content (62.5%). Furthermore, its mechanical strength reaches 11.9N, which can survive after HMA (hot mix asphalt) mixing and compressing[97].

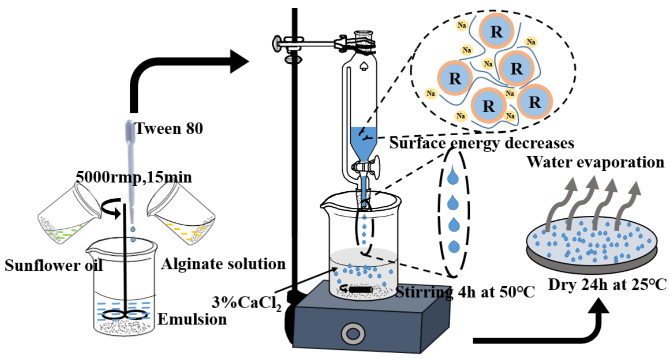


Figure 11 Synthesis of Ca-alginate capsules

Table 5 Physical properties of multi-cavity Ca-alginate capsules

Physical properties	Alginate solution (2.5wt%) : Oil	Radius /mm	Density /(g/cm^3)	Oil content /%	Mechanical strength /N
Result	10:1	0.95-1.05	1.056	62.50	11.9

Figure 6 shows the morphological changes during capsule synthesis from emulsion to ready-made capsules, which were observed by Fluorescence microscope, SEM and camera, respectively. A mixed solution of sodium alginate and sunflower oil forms an oil-in-water structure with the help of a surfactant and high shearing speed. The structure was also retained during the cross-linking process of Calcium ions. During the drying process, the water inside the capsules evaporates, and the radius of the capsules decreases. Due to the different wall thicknesses and locations of the cavity inside the capsules, the internal rejuvenator will be gradually released over time under the influence of traffic loads and environmental factors during the service process. If the asphalt ageing process matches the release rate of the rejuvenator, the aged asphalt pavement will be automatically rejuvenated *in situ*.

3.2. Preparation of samples

3.2.1. Bitumen samples

Two types of aged bitumen samples were prepared. One is Pressure Aging Vessel (PAV) aged bitumen, the other is RAP binder. The oxidative ageing in the lab was simulated for the short term-ageing by the thin film oven test (TFOT) according to EN 12607-1. Firstly, 50g of unaged virgin bitumen is placed into each plate having a diameter of 150 mm; it was then transferred to the oven for 5 hours, where temperature and fresh air flow were set at 163 °C and 4 L/min. This test simulates the high temperatures occurring during production and is linked with the initial fast-rate oxidation phase of a dual-sequential oxidation scheme. After TFOT ageing, the samples were then subjected to PAV ageing in order to simulate the state of asphalt after 5-7 years of service, according to EN 14769. The temperature was set at 100 °C with an air pressure of 2.1 MPa for a total duration of 20 hours. Regarding the RAP binder, the bitumen was extracted from the reclaimed asphalt mixture using a dichloromethane dissolving method. It was then prepared for subsequent experiments using distillation and drying.

3.2.2. Mixtures samples

AC11 dense asphalt mixture, which is normally used for the upper layers of asphalt pavement, was used in this study. The designed aggregate gradation is also shown in Figure 13. Bitumen content was 5.2%. When asphalt mixtures containing Ca-alginate capsules were prepared, 150℃ virgin bitumen, 160 ℃ aggerates and filler were added and continuously stirred for 300s. Next, Ca-alginate capsules were evenly sprinkled on the surface and continued to be stirred for 20s. Finally, the mixture was compressed into cylindrical samples (D 100mm*65mm) using rotary compaction and flat samples (300mm*300mm*50mm). Regarding reference samples without capsules, the mixing time was the same. Six types of asphalt mixture samples were prepared, as shown in Figure 12.

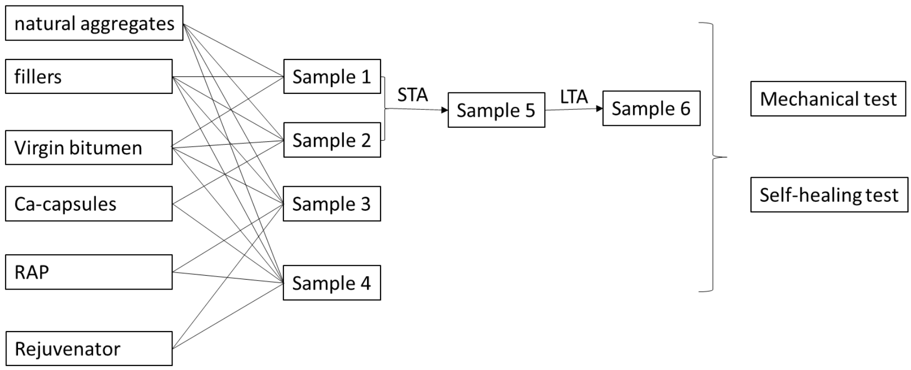


Figure 12 Preparation of asphalt mixture samples

With respect to laboratory-accelerated ageing specimens, there are two kinds of ageing methods: short-term ageing (STA) and long-term ageing (LTA). Regarding the STA, the formed asphalt mixture samples were placed in the oven at 135℃ for 5 hours, which was done to simulate the aged process between mixing and paving in the actual case. After the STA, the mixtures with and without capsules were placed into the oven at 85℃ for 5 days under forced ventilation for long-term ageing; this simulated the ageing state of asphalt mixture after 5-7 years of service. They were then used to perform various mechanical tests.

Regarding mixture samples containing RAP, natural fresh crushed stones, bitumen and rejuvenator were added separately using the sieve result and required ratio to keep the same gradation asphalt mixture with different amounts of RAP. The content of rejuvenator accounts for 6% of the bitumen content in RAP. In this paper, RAP mixture content of 0%,40%, 50%, 60% and 70% asphalt mixtures were prepared to make cylindrical and plate specimens.

According to previous studies, the diffusion of rejuvenators to aged bitumen is a time-consuming process[136]. Initially, rejuvenators form a thin layer of low viscosity surrounding the aggregates coated with aged bitumen. Subsequently, the rejuvenators gradually infiltrate the aged bitumen and induce its softening. Consequently, the incorporation of rejuvenators into the mixtures generates a lubricating layer, enabling the aggregates to move freely against each other. Therefore, to minimize the effect on virgin bitumen, it is recommended to mix rejuvenator with RAP before utilization.

During the mixing process, 160℃ RAP mixture with the corresponding rejuvenator is first stirred for 180s to confirm all RAP aggregates and binder can be stirred consistently and rejuvenated. Then, 150℃ virgin bitumen, 160 ℃ aggerates and filler are added and consistently stirred for 180s. Next, Ca-alginate capsules are evenly sprinkled on the surface, and the mixture continues to be stirred for 20s. Finally, the mixture is compressed into samples of different shapes. In the case of reference samples without RAP or capsules, the mixing time is the same.

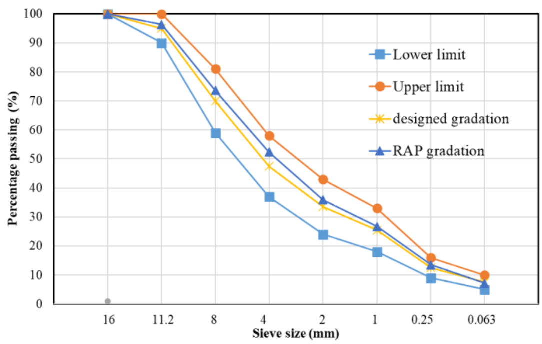


Figure 13 The designed gradation curve and RAP gradation of asphalt pavement

3.3 Test method

For asphalt mixture materials, the volumetric performance, high-temperature rutting resistance, low-temperature crack resistance and water stability are the most important mechanical performances. These properties determine the quality of the material and affect the durability, safety and lifespan of the asphalt pavement. Self-healing performance can characterize the material's ability to repair cracks, which can extend its service life. Table 6 shows the overview of test methods in relation to the research objectives. Different standard test methods were applied to test their mechanical and self-healing performance. To explain the changes in their performance (rejuvenating and self-healing), aged bitumen and extracted RAP binder were analyzed by diffusion, rheology, creep and chemical composition analysis tests. Various testing methods are introduced in detail below.

Table 6 Overview of test methods in relation to the research objectives

Asphalt mixture	Samples	Ref, aged asphalt mixture and RAP mixture with and without capsules				
	Performances	Volume performances	Dry rutting resistance	Moisture stability	crack resistance	Self-healing
	Test methods	water basket weight method	Wheel track	Marshall stability	3-point blending	fracture-healing-re-fracture
Unraveling the mechanism of rejuvenating and self-healing						
Bitumen	Samples	Aged bitumen and extracted RAP binder				
	Mechanism	Rejuvenating				Self-healing
	Index	Rheology	Diffusion	Creep	Chemical component	Flow behavior
	Test methods	DSR	Sinking time test; Softening rate test; Gravitational collapsing test	BBR	four components analysis	Frequency sweep; Numerical fitting

3.3.1 Bitumen test

(1) Penetration and softening point

The needle penetration of bitumen was tested, referring to the standard EN 1426. The softening point of bitumen was also measured using the Ring and Ball method and according to the standard EN 1427.

(2) Four components analysis

In order to clearly understand the change in chemical components of asphalt binder after ageing and capsule releasing, SARA (saturate, romantic, resin and asphaltene) analysis was performed using the TLC-FID, which has the advantage of faster detection speed (about 30 s) and a higher sensitivity level than traditional components analysis method. Bitumen samples were collected directly from the intermediate of asphalt mixture test specimens using a hot knife[18]; these were then dissolved in dichloromethane (2% mass/volume ratio). 1μL prepared solution was dropped five separate times at the origin point of a silica gel chromatography bar. Next, the prepared silica gel chromatography bars were put into three expansion slots for expansion. The expansion solvents were n-heptane, heptane/toluene mixture (volume ratio 1:4) and toluene/ethanol mixture (volume ratio 11:9), respectively. After each expansion process, the expanded silica gel chromatograph was placed in an oven at 70℃ for one minute to completely evaporate the solvent. Finally, the prepared silica gel chromatography bars were placed into TLC-FID to analyze the components of asphalt binders.

(3) Dynamic shear rheometer (DSR) test

This study uses DSR test to assess the rheological properties of bitumen. According to the different parameter settings during the test process, it is divided into temperature sweep and frequency sweep.

Temperature sweep

A temperature sweep test was performed at a constant strain of 0.5% and a constant frequency of 10 rad/s at a temperature ranging from 30℃ to 80℃ (heating rate of 2 ℃/min) by a dynamic shear rheometer (DSR). Three indicators – complex modulus (G*), phase angle (δ) and fatigue factor ($|G^*|\cdot\sin\delta$) -- were automatically calculated, respectively.

Frequency sweep

A frequency sweep test was conducted for each bitumen at nine different temperatures (increasing from 30℃ to 70℃ with an interval of 5℃). The test frequency ranged from 0.1 Hz to 100 Hz, and the constant strain was 0.5%. Complex modulus(G*), phase angle (δ) and complex viscosity (η*) were recorded as frequency increased at each temperature point.

(4) Bending Beam Rheometer (BBR) test

The Bending Beam Rheometer test principle is the measurement of the deflection of a bitumen beam using 3-point bending in an ethanol bath at low temperature. The size of the beam samples is 6.4*12.7*127mm. The distance between the supporting pins is 100 mm. The deflection at that point is measured at 8 s, 15 s, 30 s, 60 s, 120 s and 240 s. The loading is 980 ± 50 mN.

(5) Diffusion of oil in bitumen

Then, three self-designed tests were proposed to evaluate the diffusion of oil in bitumen, which was called a sinking time test, softening rate test and gravitational collapsing test. These three tests provided a concise reference to characterize the diffusion of oil using dissolving times.

Sinking time test. An aged asphalt specimen was kept floating on the surface of the sunflower oil. A stirring magnetic rotor was used during the entire testing process to keep the temperature at 40°C. The aged asphalt specimen was designed in a special shape that ensured it would float on oil. During the test, substance exchange occurred from the effects of molecular motion between the aged asphalt and oil. In the end, the specimen became soft and finally sank to the bottom. The sinking time needed to reach the bottom can be used to characterize the diffusion of rejuvenators. Figure 14 indicates the schematic diagram.

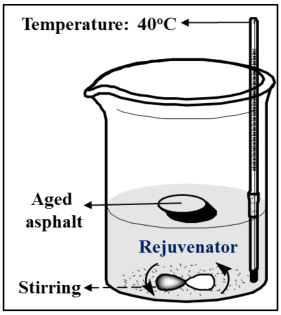


Figure 14 Schematic diagram of sinking time test

Softening rate test. It is a kind of revised softening point test. Oil replaced water and was kept at a constant temperature. The test principle is to measure the time needed for aged asphalt to completely soften and stretch to reach the bottom while under the weight of a fixed steel ball. Firstly, two specimens of aged asphalt were made by the softening point test mould; softening point balls were then placed onto the specimens individually. Secondly, the specimens were placed in a beaker with 30mm of rejuvenator. A stirring magnetic rotor and water bath heating were used to keep the system temperature uniform at 35°C. The time was recorded for the aged asphalt specimens to reach the bottom. The schematic diagram is depicted in Figure 15.

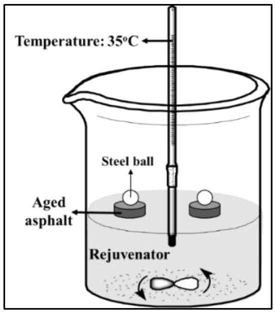


Figure 15 Schematic diagram of softening rate test

Gravitational collapsing test. It is designed to simulate the phase diffusing rate at low temperatures to keep the bitumen solid at 10°C. The aged asphalt was put into a glass pipe whose other end was blocked. Oil was then poured onto the solidified asphalt after it had cooled. At the two phases' interface, rejuvenator and aged asphalt diffuse each other until the aged asphalt fully softens and collapses. In this way, the crushing time of aged asphalt using different weights can be used to analyse the rejuvenator's diffusivity, as shown in Figure 16. The inner area of the mould is 4.23cm^2, and the used oils' quality is 1.28g. So the pressure was 30.26Pa on the diffusion interface.

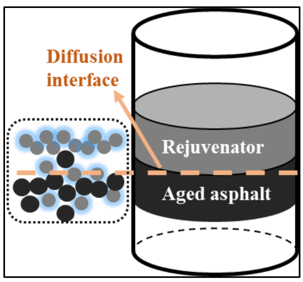


Figure 16 Schematic diagram of gravitational collapsing test

3.3.2 Mixture test

(1) Marshall stability

The Marshall stability (MS) test was used to evaluate the high temperature stability of asphalt mixtures containing different RAP content and capsules. The test process referred to NS-EN 12697-34:2020. Additionally, the Immersion Marshall test was adopted to figure out the effect of RAP and capsules on asphalt's moisture stability. o The Marshall samples are soaked in water at 60℃ for 48h, then the Marshall test is administered, which is called immersion Marshall stability (MS1). The Marshall stability ratio (RMS) was often used to express the residual Marshall stability.

$$RMS = \frac{MS_1}{MS} \times 100 \tag{8}$$

Where, RMS is the average residual moisture stability of specimens (%); MS1 is the average immersion moisture stability of specimens at 60 °C for 48 h (kN); MS is the average moisture stability of specimens at 60°C for 30 min (kN).

(2) 3-point bending

Low temperature crack resistance of asphalt mixture was measured by 3-point bending, referring to the standard NS-EN 12697-44:2019. However, in this paper, the semi-circular samples were replaced by beam samples in order to simplify experimental design; this is also the first fracture in the self-healing test. Before the test, the beam samples were placed in a thermostat at -10 ℃ for 3 h ± 0.5 h. The loading rate of the principal axis was 0.05 mm/min, which would automatically stop when the specimen fractured. The loading rate with displacement was recorded to calculate the fracture strength and fracture energy of the mixture, both with and without RAP and Ca-alginate capsules:

$$E = \frac{W}{A_{lig}} \tag{9}$$

$$W = \int F\, dx \tag{10}$$

$$A_{lig} = t(h - a) \tag{11}$$

Where E is fracture energy density (J/m^2); W is energy consumed to fracture a beam (J); A_{lig} is the ligament area (m^2); F is the load (N); dx is the differential displacement (m); h is height of samples (m).

(3) Wheel tracking test

The rutting of different asphalt mixtures containing different contents of RAP, with and without self-healing capsules, was measured using a wheel tracking test. This test refers to the standard NS EN 12697-22. Before the test, 300mm*300mm*50mm asphalt mixture plates were fixed into the mold, and the test temperature was kept at 60℃ for a minimum of 4h. The width of the rubber tire was 50mm, and the tire's thickness was 20mm. The rate of tracking was 53 passes per minute, and the wheel load was 700N. The rutting depth was recorded with passes.

(4) Self-healing test

The self-healing property of different asphalt mixtures was tested by fracture- healing-re-fracture method to evaluate the crack auto-repair capability. The test flow chart is shown in Figure 17. The fracture and re-fracture methods were used in the 3-point bending test method. The self-healing process of asphalt mixture beam is to keep the fractured beam under closed conditions at 20℃ for 48h. To evaluate the effect of Ca-alginate on the self-healing property of asphalt mixture with RAP, especially oil release in capsules, two kinds of healing methods were used. One method involved applying 20,000 passes of wheel track rutting to promote oil release in capsules before healing, while the other had no wheel track rutting and was allowed to heal for 48h at 20℃. The oil release mechanism of Ca-alginate capsules is considered to offer two possibilities; one involves broken capsules, while the other involves elastic contraction-expansion (similar to the contraction-recovery of a sponge before and after stress)[107]. Wheel track rutting simulates vehicle driving-loading to promote oil release in capsules.

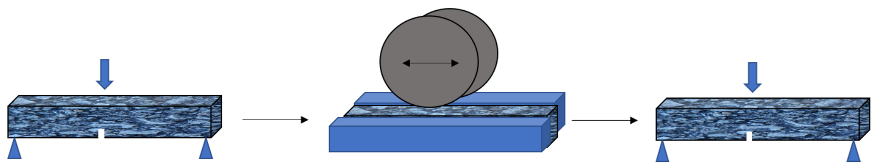


Figure 17 Self-healing test of asphalt mixture beams

The ratio of performances before and after self-healing is used as an evaluation index of the self-healing ability of asphalt mixtures. Fracture strength and energy were selected for study because they are the most important critical conditions of crack generation. The calculation of healing ratio is shown in Eq.

$$SHL_i = \frac{F_{first}}{F_{second}} \times 100\% \quad (12)$$

$$EHL_i = \frac{E_{first}}{E_{second}} \times 100\% \quad (13)$$

Where, i=1 and 2, SHL_1 and SHL_2 are the fracture strength healing ratios without and with 20,000 track rutting, respectively. EHL_1 and EHL_2 are the fracture energy healing ratios without and with 20,000 track rutting, respectively. F_{first} and E_{first} are the fracture strength and energy of the first fracture. F_{second} and E_{second} are the fracture strength and energy of the second fracture after 2d of self-healing.

4. Results and Discussion

4.1. Mechanical and self-healing performances of asphalt mixtures after laboratory-accelerated ageing

4.1.1. Basic mechanical performances

(1) Volumetric performances of asphalt mixtures

Table 7 shows the void volume (VV) and voids in mineral aggregate filled with asphalt (VFA) of different aged asphalt mixtures both with and without Ca-capsules. It was found that the capsules have a slight effect on the volume of the asphalt mixture; this is mainly because capsules are mixed into asphalt concrete as an aggregate, accounting for only 0.5% of the total aggregate, a reading that is also reported in Norambuena-Contreras's study[20]. At the same time, the ageing processes (STA and LTA) had no effect on the volume performance of asphalt mixture both with and without capsules. The formed asphalt mixtures are only in the process of accelerating thermal oxygen, and without any loading, their internal structure does not change; as a result, the volume performance does not change. It is also indirectly indicated that the capsules show no volume changes during the ageing process.

Table 7 VV and VFA of aged asphalt mixtures

	virgin	virgin with capsules	STA	STA with capsules	LTA	LTA capsules
VV (%)	3.54	3.68	3.55	3.69	3.54	3.7
VFM (%)	74.1	73.4	73.9	73.4	74.1	73.7

(2) Dry rutting resistance

After going through the STA and LTA, the rutting depth of different asphalt mixtures is shown in Figure 18. Undoubtedly, the rutting depth of asphalt mixtures decreases with advanced ageing, as aged asphalt mixtures exhibit better rutting resistance. Further, the rutting resistance of asphalt mixtures with capsules is significantly weaker than the samples without capsules at any ageing stage. This is mainly because during the rutting process, the internal structure of asphalt concrete changes, and the capsule is then squeezed to promote the release of internal oil under loading, which will further soften the asphalt and reduce the permanent deformation resistance of asphalt=concrete. The optimal design of the self-healing Ca-alginate capsule allows the capsule's release to match the asphalt's ageing process, so that it will not be released early and damage the early anti-rutting performance of asphalt concrete. Therefore, it is necessary to improve the early rutting resistance of asphalt-concrete when applying capsules to asphalt.

It also shows that the rutting depth of the LTA sample with capsules is almost the same as the virgin samples without capsules. To explain, LTA samples with capsules still have the same hardness as virgin samples without capsules; so although the capsule has a negative effect on the rutting resistance of asphalt-concrete, it has a positive effect on softening the bitumen. After LTA, the rutting depth of asphalt mixtures with capsules decreases by 17.35% (from17.11mm to 14.14mm), while the samples without capsules are reduced by 20.38% (from 14.18mm to 11.29mm). The capsules could slow down the hardening process of asphalt during the ageing process.

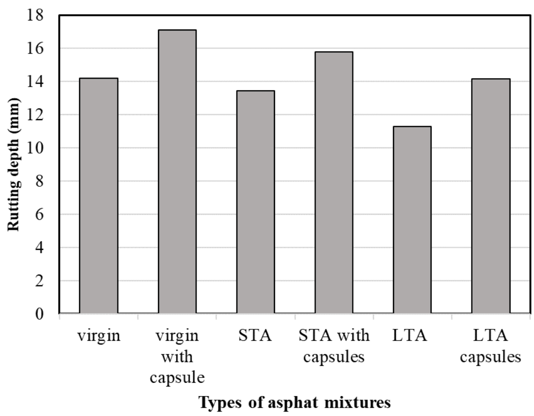


Figure 18 The rutting depth of different aged asphalt mixtures with and without capsules

(3) Marshall stability and residual Marshall stability

The residual Marshall stability (RMS) is the residual ratio of Marshall stability of asphalt-concrete samples after soaking in 60°C water for 48 hours, which is better at preventing the samples' moisture damage resistance. Firstly, as seen in Figure 19, the MS and RMS of samples both with and without capsules both decrease with advanced ageing. Indeed, the LTA is more pronounced than STA because the aged bitumen has poorer adhesion with aggregates.

Also, the MS and RMS of samples with capsules are lower than samples without capsules, which have a slight negative effect on asphalt mixtures' water stability. The capsule's surface is smooth and oily, and the adhesion to bitumen is significantly lower than that of bitumen to stones. There is also a small amount of oil (about 4%) released from capsules during mixing and compaction[20]. This factor may be the reason why capsules affect the stability of asphalt water stability.

After STA and LTA, the MS and RMS show the same trend with regard to rutting results; the change of LTA samples with capsules is lower than the samples without capsules. This means that capsules still partially slow down the ageing of asphalt-concrete without rutting loads, and laboratory-accelerated ageing (135℃ for 5h and 85℃ for 5d) might also promote the release of a small amount of oil in the capsule.

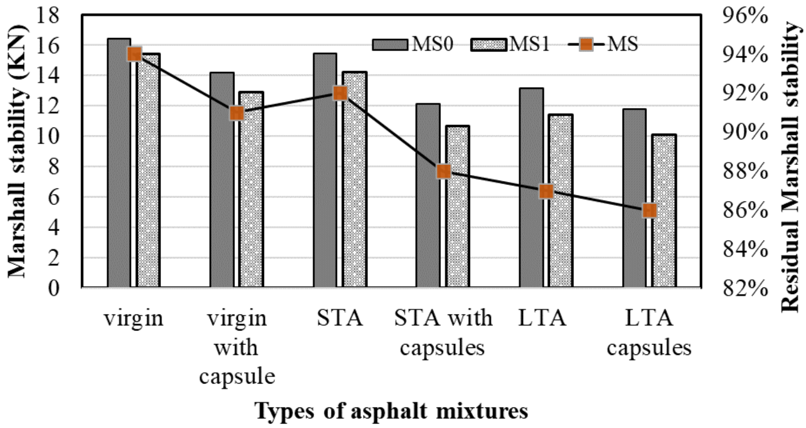


Figure 19 The Marshall stability of different aged asphalt mixtures with and without capsules

(4) Low temperature crack resistance

In order to investigate the effect of ageing on the fracture behavior of asphalt mixtures with/without capsules, at least 6 beams for each sample were tested, and the average values of the results were recorded, as shown in Figure 20. Regarding virgin samples, it can be seen from Figure 20 (a) that the critical load at fracture increases in accordance with the increase of thermal oxygen ageing degree. The critical load is 5.09KN, 5.18KN and 5.84KN for virgin, STA and LTA, respectively. At the same time, with the increase of thermal oxidative ageing, their stiffness also increases, and the fracture energy decreases, as shown in Figure 20 (b) and (c). In addition, the difference value between LTA and STA (0.66KN, 4.5KN/mm and 0.0267J/cm^2) is much greater than that between STA and virgin (0.11KN, 1.8KN/mm and 0.0118J/cm^2). This could indicate that the long-term ageing procedure as specified in AASHTO R30 has a very significant effect on the mixtures. The above phenomenon is mainly due to the hardening effect of ageing on bitumen. Thus, although the aged mixture has the highest load at fracture, once the crack begins, it propagates rapidly within the fracture zone. The high crack propagation rate reduces the fracture energy in Figure 20 (c). The trend of hardening also increases with ageing, but short-term ageing shows minor changes. The STA samples' stiffness resembles that of virgin samples, while the stiffness of LTA samples increases significantly. At the same time, when comparing the above physical parameters of the encapsulated asphalt concrete with the reference beams on different ageing degrees, it can be seen in Figure 20 that the different ageing rates on the critical load, stiffness and fracture energy of mixtures containing capsules are similar to those of the reference group. Simply stated, as ageing advances, critical load and stiffness increase while fracture energy decreases.

It can be seen that the calcium alginate capsule has almost no effect on the initial mechanical properties of the asphalt concrete. Regarding different ageing asphalt beams with and without capsules, it can be found that the critical load and stiffness of all beams with capsules are slightly less than their corresponding reference groups, while their fracture energy is slightly larger. The difference is caused by the one-time release of the oil, making the bitumen containing the capsules relatively softer. Comparing LTA and STA samples, it has also been found that the increase in critical load and stiffness and decrease in fracture energy of the beams with capsules is less than reference beams. It is highly likely that the 135 ℃ and 85 ℃ temperatures during the ageing process caused some of the oil in the capsule to escape. However, the pavement temperature cannot reach 85 ℃ during the actual service; thus, the laboratory-accelerated mixture's ageing process could not be fully applied to the ageing process of asphalt mixtures containing calcium alginate capsules. In addition, the more serious the ageing, the greater the difference between beams with capsules and without capsules. This indicates that self-healing capsules have a significant effect on the crack resistance of asphalt mixtures, especially in aged asphalt mixtures.

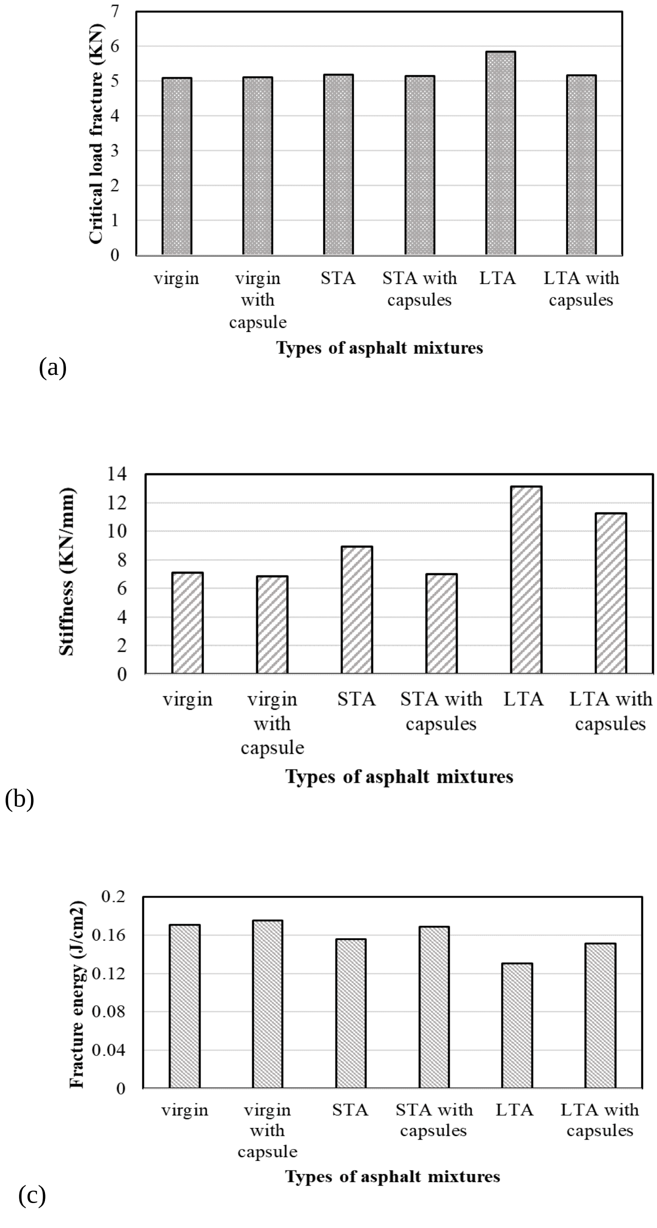


Figure 20 Mechanical properties of asphalt mixtures with different ageing types: (a) critical load at fracture; (b) stiffness; (c) fracture energy

4.1.2. Self-healing properties

The self-healing behavior of the aged asphalt mixtures with and without capsules was also investigated using a fracture-healing-refracture test. After the first fracture, the aged beams were subjected to rutting, and a second fracture test was performed after 48 hours of self-healing at 20℃[22]. The strength recovery ratio and energy recovery ratio are shown in Figure 21 and Figure 22. With the deepening of thermal-oxygen ageing, the strength recovery ratio and fracture energy recovery ratio of asphalt beams with/without capsules both decrease significantly. This is primarily because ageing reduces the self-healing ability of the asphalt itself. The main reason is that ageing makes the fluidity of asphalt mortar in asphalt concrete worse; consequently, it cannot achieve the healing level of virgin asphalt under the same conditions.

It can be seen that the strength recovery ratio of the beams containing capsules obviously improves after the sunflower oil inside the capsules is released; the LTA is increased from 23.8% to 59.8%, returning to the state with the STA. It indicates that the fracture energy recovery ratio of aged and unaged beams containing capsules is also greater than that of the asphalt mixtures' ratios without capsules. The energy healing rate of asphalt-concrete containing capsules is as high as 134.6%, which is mainly due to the asphalt's softening – after the release of sunflower oil – into binder, which increases the viscosity of asphalt mastic at room temperature. As ageing advances, the difference between the energy recovery rate of the beams with and without capsules decreases. This is because sunflower oil in the capsules also ages during the ageing process, reducing the enhancement for asphalt's self-healing performance[20].

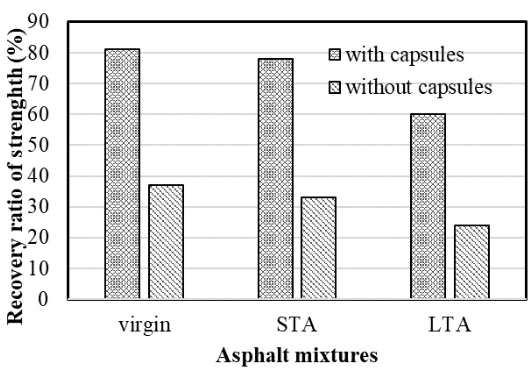


Figure 21 Recovery ratio of strength for asphalt mixture beams

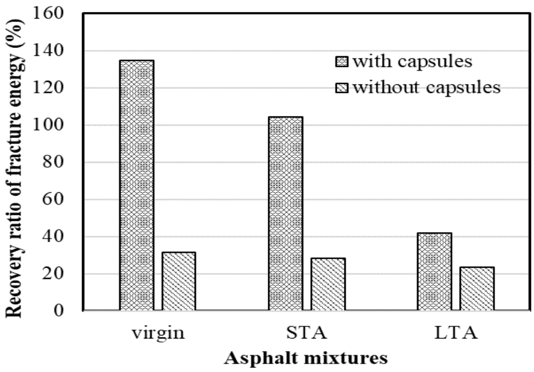


Figure 22 Recovery ratio of fracture energy for asphalt mixture beams

4.2. Mechanical and self-healing performances of asphalt mixtures with both RAP and Ca-alginate capsules

4.2.1 Determination of rejuvenator content

Rejuvenator was applied to rejuvenate aged bitumen in the RAP mixture to reach properties of virgin bitumen. Different rejuvenator contents (0wt%, 2%wt%, 4wt%, 6wt% and 8wt%) were added into extracted reclaimed bitumen. A general mixing procedure was used for adding rejuvenators to reclaimed bitumen. First, after having been extracted for two weeks, the weighed reclaimed bitumen was preheated in a heating cabinet (130°C) for 1 h. Then, the rejuvenators were mixed and stirred for 2mins by hand using a glass rod. The mixed bitumen was to be tested to find the softening point after standing still for over 2 weeks to ensure even diffusion.

The softening point is one of the most important properties that can affect the performance, durability, and workability of bituminous materials. It is also an important index used to show bitumen's hardness and degree of ageing. The softening point of bitumen increases in accordance with the speed at which asphalt ages. Conversely, when ageing asphalt is regenerated, the softening point also decreases.

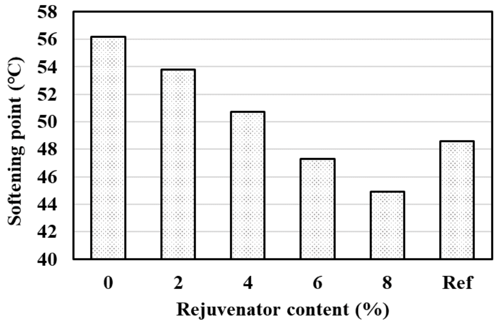


Figure 23 Softening point of RAP binder with different rejuvenator content

Figure 23 shows the softening points of reclaimed bitumen containing different rejuvenators. The softening point of reclaimed bitumen may be found when the temperature reaches 56.2℃; the softening point keeps dropping by 2-3℃ for each 2% of rejuvenator added. When 6% of rejuvenator was added, the softening point decreased by 47.3 ℃, just slightly below the softening point of 48.6℃ for virgin bitumen. Considering that dichloromethane cannot be completely distilled during the extraction of reclaimed bitumen, the tested softening point is slightly lower than the real value. The authors think that adding 6% of rejuvenator can rejuvenate the reclaimed bitumen so it will reach the hardness of virgin bitumen. So 6wt% rejuvenator, corresponding to reclaimed bitumen, will be added when designing and preparing asphalt mixtures with RAP.

4.2.2 Basic mechanical performances

(1) Volumetric performances characterization of mixture

Table 8 showed the void volume (VV), and voids in mineral aggregate filled with asphalt (VFA) of different asphalt mixtures. VFA refers to the volume of free asphalt within a mixture, which is essential for self-healing. A higher level of VFA often leads to more free asphalt that can flow and fill into cracks.

Firstly, the effect of the high content of RAP mixtures without capsules on the volumetric property of asphalt concrete without capsules was observed. The VV basically kept a steady rate (from 3.58-3.73%), with RAP content increasing from 40%-70% (referring to ref samples). The VFA also showed little decrease; this fact indicated that the design method of maintaining the same graduation and binder content had no effect on the volumetric properties of asphalt mixtures containing RAP. It might also indicate that the RAP was fully stirred and rejuvenated. Secondly, the effect of Ca-alginate capsules' addition to the volumetric property was observed. The VV showed a slight increase while the VFA showed a slight decrease. This is because the capsules were added directly without any change of graduation. At the same time, the capsules' content was only 0.5% of the asphalt mixture, so the slight effect it had on the volumetric property can basically be ignored.

Table 8 VV and VFA of asphalt mixtures

	ref	ref+ cap	ref+ RAP (40%)	ref+RAP (40%) + cap	ref+ RAP (50%)	ref+RAP (50%) + cap	ref+ RAP (60%)	ref+RAP (60%) + cap	ref+ RAP (70%)	ref+RAP (70%) + cap
VV(%)	3.58	3.68	3.64	3.69	3.62	3.73	3.62	3.64	3.62	3.66
VFA(%)	74.1	73.4	73.6	72.6	73.2	73.3	73.2	72.5	71.9	71.2

(2) Dry rutting resistance

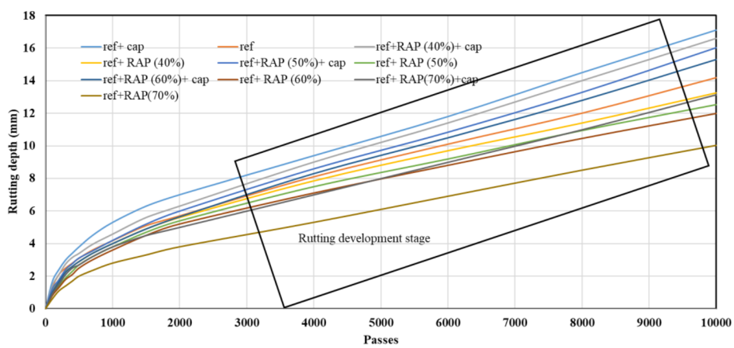


Figure 24 The rutting depth with passes of different asphalt mixtures at 60°C.

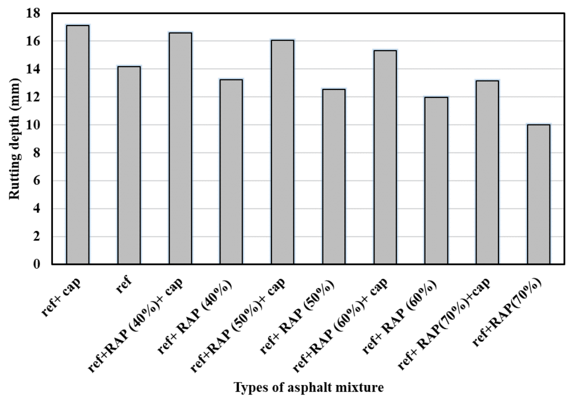


Figure 25 Rutting depth of different asphalt mixtures.

Figure 24 and Figure 25 show the rutting depth curves with passes and rutting depth results of different asphalt mixtures, respectively. Firstly, the effect of capsules on high temperature stability is discussed. As can be seen from the rutting depth results, the rutting depth of asphalt mixtures containing capsules is obviously greater than the depth of the asphalt mixture without capsules under any RAP content; further, the value of depth is increased by 20%-30% owing to the addition of capsules. This is an unavoidable shortcoming of capsule application; Figure 24 demonstrates this phenomenon. During the rutting process, there is a stage where the rut depth increases steadily, which is defined as the rutting development stage.

The result of the linear fitting of this curve is shown in Table 9; in this case, all slopes were calculated. The slopes of asphalt mixtures containing capsules ranged from 1.24×10^{-3} mm/pass to 1.33×10^{-3} mm/pass, while the slopes of asphalt mixtures without capsules ranged from 0.81×10^{-3} mm/pass to 1.11×10^{-3} mm/pass. This discrepancy indicates that capsules promote a steady increase in rut depth over the tested range, primarily because rutting promotes the release of oil from capsules, which further softens the bitumen and reduces its rutting resistance. Each time the tire passes over the surface, the capsules in the mixture deform accordingly, and oil is released, similar to when water is released from a sponge before and after pressure is applied to it.

Table 9 Rutting curves in relation to fitting of different asphalt pavements during the rutting development stage

	ref+ cap	ref	ref +RAP (40%) + cap	ref+ RAP (40%)	ref +RAP (50%) + cap	ref+ RAP (50%)	Ref +RAP (60%) + cap	ref+ RAP (60%)	Ref +RAP (70%) +cap	ref + RAP (70%)
Fitted line	y=0.0 0131x +4.06	y=0.0 0111x +3.27	y=0.0 0133x +3.41	Y=0.0 0103x +3.22	y=0.0 0130x +3.07	Y=0.0 0098x +3.08	y=0.0 0125x +2.91	y=0.0 0094x +2.93	y=0.0 0124x +2.77	y=0.0 0081x +2.01
R2	0.997	0.994	0.997	0.99	0.996	0.988	0.997	0.987	0.99	0.998
Slope× 10^{-3}/(mm/pass)	**1.31**	**1.11**	**1.33**	**1.03**	**1.3**	**0.98**	**1.25**	**0.94**	**1.24**	**0.81**

Secondly, only the effect of RAP content on rutting resistance has been discussed. When the RAP content has increased from 0 to 70%, the rutting depth has also significantly decreased. The results indicate that RAP has a higher level of stiffness and can enhance asphalt mixtures' rutting resistance. It demonstrates that the enhancement function of RAP on permanent deformation seems more prominent than the attenuation effects of rejuvenators. More specifically, the rutting depth decreased from 14.18mm to 13.25mm when 40% RAP was replaced. The value of reduction was only 0.93mm, while the value of reduction reached 3.23mm when RAP replacement increased from 40% to 70%. This indicates that the effect of replacing a large amount of RAP is more significant than that of a small amount for improving the dry rutting resistance of asphalt mixtures.

When considering the overall impact of capsules and RAP on asphalt rutting resistance, the rutting depth of asphalt mixtures containing both RAP and capsules is deeper than those containing only RAP but lower than those containing only capsules. So the reduction of asphalt rutting resistance using capsules can be partially offset by the increase owing to RAP's addition.

(3) Marshall stability and residual Marshall stability

Next, Figure 26 shows that RAP replacement has a negative effect on both Marshall stability and residual Marshall stability; this becomes more obvious as RAP content increases. For instance, when RAP content increased from 0% to 40% and from 40% to 70%, the MS decreased from 16.42KN to 14.1KN, then to 12.4KN, while the RMS decreased from 94% to

90%, then to 86.3%. This might be due to the lower fatigue endurance of asphalt mixes containing a higher content of heavily aged RAP.

At the same time, the addition of capsules not only reduced the initial Marshall stability of asphalt mixtures, but also reduced its residual stability in any RAP content. More specifically, when capsules were added to the reference asphalt mixture, the MS decreased from 16.42KN to 14.21KN, and the RMS decreased from 94% to 91%. When using different RAP content, the MS and RMS of asphalt mixtures containing capsules had a corresponding decline relative to samples without capsules. The capsules reduced the Marshall stability of asphalt mixtures, the most likely reason being that the capsules were smooth and oily on the surface, and the bonding force between asphalt mortar and it was much lower than that between asphalt mortar and aggregates. Also, soaking in 60°C water for 48 hours may have also caused a small amount of rejuvenator in the capsule to flow out, further affecting the adhesion of the sample.

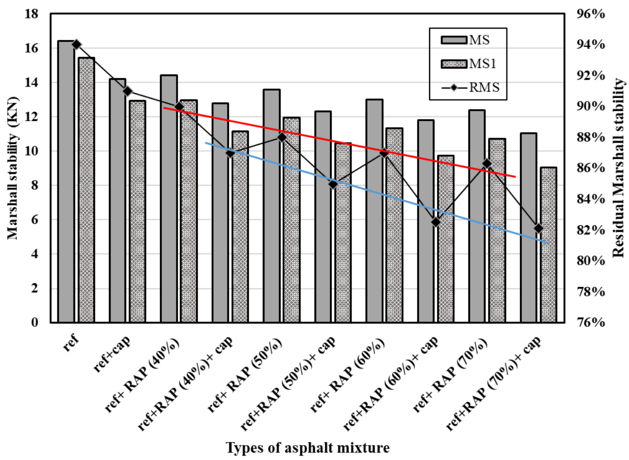


Figure 26 Moisture stability results of different asphalt mixtures

Figure 26 also shows the hazards of capsules and RAP for RMS resistance to asphalt mixtures. It may be observed that the slope of the curve of the RMS with RAP replacement content of the sample containing the capsules (the blue line) is larger than that of the sample without the capsules (the red line). Due to this combined effect, MS and RMS became the most important mechanical index of RAP replacement quantity in asphalt mixtures containing Ca-alginate capsules. When the RAP replacement exceeded 40%, the RMS reduced to 84.2%, thereby not meeting the technical requirements listed in the specifications.

(4) Low temperature crack resistance

Based on the above results, both RAP and capsules have a negative effect on the moisture stability of asphalt mixtures; when the RAP content of asphalt mixtures containing capsules exceeds 40%, neither the Marshall stability nor the residual stability fulfills the technical requirements listed in the specifications. Therefore, when studying its low temperature and self-healing properties, a RAP content of 40% was the only option considered.

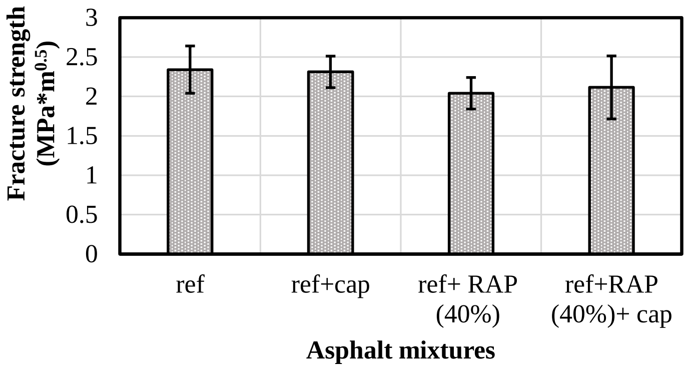


Figure 27 Fracture strength at -10℃

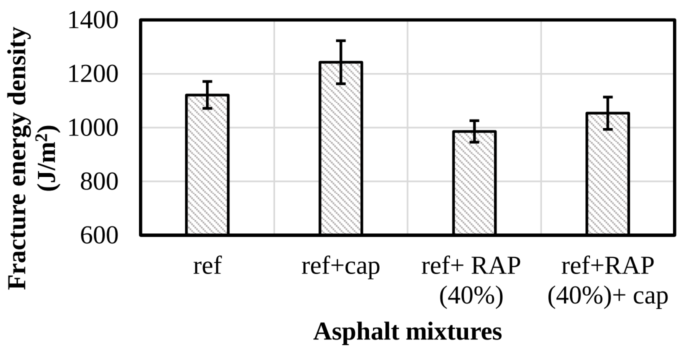


Figure 28 Fracture energy density at -10℃

Figure 27 and Figure 28 show the fracture strength and fracture energy of different asphalt mixtures at -10°C. Accordingly, a 40% RAP replacement reduced its fracture strength from 2.341 MPa*$m^{0.5}$ to 2.041 MPa*$m^{0.5}$, while the fracture energy was also reduced from 1121.2 J/m^2 to 985 J/m^2. This indicates that the addition of RAP resulted in significantly lower flexibility due to the oxidized binder in the RAP. So the asphalt mixtures with RAP were more rigid, brittle and less flexible than those without RAP, which was also reported in the study by Costa et al.[137]. On the other hand, although the addition of capsules has little effect on fracture toughness, it increases the fracture energy of asphalt mixture. This may be because some capsules were broken or deformed during the mixing and compacting of asphalt mixtures, causing a small amount of oil to flow out (to improve the flexibility of asphalt mixtures at low temperatures). According to a study by Norambuena-Contreras et al.[20], only 4% oil flowed out during this process.

When both 40% RAP and capsules were added to asphalt mixtures at the same time, the results showed that their respective effects on the crack resistance of asphalt mixtures could be neutralized. The fracture toughness and energy of asphalt mixtures with 40% RAP and capsules can recover to the same level as virgin asphalt mixtures.

4.2.3. Self-healing capability

Figure 29 and Figure 30 show the self-healing ratios of asphalt mixture beam without tracking rutting during the healing process. The fracture strength self-healing ratio (SHL) and fracture energy self-healing ratio (EHL) decreased from 32.8% to 25.5%, and 28.2% to 23.5%, respectively, due to the replacement of 40% RAP; yet they increased to 48.7% and 52.2% because of the addition of Ca-alginate capsules. It can be seen that the self-healing ability of rejuvenated RAP is lower than that of the virgin asphalt mixture. At the same time, capsules can effectively increase the self-healing ability of asphalt mixtures, especially fracture energy. The results also show that the SHL and EHL of asphalt mixtures containing both RAP and capsules are higher than the reference samples. The positive effect of capsules on the self-healing ability of asphalt mixtures outweighs the negative effects of RAP. However, this is only when the sample had not considered rutting and the capsule had not released a large amount of rejuvenator.

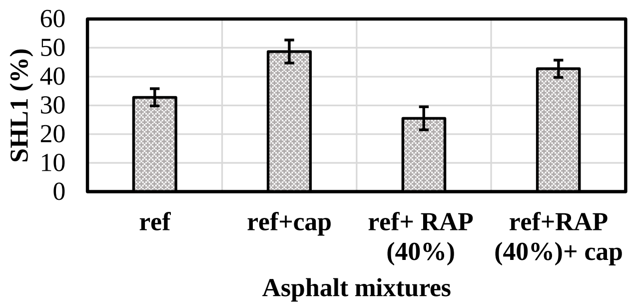


Figure 29 Fracture strength healing ratio without track rutting

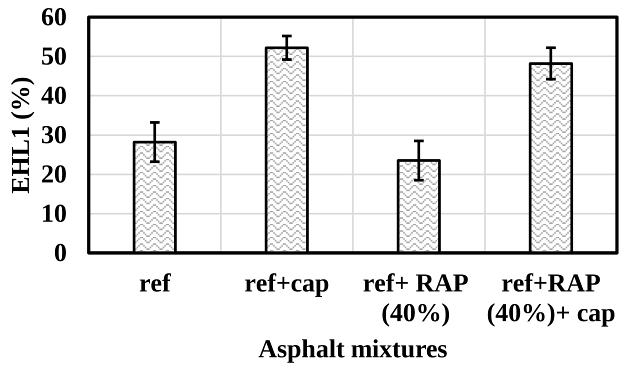


Figure 30 Fracture energy healing ratio without track rutting

Further, the self-healing ratio of the asphalt mixture beam has also been calculated after 20000 passes tracking rutting during the healing process to promote capsules' oil release. The results are shown in Figure 31 and Figure 32.

It has been determined that wheel track rutting has no effect on asphalt mixtures without capsules on self-healing ability, regardless of whether RAP has been replaced. The vertical stresses perpendicular to the crack direction from rutting have no effect on the healing of cracks in asphalt; they help significantly to improve the self-healing ability of asphalt mixtures containing capsules. The SHL and EHL of asphalt mixtures containing capsules reached 81.1% and 134.6%, respectively. The crack-related self-healing ability of asphalt mixtures showed a significant improvement.

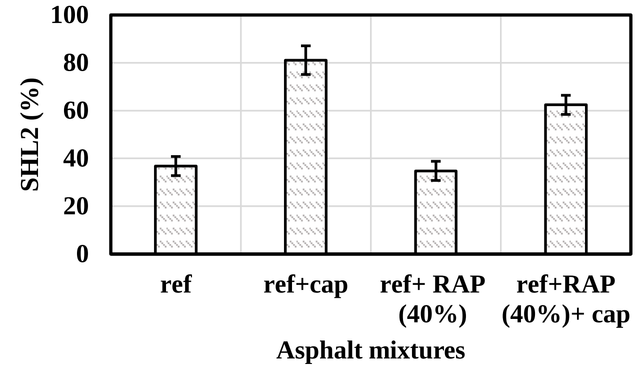


Figure 31 Fracture strength healing ratio with 20000 passes track rutting

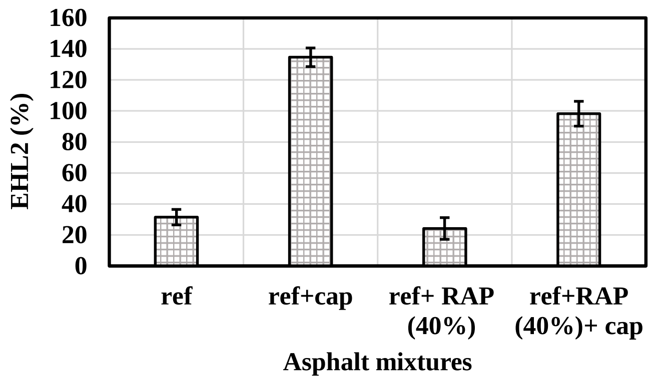


Figure 32 Fracture energy healing ratio with 20000 passes track rutting

There is no doubt that wheel rutting significantly increases the self-healing ability of asphalt mixtures containing capsules. The samples could not withstand wheel track rutting; indeed, only a small amount of oil flowed out from capsules broken during crack interface. This is because of the capsules' multi-chambered structure. When a capsule is split in two, only a few chambers are damaged; the other chambers remain largely intact, and the oil does not flow out. The increase of self-healing is only due to the small amounts of rejuvenators released by the mixing, compression, and rupture of the capsules' cracks. However, wheeling rutting in the laboratory can effectively simulate the driving load of an actual road surface, which can also promote oil flow from capsules that softens the bitumen, especially crack surfaces, to improve cracks' self-healing ability. This is why the self-healing ratio of samples containing capsules after rutting is higher than that without rutting. In addition, the softener asphalt mixtures had longer displacement when they were subjected to the fracture test, which indicated higher fracture energy. It is well known that fracture is the reverse process of healing, and the release of capsules not only increases the self-healing ability of cracks but also increases the crack resistance of asphalt mixtures containing capsules.

More importantly, the SHL and EHL of asphalt mixtures containing both capsules and RAP also increase to 62.4% and 98.2%, showing a much higher growth rate than the self-healing ability of virgin asphalt mixtures. This expanded self-healing ability should be consistent with the self-healing ability without RAP. The positive effect brought about by the capsule's full release on self-healing of cracks in asphalt mixtures is far better than the negative effect brought about by replacing RAP. During actual road service, the outflow of oil in the Ca-alginate capsules is a long-term process of multiple instances of sustained release depending on time and load factors; also, they are not released all at once due to the multi-chamber structure. At the same time, RAP rejuvenation and asphalt ageing are also time-dependent. The comprehensive utilization of capsules and RAP can better make the asphalt mixtures containing RAP maintain their extremely high level of self-healing ability for a long time, overcoming the shortcomings of RAP utilization. This also provides a better solution for the design and utilization of long-life asphalt pavement containing RAP, which can be fully utilized while also ensuring asphalt pavement's durability and service life.

4.3. Diffusion of oil from capsules in bitumen

Ca-alginate capsules can both rejuvenate aged asphalt and RAP, and improve their self-healing capabilities; in this process, the core material (sunflower oil) plays the most important role. Based on the above rejuvenating and self-healing theories, the tiny molecules in the aged bitumen are replenished with the capsules' oil through a process of physical diffusion, which regeneration and softening to heal cracks. In order to reveal capsules' diffusion capabilities as well as their rejuvenating and self-healing properties in relation to aged asphalt and RAP, sunflower oil and broken capsules were added to aged bitumen so that we could discuss any diffusion that took place in addition to the mixture's rheological properties, flow behavior and low temperature creep.

Table 10 shows the results of diffusion tests where sunflower oil was added to different bitumen. In the sinking time test, the bitumen specimen became soft and deformed because of molecular exchange and buoyancy; thus, it sank to the bottom. It took 982s, 1542s and 1436s to immerse the bitumen samples for virgin, PAV and RAP, respectively. The results show that the sunflower oil diffusion rate in virgin asphalt is greater than in aged bitumen, including PAV bitumen and RAP bitumen. At the same time, the diffusion rates of oil in PAV and RAP are similar. The softening rate test and gravitational collapsing test achieved the same results.

Table 10 The results of diffusion tests

	Sinking time (s)	Softening time (s)	Collapsing time (s)
Oil in virgin bitumen	982	726	1128
Oil in PAV bitumen	1542	1265	1934
Oil in RAP bitumen	1436	1156	1826

Diffusion that takes place when the rejuvenator penetrates asphalt can be interpreted as the result of random molecular movements called Brownian motions. Cussler[138] has concluded that the significant factors that influence the rejuvenator diffusion rate primarily involve the size and shape of molecules or agglomerations, intermolecular forces, temperature and so forth.

Next, based on Fick's law and Stoke-Einstein's equation[139], which have been used for modelling the diffusion process with proper applicability, are shown in Equation (16) and Equation (17) below. According to Equation (16), which focuses on the rejuvenating process itself, the diffusion coefficient can account for a large part of enhancing the penetration rate. Meanwhile, Equation (17) explains the relative factors influencing diffusion rates, illustrating that smaller viscosity and molecular size generally increase the diffusion coefficient. The diffusion of sunflower oil in virgin asphalt is greater than that in aged asphalt under the same conditions, most likely because the molecular size of aged asphalt is much larger than that found in virgin asphalt. It also indicated that the rate of oil diffusion in bitumen and penetration of inorganic molecules in solution are different; moreover, the difference in molecular size concentration of the two phases does not play a major role in this process.

Fick's law:

$$J = -D * \frac{\partial c}{\partial x} \tag{16}$$

Where J is diffusion flux (mol/m^2·s), c is concentration (mol/m^3), x is the diffusion depth (m), and D is the diffusion coefficient.

Stoke-Einstein equation:

$$\mathrm{D} = \frac{k_B T}{6\pi\mu(R)} \tag{17}$$

Where D is diffusion rate (m^2/s), R is the mean molecular radius, μ is dynamic viscosity (Pa·s), k_B is Boltzmann's constant ($1.3807*10^{-23}$J/K), and T is absolute temperature (K).

4.4. Rheological properties

4.4.1. PAV aged bitumen

Any changes made to the chemical composition of asphalt binder will definitely affect the rheological properties of asphalt. In order to analyze the mechanism of self-healing improvement from a rheological property point of view, Figure 33 and Figure 34 show the temperature sweep results and frequency sweep results of different asphalt mortars, respectively. The main curves of different binders were constructed by Williams–Landel–Ferry (WLF) Time-Temperature Superposition principle (see Eq. (18)) based on the frequency sweep analysis results in order to study rheological properties over a wide frequency range.

$$\log\alpha_T = \frac{-C_1(T-T_0)}{C_2+(T-T_0)} \tag{18}$$

where α_T is the horizon shift factor, T is the actual measured temperature, C_1 and C_2 are constants, and T_0 is reference temperature.

During construction, 30℃ was selected as the reference temperature. The formula for calculating replaced frequency (f_R), complex modulus (G*) and phase angle (δ) were shown in Eq. (19), Eq. (20) and Eq. (21), respectively[140].

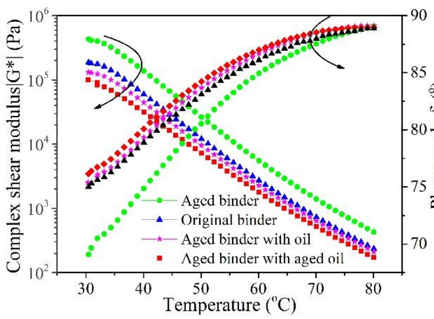
$$f_R = f \times \alpha_T \tag{19}$$

$$G^* = G_{min} + (G_{max} - G_{min}) \times (1 - \exp(-\left(\frac{f_R}{\beta_G}\right)^{\gamma_G})) \tag{20}$$

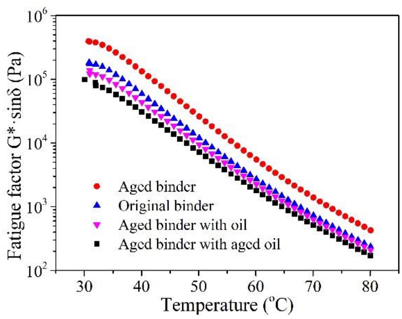
$$\delta^* = \delta_{min} + (\delta_{max} - \delta_{min}) \times (1 - \exp(-\left(\frac{f_R}{\beta_\delta}\right)^{\gamma_\delta})) \tag{21}$$

where f is the testing frequency in DSR apparatus, G* is the complex modulus in master curves, G_{min} and G_{max} are the complex modulus when f_R is 0 and infinity, δ* is the phase angle in master curves, δ_{min} and δ_{max} are the phase angles when f_R is infinity and 0, β_G β_δ γ_G γ_δ are the curve parameters.

At the same time, in order to make additional comparisons, a set of reference groups was added to the experiment's design process. After the sunflower oil in the capsules' core material had aged under the same conditions as the asphalt binder, it was added to the aged asphalt in the same proportion. It can be seen from the temperature sweep results in Figure 33, the difference in complex shear viscosity, phase angle and fatigue factor of different types of asphalt binder samples at low temperatures is much greater than that at high temperatures, which are caused by asphalt's basic properties. While the asphalt-concrete pavement containing capsules is paved to a higher degree under relatively low temperature conditions, the property's difference and recovery should be further studied at low temperatures. At the same time, the rheological properties of the aged bitumen samples are worse than those of the other three types of samples; in addition, aged binder containing oil and aged binder containing aged oil can both recover the rheological properties to the same level as virgin bitumen. It can be seen that when sunflower oil is released from the capsules and physically penetrates aged asphalt, this effectively restores its rheological properties and rejuvenates aged asphalt concrete pavement. Furthermore, its self-healing performance noticeably improves.



(a)



(b)

Figure 33 Results of DSR temperature sweep test: (a) Complex shear modulus and Phase angle; (b) Fatigue factor

The results also show that the sample of aged binder containing aged oil and the sample of aged binder containing oil basically makes no difference to the rejuvenation of the rheological properties of the aged asphalt concrete. It can be seen from the curve that the rheological properties indexes of aged binder containing aged oil are slightly better than that of aged binder containing oil, which may be due to the fact that the directly aged sunflower oil volatilizes the ultra-light components with very little internal content, so the effective proportion of adding aged oil is slightly higher than that of simultaneously adding ageing oil and asphalt in the same proportion.

The main curve in Figure 34 also shows that the results are basically consistent with the temperature sweep. The reference temperature for constructing the master curves is 30℃. Further, in the entire frequency range, the complex shear modulus of the aged asphalt binder is about 5 times higher than that of the other three samples at the same frequency. And the phase angle is also lower than the other three samples. This indicates that ageing reduces the complex shear modulus of the bitumen and increases the sensitivity of the phase angle; in addition, the bitumen becomes harder. At the same time, the addition of oil from capsules makes the modulus recover more than the results before being aged; as a result, the sensitivity of the phase angle is more obvious. This is because the light components supplemented by the oil are still stronger than those lost during ageing, and these light components have a relative significance to the phase angle. Sunflower oil can effectively restore the complex shear modulus and phase angle of the aged asphalt-concrete over the full frequency sweep range. Aged bitumen can also be rejuvenated and softened to improve its self-healing capability.

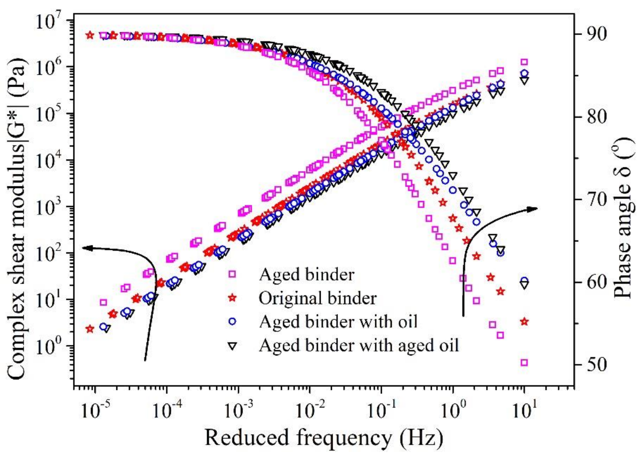


Figure 34 Master curves of complex modulus and phase angle of different asphalt binders

4.4.2. RAP bitumen

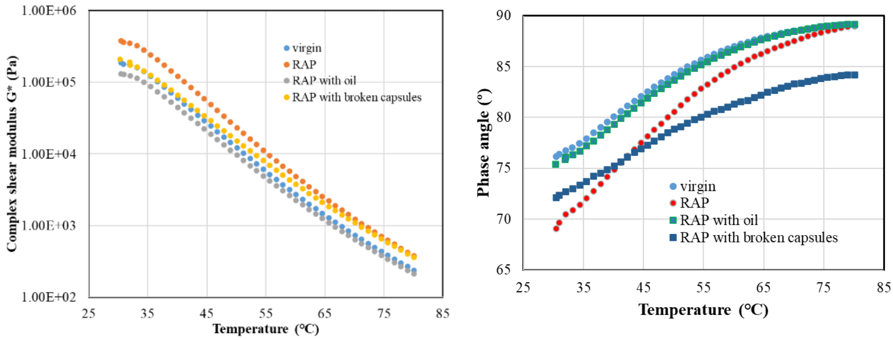


Figure 35 Results of DSR temperature sweep test of different RAP bitumen: (a) Complex shear modulus (b) Phase angle

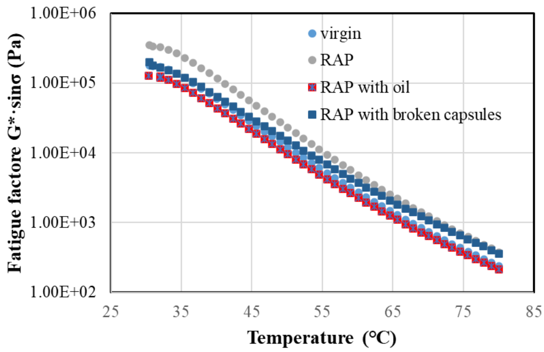


Figure 36 Fatigue factor of different RAP bitumen

Regarding RAP samples, the sample rejuvenated RAP by directly using oil; it also rejuvenated RAP by using broken capsules containing the same oil. In addition, the same temperature and frequency sweep were applied to PAV bitumen. Figure 35 and Figure 36 show the temperature sweep results. The complex shear modulus and phase angle of RAP are obviously lower than those of virgin samples. This is primarily because RAP has been aged, and its rheological properties have declined severely. For instance, especially at low temperatures, RAP's phase angle and fatigue factor are significantly lower than virgin samples, which means that RAP asphalt samples are more prone to fatigue cracking at low temperatures. But after rejuvenating RAP with sunflower oil extracted from capsules, the modulus, phase angle and fatigue factor of RAP bitumen can recover to the virgin level, which shows similar laboratory-accelerated ageing samples. Broken capsules containing oil were also added to RAP bitumen; consequently, the appearance of the capsule shell material, which is incompatible with the bitumen material, leads to a phenomenon known as phase angle shift. When compared to the RAP sample, the inner core material assumes a more prominent role at low temperatures, resulting in a higher phase angle of rejuvenated samples by broken capsules. However, at high temperatures, the broken shell material remains unaffected by temperature; however, bitumen's viscosity decreases rapidly, and its effects are also highlighted. This phenomenon is particularly evident in the main curve image of the asphalt material (Figure 36). By using the WLF model, the temperature is replaced by frequency. It may be observed that at low frequencies (high temperatures), the phase angle of RAP containing broken capsules is significantly lower than that of the other three samples. Conversely, at high frequencies (low temperatures), the rheological properties of the rejuvenated bitumen containing broken capsules are still superior to those of RAP.

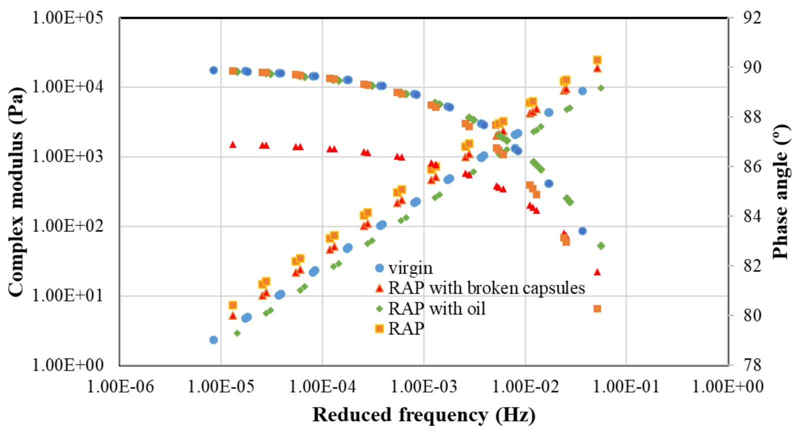


Figure 37 Master curves of complex modulus and phase angle of different RAP bitumen

The primary function of calcium alginate capsules is to reduce the viscosity of asphalt at low temperatures. Simultaneously, because of the capsules' release mechanism, during the service life of asphalt pavement containing capsules, the capsules experience minimal breakage that could affect the asphalt's rheological properties. Instead, they mostly deform or break into small pieces. Thus, it may be observed that the capsules do not impede the regeneration of aged asphalt-concrete or the enhancement of its self-healing performance.

4.5. Self-healing mechanism

4.5.1. Flow behavior of PAV bitumen

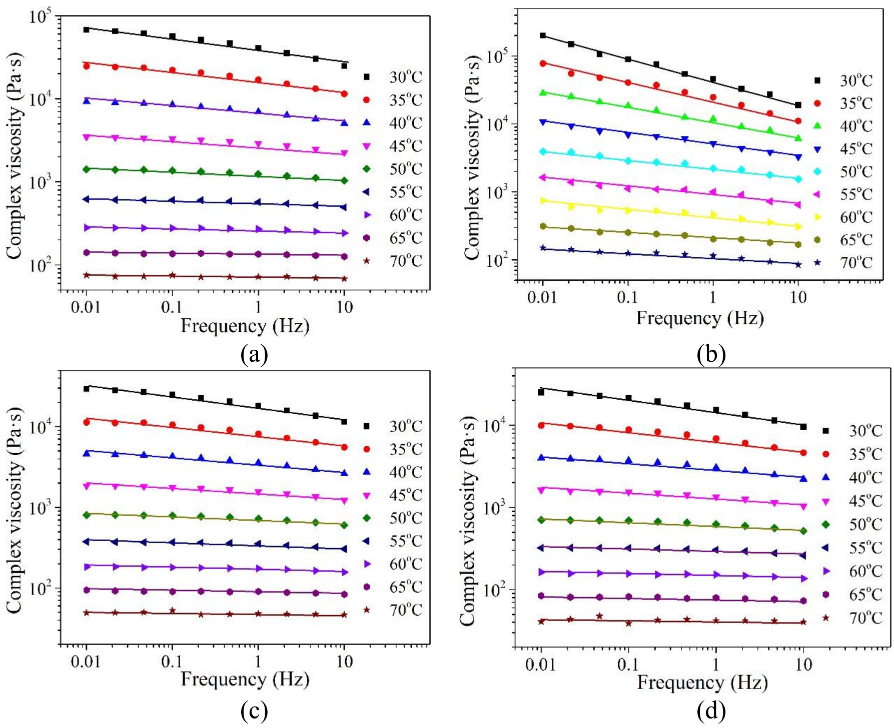


Figure 38 Complex viscosity-frequency curves of different asphalt binders: (a) Original binder; (b) Aged binder; (c) Aged binder with oil; (d) Aged binder with aged oil

In the frequency sweep results, the frequency-complex viscosity curves of the four binder samples are listed separately as shown in Figure 11. The flow behavior index (n) of different binders could be obtained at each tested temperature by fitting a power-law model (Ostwald-De Waele model) according to Eq. (22) [141,142].

$$\eta^* = m \cdot f^{n-1} \tag{22}$$

where η* is the complex viscosity (Pa·s), f is the testing frequency (Hz), m and n are the fitting parameters.

The sensitivity of the complex viscosity to frequency fit is different at different temperatures, the slope of which represents an indicator of bitumen's prevailing behavior. Table 11 and Figure 38 show the fitting results. It is found that the values of R^2 are high, which shows complex viscosity and sweep frequency have a good exponential fit at all temperature ranges. The parameter "n" is the slope of the viscosity-frequency curve, which is usually used to present the flow behavior index of Newtonian fluids. Its value is between 0 and 1; to explain, a value of 0 indicates that the material is solid, while a value of 1 indicates that the material is an absolute fluid[38].

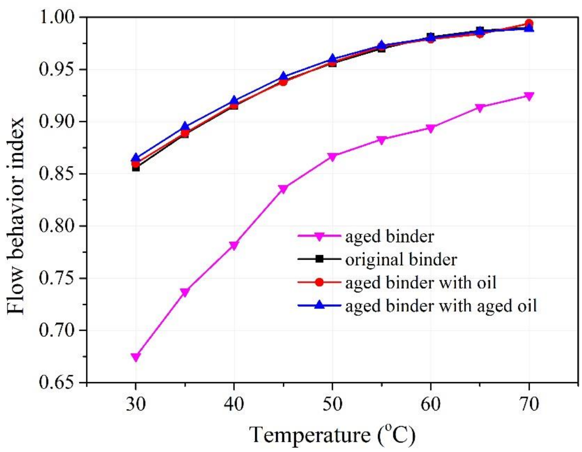


Figure 39 Flow behavior index of different asphalt binders

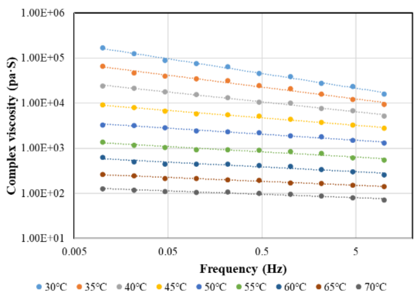
According to Figure 39, it may be found that the flow behavior index of several asphalt binders increases along with increasing temperature, which is determined by asphalt's temperature sensitivity. It is difficult for asphalt pavements to reach very high temperatures during practical application, especially in northern climates. In order to improve asphalt's self-healing properties, the best method is increasing flow capability at low temperatures. Figure 39 shows that aged asphalt binder has worse flow capability than virgin binder at all test temperature ranges, which means that ageing has severely reduced the self-healing capability of asphalt. However, flow capability has been recovered to the reference level for encapsulated oil that is added to aged asphalt binder after the capsules break. It may be posited that the healing mechanism found in calcium-alginate capsules is the following: in the crack's local microenvironment, the cracks in the asphalt mixture pass through the asphalt binder, affecting the capsules; compressive forces make the rejuvenator flow out of the capsules in small amounts, reducing the viscosity of bitumen around them; finally, bitumen flows into the crack, sealing it. Then, with the rejuvenator's further diffusion, the rheological properties of the aged asphalt are also restored.

Table 11 Fitting results of flow behavior index of different asphalt binders at different temperatures

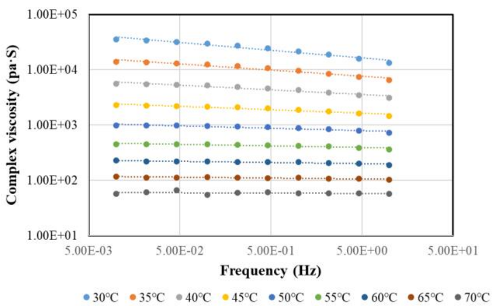
Binder	Temperature (℃)	Fitting formula ($y=a\cdot x^b$)	R^2	Flow behavior index
Original binder	30	$y = 38614x^{-0.144}$	0.9622	0.856
	35	$y = 16195x^{-0.112}$	0.946	0.888
	40	$y = 6673.6x^{-0.085}$	0.9425	0.915
	45	$y = 2788x^{-0.061}$	0.9139	0.939
	50	$y = 1205x^{-0.044}$	0.9054	0.956
	55	$y = 554.13x^{-0.03}$	0.8493	0.97
	60	$y = 263.5x^{-0.019}$	0.8825	0.981
	65	$y = 132.84x^{-0.013}$	0.9344	0.987
	70	$y = 71.158x^{-0.01}$	0.8865	0.99
Aged binder	30	$y = 42996x^{-0.325}$	0.9941	0.675
	35	$y = 22434x^{-0.263}$	0.9845	0.737
	40	$y = 10868x^{-0.218}$	0.8915	0.782
	45	$y = 4991.1x^{-0.164}$	0.9881	0.836
	50	$y = 2218.1x^{-0.133}$	0.9793	0.867
	55	$y = 913.26x^{-0.117}$	0.939	0.883
	60	$y = 426.07x^{-0.106}$	0.9255	0.894
	65	$y = 206.82x^{-0.086}$	0.8839	0.914
	70	$y = 107.69x^{-0.075}$	0.9375	0.925
Aged binder with oil	30	$y = 16651x^{-0.14}$	0.9585	0.86
	35	$y = 7543.8x^{-0.111}$	0.946	0.889
	40	$y = 3226.6x^{-0.084}$	0.9282	0.916
	45	$y = 1496.8x^{-0.062}$	0.9065	0.938
	50	$y = 707.7x^{-0.043}$	0.8812	0.957
	55	$y = 343.89x^{-0.028}$	0.9072	0.972
	60	$y = 168.06x^{-0.021}$	0.866	0.979
	65	$y = 87.707x^{-0.016}$	0.8423	0.984
	70	$y = 46.849x^{-0.006}$	0.8628	0.994
Aged binder with aged oil	30	$y = 15383x^{-0.135}$	0.9593	0.865
	35	$y = 6782.4x^{-0.105}$	0.925	0.895
	40	$y = 3021.9x^{-0.08}$	0.9307	0.92
	45	$y = 1413.9x^{-0.057}$	0.9046	0.943
	50	$y = 602.52x^{-0.04}$	0.8695	0.96
	55	$y = 311.33x^{-0.027}$	0.9246	0.973
	60	$y = 150.42x^{-0.02}$	0.8416	0.98
	65	$y = 78.161x^{-0.014}$	0.9322	0.986
	70	$y = 45.852x^{-0.011}$	0.8983	0.989

4.5.2. Flow behavior of RAP binder

Since the broken capsule shell materials do not flow into asphalt concrete, their flow behavior is not discussed in this section. Figure 39 depicts viscosity-frequency plots for RAP bitumen and rejuvenated RAP bitumen. Next, as shown in Figure 40, by fitting Equation 22, the flow behavior index of RAP asphalt is obtained; its fundamental behavior follows a pattern similar to PAV ageing. The flow behavior of RAP is significantly lower than that of virgin bitumen, especially at low temperatures, which indicates the RAP bitumen has aged. However, after being rejuvenated, its flow behavior returns to almost the same level as virgin bitumen. The mechanism by which Ca-alginate improves the self-healing performance of RAP is akin to that of PAV. Over time, when the asphalt pavement containing capsules has been in service for many years, the internal bitumen will have aged. During this period, the internal capsules release sunflower oil under the stress load, which may restore the aged bitumen's flow performance. In the event of a crack, bitumen can flow into the crack under capillary force, effectively healing it.



(a)



(b)

Figure 40 Complex viscosity-frequency curves of bitumen: (a) RAP; (b) rejuvenated RAP by oil

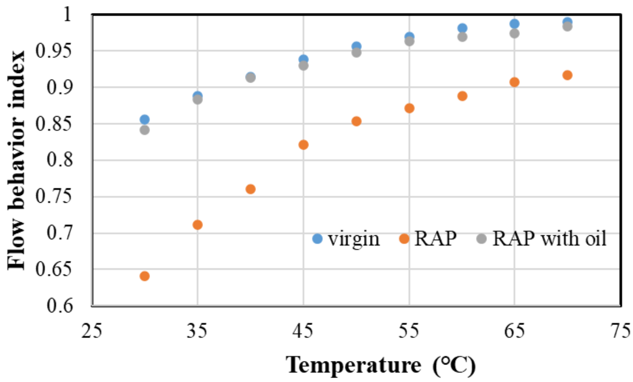


Figure 41 Flow behavior index of different RAP bitumen

4.5.3. Chemical component supplement

In order to clearly understand how components change asphalt binder in the mixture after going through different processes such as ageing and capsules release, Table 12 shows the four-component (SARA) content of asphalt binder extracted from different asphalt mixtures. As ageing increases, the content of saturates in the asphalt continue to decrease while the asphaltene increases significantly: however, the aromatics and resins experience only minor change. This phenomenon might be caused by the fact that the aromatics were first condensed to resins, and the resins were then condensed to asphaltene, which led to the increase of asphaltene during the ageing process[143]. The "Colloidal Instability Index" (C_{II}) has also been used to describe the bitumen using the dispersed polar fluid model, which calculates by Eq18. Lesser values of the index indicate higher stability and more widespread dispersion of the micelle fractions in the bitumen[144]. Thermal oxidative ageing has also exacerbated the colloidal instability of asphalt from type-0 results. Comparing different asphalt binders extracted from concrete both containing capsules and without capsules (data type-0 and type-1 group), the SARA component and C_{II} are similar, which shows that the capsules are basically not released during the concrete mixing, compacting and ageing process, having a certain level of weather resistance and long-term storage ability.

When the sunflower oil found in the capsules flows into the asphalt binder after the fatigue load, where oil currently accounts for about 5% of binders [22], it may be seen that the saturates and aromatics are increased; thus, the aged asphalt binder is rejuvenated.

The self-healing ability of STA-2, LTA-2 and virgin-2 significantly increases compared to STA-0, LTA-0 and UVA-0; in contrast, the asphaltene content after rejuvenation did not decrease a great deal, yet the lightweight asphalt increased to a certain degree. It may be found that the improvement of the asphalt binder's self-healing ability mainly depends on the lightweight components. Therefore, the sunflower oil in the calcium alginate capsules can significantly improve the self-healing and rejuvenation ability of the aged asphalt mixture.

$$C_{II} = (Saturate + Asphaltness)/(Aromatic + Resin) \tag{18}$$

Table 12 Four components (SARA) percentage of different asphalt binders

Samples		Saturate (%)	Aromatic (%)	Resin (%)	Asphaltene (%)	C_{II}
virgin-0	Without capsules	15.46	39.94	30.7	13.9	0.416
STA-0		14.72	38.32	29.75	17.21	0.469
LTA-0		13.4	35.04	26.89	24.67	**0.617**
virgin-1	With capsules	15.34	40.01	29.98	14.67	0.429
STA-1		15.01	38.87	28.85	17.27	0.477
LTA-1		13.02	36.59	27.05	23.34	0.571
virgin-2	Capsule release	17.01	43.2	30.07	9.72	0.365
STA-2		16.45	42.04	29.16	12.35	0.405
LTA-2		14.34	40.21	27.03	18.42	**0.487**

4.6. Low temperature creep

BBR tests asphalt binder's creep stiffness (S) and creep rate (m-value). Creep stiffness modulus indicates the ability of asphalt mixtures to resist permanent deformation. Creep rate indicates asphalt's stress relaxation ability at low temperatures. Samples reflect a better low temperature crack resistance, with S being smaller and m-value being higher. In this particular research project, the asphalt beams were tested at -12^{o} C.

According to the Strategic Highway Research Program, the stiffness modulus of asphalt samples ought to be smaller than 300MPa at measuring temperature, and the samples' creep rate should be greater than 0.3. Table 13 shows that in the test results, there appeared an excess creep rate at the testing temperature; this was because rejuvenators caused the asphalt beams to soften and deform beyond the test range. Although the S value of RAP and PAV is higher than that of virgin samples, both of them return to virgin level (or even lower). The results fulfil the rutting test requirements of asphalt mixtures. This is also an unavoidable weakening of the capsule's ability to resist permanent deformation of asphalt concrete. However, this value expresses the result after the capsule has been completely released; this defect can be solved as long as the capsule is released early stage. The similar law was shown for m-value, which indicated that oil from capsules could soften and increase the aged asphalt's creep rate. Further, at low temperatures and once released, oil from capsules still works to increase the viscoelasticity of bitumen.

Table 13 BBR test results

Samples	S (MPa)	m-value
Virgin bitumen	142	0.481
PAV aged bitumen	201	0.417
RAP bitumen	212	0.409
Rejuvenated PAV	136	0.521
Rejuvenated RAP	124	0.552

5. Final conclusions

5.1. Conclusions

There has been limited research on the mechanical and self-healing properties of aged asphalt concrete containing Ca-capsules and it has been unclear what effect the capsules have on RAP asphalt mixture performance. The lack of knowledge has limited the application of Ca-alginate capsules to extend the service life of asphalt concrete pavements. The objectives of the work were to assess the effect of capsules on the mechanical properties and the self-healing ability improvement of laboratory-accelerated ageing asphalt mixture and asphalt mixture containing RAP and unravel the mechanism of rejuvenating and self-healing of Ca-alginate capsules.

This study contributes to a deeper comprehension of how capsules affect concrete properties throughout the entire lifespan of asphalt concrete, offering practical guidance for their application. Specifically, the Marshall stability test was employed to determine the Marshall stability (MS) and the average residual stability (RMS), providing insight into the moisture stability of asphalt mixtures. The 3-point bending test was utilized to assess the fracture strength and energy of asphalt mixtures, evaluating their resistance to low-temperature cracking. Additionally, the wheel track test was performed to measure rutting depth, thereby assessing rutting resistance. Furthermore, the fracture and re-fracture test was conducted to measure the strength healing ratio (SHL) and the energy healing ratio (EHL), showing the self-healing ability of asphalt mixtures. The detailed conclusions are as follows:

- The presence of Ca-alginate capsules and the application of laboratory-accelerated thermo-oxidative ageing had minimal impact on the volumetric properties of asphalt mixtures by VV and VFA.
- Before ageing, the capsules reduce the resistance to permanent deformation in asphalt mixtures primarily due to the release of softening oils bitumen during rutting. Concurrently, these capsules diminish water stability while enhancing the crack resistance of asphalt mixtures at low temperatures.
- After laboratory- accelerated ageing, the resistance to permanent deformation increased in all asphalt concrete samples. However, water stability and low-temperature crack resistance declined. In the case of asphalt mixture containing

capsules, the anti-rutting performance decreased to the level of normal asphalt mixtures, and water stability, as well as low-temperature crack resistance, were reduced. Nonetheless, these properties remained superior compared to asphalt mixtures without capsules. The presence of a small quantity of capsules is likely responsible for the observed effects.

- The Ca-capsules can effectively improve the strength healing rate and fracture energy healing rate of asphalt mixtures before and after long-term, laboratory-accelerated thermo-oxidative ageing, which is mainly caused by the oil found in the capsules flowing into the asphalt to soften it. The strength recovery and fracture energy recovery rates of the aged asphalt mixtures containing capsules can also reach the level of ordinary virgin asphalt concrete without capsules.

By utilizing various contents of RAP and capsules, the mechanical and self-healing properties of different asphalt concretes were evaluated using the aforementioned test methods and parameters. This research aims to enhance the performance of asphalt mixtures containing RAP and prolong the service life of such mixtures. The detailed conclusions are as follows:

- Both replacing RAP proportionally according to sieve results and adding 0.5wt% Ca-alginate capsules (or doing just one of these actions) had no effect on the asphalt mixtures' volume performances.
- Replacing RAP and Ca-capsules decreased the Marshall stability and residual Marshall stability of asphalt mixtures; its negative effect became more serious as the amount of RAP replacement increased. Notably, Marshall stability has also become the most important mechanical index of RAP replacement quantity in asphalt mixtures containing Ca-alginate capsules.
- The capsules decrease rutting resistance but increase the crack resistance, RAP has the opposite effect. The comprehensive utilization of the two can effectively cancel out their respective shortcomings, and it is possible to find a balance that gives basically the same performance as that of the reference samples.
- The self-healing ability of asphalt containing RAP is lower than that of virgin samples, but Ca-alginate capsules have significantly improved the mixtures' self-healing ability. The SHL and EHL of asphalt mixtures containing both RAP and

capsules reach 62.4% and 98.2%, respectively. The comprehensive utilization of capsules and RAP can more noticeably help the asphalt mixtures containing RAP maintain their excellent self-healing ability for a long time, thereby overcoming the limitations of RAP utilization.

To show the effect of Ca-alginate capsules on the rejuvenation and self-healing enhancements of aged bitumen and asphalt mixture, the mechanism of diffusion, rejuvenation, and self-healing facilitated by capsules in aged bitumen has been investigated through diffusion, DSR tests, and creep tests. This research can contribute to optimize capsule design in rejuvenator, enabling broader and tailored application to enhance the life of various asphalt concretes. Specifically, three self-designed tests (Sinking Time, Softening Rate, and Gravitational Collapsing) were conducted to determine the diffusion time of oil from capsules in various bitumen. The rheological properties of bitumen, indicating whether aged bitumen has been rejuvenated, were assessed through complex modulus (G*), phase angle (δ), and fatigue factor obtained from DSR temperature sweep tests, along with the master curves derived from DSR frequency sweep tests. The creep stiffness (S) and creep rate (m-value) of bitumen, obtained from the BBR test, were utilized to ascertain whether the low-temperature crack resistance of aged bitumen has been restored. Furthermore, the flow behavior index, calculated from bitumen viscosity acquired through DSR frequency sweep tests, serves as an indicator of the self-healing ability of bitumen. Four components analysis obtain changes in bitumen composition to determine whether aged bitumen has been rejuvenated. The detailed conclusions are as follows:

- Calcium alginate capsules can effectively rejuvenate aged asphalt concrete (Both laboratory-accelerated ageing and RAP) primarily because the sunflower oil found within the capsules diffuses and penetrates the aged bitumen after capsule release. This process helps replenish the saturates and aromatics in the aged bitumen.
- Additionally, based on temperature and frequency sweep results, it may be demonstrated that the rheological properties and low-temperature creep of the aged bitumen rejuvenated by the capsules can be restored to the level of virgin asphalt.
- After the capsule is released and diffusion, the flow behavior index of aged bitumen increases significantly, even higher than the level of virgin asphalt. This shows that

its self-healing ability has also been significantly increased, even higher than that of virgin asphalt.

5.2. Limitation of the thesis and recommendations for future work

In this thesis, all tests are based on laboratory research, and the selected materials are limited; there is still a long way to go before large-scale application of calcium alginate self-healing capsules becomes a reality.

Based on the conclusions of this study, the capsule's structure design can be optimized to minimize the release of oil from the capsule during the early stages of the paving process. At the same time, the capsules' release should preferably coincide with the asphalt's ageing process.

Considering economic and environmental sustainability, there are many options for capsule core materials, including waste oil, rejuvenator, and other agents that could help soften bitumen.

The release of the capsules is closely related to the stresses in the asphalt mixtures, while temperature strongly affects the modulus change of the asphalt-concrete. More and wider temperature ranges and load ranges should be studied to clearly present the release process and mechanism of calcium alginate self-healing capsules in asphalt mixtures.

The mechanical and thermal conditions of mixing, compaction and accelerated ageing under laboratory conditions are still somewhat different from those in field conditions, especially since it is difficult for the laboratory to simulate actual traffic load, which is important for the release of Ca-capsules.

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Appendix A - Paper I

Lei Zhang, Inge Hoff, Xuemei Zhang, Jianan Liu, Chao Yang, Fusong Wang.

A Methodological Review on Development of Crack Healing Technologies of Asphalt Pavement.

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Review

A Methodological Review on Development of Crack Healing Technologies of Asphalt Pavement

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Abstract: Crack healing has been a key area of asphalt pavement research. In this review, different crack-healing theories and crack-healing evaluation methods in bitumen and asphalt mixtures are summarized and presented. Then different crack healing technologies have highlighted the problems and solutions associated with their implementation. Detailly, traditional technologies (hot pouring and fog seal) are introduced. They mainly fill cracks from the outside, which can effectively prevent further damage to the asphalt pavement, when the cracks have generally developed to the middle and late stages of practical engineering. Their extension of the life of the asphalt pavement is relatively limited. Energy supply technologies (induction and microwave heating) have demonstrated significant efficacy in enhancing the crack healing capability of asphalt pavement, particularly in microcracks. Now, Extensive laboratory testing and some field test sections have been conducted and they are waiting for the promotion from the industry. The agents encapsulated technologies (Saturated porous aggregates encapsulate rejuvenators, Core-shell polymeric microcapsules, Ca-alginate capsule, Hollow fibers and Compartment fibers) not only heal cracks but rejuvenate the aged asphalt pavement. In order to promote industrial application, more field test sections and large industrial mixing and compaction equipment applications need to be implemented. Finally, some other potential crack healing techniques (coupling application, electrical conductivity, 3D printing, and modifications) are also mentioned.

Keywords: asphalt pavement; cracks; self-healing technologies; induction and microwave heating; encapsulated agents

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1. Background

After thousands of years of development, the road has experienced the original dirt road, flagstone road, gravel road, cement concrete road, and asphalt road. Asphalt pavement consists of an asphalt mixture surface layer, base layer and subbase layer. The asphalt layer is formed by mixing and compacting bitumen, aggregates, filler, and other additives at high temperatures [1]. Asphalt pavement is now the most common surface of roads especially in high-grade road because of its irreplaceable advantages, such as comfort, safety, and low noise.

However, asphalt pavement is also prone to aging and cracking. Water can also enter through cracks and further damage the pavement's base layer [2]. Continuous maintenance is therefore required to ensure quality. And infrastructure related to road construction has basically become the largest expenditure and energy consumption area in most countries and regions [3,4]. More research focused on finding technological solutions to enhance the reliability and sustainability of pavement materials [5]. Long-lifespan, energy-saving, and functional asphalt pavement are continued research and become the main direction of road development [6]. Crack healing technologies can effectively prolong the service life of asphalt pavement, thereby further reducing the damage to the environment caused by road engineering, reducing energy consumption and CO_2 emissions [7]. Making asphalt pavements more environmentally sustainable. Most asphalt pavement distresses and failures start from cracks (fatigue cracks, reflected cracks and low-temperature cracks), so healing cracks in earlier stage can effectively extend serves lifespan of pavement [8]. Although asphalt binder is a kind of self-healing material which can heal spontaneously under special conditions, it is difficult for common asphalt pavement to ensure a heal rate faster than the crack rate in a practical application environment including aging, temperature, traffic loading and moisture [9]. This is mainly because asphalt molecules are hard to attain sufficient moving speed or time to healing cracks by a series of healing theories, including: surface energy theory, molecular diffusion theory and flow behavior and so on [10]. Modifying, external energy supplementary and additives all become methods to accelerate molecular motion and enhance the crack-healing capability of asphalt pavement [11].

Based on the above concepts, many self-healing technologies have been developed in past decades, and some of them have been used in practical engineering field and played significant role until present [12]. Undeniably, fog sealing and pouring asphalt binder are most traditional and universal methods to heal crack in the current actual road maintenance. However, both of them are applied when the cracks have developed for a period of time and macroscopically visible pavement distresses have appeared. They are generally expensive and extended pavement life is limited. Induction heat technology and microwave heating technology can quickly heal cracks by heating asphalt concrete to reduce the viscosity of asphalt binder based on the temperature sensitivity of asphalt binder [13]. Metallic additives are necessary for induction heating, and microwave heating is also very inefficient if no additional absorbing material is added. Rejuvenator encapsulated technology is to encapsulate the agents in capsules or fibres, and then they will be mixed into bitumen or asphalt mixtures. The agents will release and flow into the crack to soften the binder and promote flow, resulting in healing the crack. Once the crack occurs, the capsules or fibres will break. This will be the most effective way to prolong the life of the road. The key point is to control the release time of capsules, which need to meet the bitumen ageing process. Otherwise, it will affect the permanent deformation resistance of asphalt pavement when the capsule is released early. It also solves the shortcomings of difficult penetration and uneven rejuvenation compared with spraying rejuvenator on the surface. There have been many different types of capsule morphologies developed, including saturated porous aggregates that encapsulate rejuvenators, core-shell polymeric microcapsules, hollow fibres, vascular fibres, and multi-cavity Ca-alginate capsules [14]. Apart from the above-mentioned popular technologies, researchers also try other methods to heal cracks. Combination of two or more of the above technologies to improve effectiveness, application of modified binder, and electrically conductive asphalt concrete are proposed to heal cracks. In this paper, asphalt self-healing theories and self-healing evaluation methods are summarized and presented first. Subsequently, various crack healing technologies are introduced, addressing the challenges and proposing solutions related to their implementation.

2. Crack Healing Theories

The macroscopic manifestation of crack healing is that the generated crack gradually disappears, and the interfaces on both sides of the crack are integrated until the interface disappears. In this process, a series of physicochemical reactions will occur inside the material, accompanied by the migration of substances and the change of energy [10]. Researchers described the crack healing process in asphalt materials from different perspectives and developed some asphalt crack healing theories based on asphalt's own properties.The Molecular Diffusion Healing Model presents the diffusion process of asphalt molecules on both sides of the interface with each other until the interface disappears on the basis of polymer chain dynamics [15,16]. Bitumen is a kind of liquid material composed of polymer molecules of different sizes, and its viscosity is sensitive to temperature. Wool et al. proposed that the crack healing process of polymers from the perspective of molecular diffusion consists of five consecutive stages: surface rearrangement, surface approach, wetting, diffusion, and randomization [15,17]. During this process, the mechanical force will be rebuilt due to the secondary bonds being restored among molecules or microstructural components by Rouse diffusion or reptation [18]. In addition to the chemical molecular composition of the asphalt material itself, the two most important factors that determine crack healing are temperature and time. In brief, a higher temperature response leads to a shorter healing time. Sun et al. proposed a recovery function of asphalt binder based on the molecular diffusion by fatigue-rest-fatigue test, which can consider the effect of healing time and temperature [19], shown in Equation (1).

$$HI(t,T) = HI_0(T) + D_0 \exp\left(-\frac{E_h}{RT}\right) \cdot t^{0.25} \quad (1)$$

where $HI(t, T)$ is the crack healing ratio. $HI_0(T)$ is instant healing ratio. D_0 is a diffusion parameter, R is the universal gas constant (8.314 J/mol/K), E_h is the activation energy. The function adds the material parameter, activation energy, which is determined by the chemical composition of the material itself. It also can define the self-healing potential of asphalt binder. Zhang et al. tested the self-heal capability and calculated the activation energy of different aged levels asphalt binder, resulted in self-healing capability and activation energy both decrease with ageing increases [20].

Phase field healing theory describes that the separated phases will be reconfigured and tend to be isotropic during the heating process. The phases on both sides of the crack are unevenly distributed. The motive force of its driving is that in the process of mixing fluid substances, it always tends to the minimum entropy to move. The mechanical properties of asphalt can be restored when the temperature is reduced [21]. Small molecules and long-chain polymeric molecules are not common to be found in asphalt, and the diffusion model doesn't describe all the crack healing behavior completely. Kringos et al. developed the phase field healing theory by observing the phase movement of asphalt surfaces by AFM (atomic force microscopy) investigations [22]. Other researchers also observed the two phases getting separated and reaching equilibrium by AFM images [23]. Microcracks usually occur at the interfaces between the phases due to stress concentrations. The phase will reconfigure to a new homogeneous mix once the thermodynamic conditions change due to energy application.The surface energy healing theory presents that the decrease of crack surface energy during the crack-healing process of asphalt. Simply put, calculating the energy required due to the reduction in surface area. Lytton et al. derived the energy balance of the crack interface during the disappearance process from fracture mechanics during the fatigue process of viscoelastic materials [24], shown in equations below.

$$2\Gamma_h = E_R D_h(t_a) H_v \quad (2)$$

$$D_h(t) = D_{0h} + D_{1h} t^{mh} \quad (3)$$

$$2\Gamma_f = E_R D_f(t_a) J_v \quad (4)$$

where Γ_f is the fracture surface energy density, Γ_h is healing surface energy density of a crack surface, E_R is the reference modulus, $D_f(t_\alpha)$ is the tensile creep compliance, $D_h(t_\alpha)$ is compressive creep compliance, J_v is the integral of J, and H_v is H integral of H. m_h is the slope of creep compliance of concrete with log time.

Through the derivation of the above equations, Si et al. defined two healing rates (h_1, h_2) by different mechanisms and fatigue cracking processes for vicoelastic medium derived by Schapery [25,26]. h_1 is the short-term healing rate decided by non-polars; it usually occurs quickly. h_2 is the long-term healing rate determined by polar; it is time-dependent. The total healing h is shown in the below equations.

$$h = h_2 + \frac{h_1 - h_2}{1 + \frac{h_1 - h_2}{h_\beta}(\Delta t)_h} \quad (5)$$

$$h_2 = [\frac{2r_m E_R^2 D_{1h} \Gamma^{AB}}{(1 - v^2) C_m^{1/mh} H_v}]\beta \quad (6)$$

$$h_1 = [\frac{K_h E_R D_{1h} H_v}{2\Gamma^{LW}}]^{\frac{1}{mh}}\beta \quad (7)$$

where $(\Delta t)h$ is the rest period, and $h\beta$ is maximum healing ratio of bitumen

Si et al. investigated healing rate of 12 kinds of asphalt concrete, it was found that short-term healing rate (h_1) had significant difference while the long-term healing rate (h_2) were relatively same [26].

The capillary flow healing theory states that the asphalt binder can flow and fill an open crack automatically due to capillary force, based on the fact that asphalt is a kind of liquid material. When the crack growth reaches a certain size, molecular diffusion cannot occur through a large gap. The healing of the cracks can also be observed at this time, mainly because the liquid bitumen fills the cracks under capillary pressure. The capillary flow healing theory can present healing efficiency through a modification of the Lucas-Washburn equation [27]. It can be found that increasing the surface tension force of asphalt can effectively promote the flow of asphalt into cracks. As the temperature increases, the viscosity of the asphalt decreases, and its surface tension also increases. This healing therefore occurs at relatively high temperatures or when the viscosity of the asphalt interface decreases due to infiltration by the rejuvenator.

3. Evaluation Methods of Crack Healing

Several evaluation methods have been used to quantify the crack healing level (HL) by measuring the performance of asphalt before and after the healing process. Table 1 summarises the evaluation methods for asphalt binder and mixture. It is found that the healing evaluation of bitumen is based on its own performance recovery by material properties, like complex modulus, dissipated energy, fatigue life, etc. These are mainly due to changes in the microstructure and uneven phase distribution in the bitumen under loading conditions. After a period of rest, bitumen becomes a homogeneous mix again through molecular diffusion and phase field reconfiguration, resulting in performance recovery. As for mixture, crack healing level (HL) is based on mechanical property recovery, mainly because this meets the pavement design theories of mechanical property attenuation and distress.

Table 1. Self-healing evaluation methods on asphalt binder and mixture.

Materials Types	Test Method	Healing Parameter	Healing Indicator	Notes	Ref.
Binders	Ductility	Ductility value	HI = $\frac{L_{healed}}{L_{original}}$	L_{healed} and $L_{original}$ are ductility test result before and after break-healing	Qiu, J. et al. [28]
	DSR sweep test	Complex modulus and number of cycles	HI = $100 \cdot \frac{G*_{Terminal}}{G*_{initial}} \frac{N_{after} - N_{before}}{N_{before}}$	$G_{initial}$ and $G_{terminal}$ are the dynamic modulus before and after loading test; N_{before} and N_{after} are the numbers of cycles before and after rest period;	Tan, Y. et al. [29]
	Fatigue-rest-fatigue test using DSR sweep test	Area under the curve	HI = $\frac{A_d}{A_{before}}$	A_{before} and A_d is the area between the curves of the modulus versus the number of load cycles and the line of 1/2 modulus before and after rest;	Shan, L. et al. [30]
	Fatigue-rest-fatigue test	Complex shear modulus	HI = $100 \cdot \frac{G*_{h0}}{G*_0}$	$G*_0$ and $G*_{h0}$ are the complex shear modulus before and after healing;	Qiu, X. et al. [31]
	Fatigue-rest-fatigue test	Dissipated energy	HI = $100 \cdot \frac{W_{after}}{W_{before}} \frac{N_{after}}{Nbefore}$	W_{before} and W_{after} are the initial dissipative energy before and after healing	Qiu, X. et al. [31]
	Fatigue-rest-fatigue test	Fatigue life	HI = $\frac{\sum N_{fo}}{\sum N_{f1}}$	$\sum N_{fo}$ and $\sum N_{f1}$ are the fatigue life after and before rest	Liu, G. et al. [32]

Table 1. *Cont.*

Materials Types	Test Method	Healing Parameter	Healing Indicator	Notes	Ref.
Asphalt mixture	IDT	Resilient modulus	HI = $\frac{MR(t)-MR0}{MR_{undamaged}-MR0}$	$MR(t)$ is the normalised resilient modulus at time t; $MR0$ is the normalised resilient modulus at t = 0; and $MR_{undamaged}$ is the undamaged normalised resilient modulus	Chen, Y. et al. [33]
	SCB test or 3-point bending test	Strength	HI = $\frac{F_{after}}{F_{before}}$	F_{after} and F_{before} are fracture peak load after and before healing	Riara, M. et al. [34]
	SCB test or 3-point bending test	Stiffness	HI = $\frac{S_{after}}{S_{before}}$	S_{after} and S_{before} are stiffness after and before healing	Riara, M.et al. [34]
	SCB test or 3-point bending test	Fracture energy	HI = $\frac{E_{after}}{E_{before}}$	E_{after} and E_{before} are fracture energy after and before healing	Riara, M. et al. [34]
	Four-point bending fatigue-healing-fatigue test	Stiffness modulus	HI = $\frac{S2-SS}{S1-SS}$	$S1$ and $S2$ are the initial stiffness modulus before and after rest; SS is stiffness modulus when beam reaches fatigue condition	Xiang, H. et al. [35]
	Four-point bending fatigue-healing-fatigue test	Fatigue life	HI = $\frac{N_{f-after}}{N_{f-initial}}$	$N_{f\text{-}after}$ and $N_{f\text{-}initial}$ are fatigue life after and before resting	Liu, Q. et al. [36]

4. Crack Healing Technologies

4.1. Hot Pouring

Hot pouring and fog sealing are the most traditional and universal methods to heal cracks in the current road maintenance. Hot pouring is usually applied for big and long structure cracks, while fog sealing is used for fatigue cracks and aged pavement surfaces [37]. The pavement heat pouring technology is mainly used to pour hot polymer materials with strong cohesion and elasticity into the cracks of the asphalt pavement. The polymer material is usually made of base asphalt, high molecular weight polymers, stabilizers, additives, and other materials. The method is used to repair large and long transverse cracks and horizontal cracks [37]. The road can be maintained in time to prevent the damage caused by the entry of rainwater and impurities and the appearance of potholes inside, thus extending its service life [38]. However, it can only be done completely manually, which is expensive and inefficient. And the cracks have extended to the last period when the materials can pot into the cracks. Hot pouring technology can not extend service life too much (Figure 1).

4.2. Fog Sealing

A fog seal is an application of asphalt emulsion to an existing asphalt pavement surface that has aged and developed cracks or other distresses (Figure 2). After the asphalt emulsion is demulsified, the fog seal material can penetrate the aged asphalt concrete and also flow into the micro-cracks. It can rejuvenate aged asphalt concrete, close interconnected voids, heal cracks, and prevent moisture damage [39]. The technology could usually extend the surface performance of asphalt pavement for 2–3 years [40].

There are still certain disadvantages to the application process. After the asphalt emulsion breaks and cures, the cracks and voids are closed, and the skid resistance of the asphalt pavement surface will reduce significantly. Traditional fog seal materials face adhesion loss and spalling failure because of low mechanical strength and inadequate cracking resistance [41,42]. Islam's research has shown that spraying fog seal reduces the coefficient of friction of pavements by 20% to 40% [42]. Low diffusion and uneven spraying combined with the decline of anti-skid resistance will not only affect the damage to the pavement structure but also seriously affect the safety of driving. Modified emulsified bitumen with polymer material (like styrene-butadiene-rubber (SBR) or styrene-butadiene-styrene (SBS)), which helps to increase the adhesion of the fog seal material [43]. Xu et al. found that waterborne additives (acrylates, cationic acrylates, and polyurethane) can improve the thermal cracking resistance of SBS-modified asphalt emulsions through the synergy effect [41]. Liu et al. used epoxy resin to modify fog seal materials and found it could shorten the surface dry time and increase the waterproofing and durability of asphalt pavement [44]. In order to increase the skid resistance performance of the pavement surface after fog sealing, a sand fog seal concept was proposed, which is composed of fog seal materials and fine sand. Ma et al. designed sand fog seal materials with different sand contents and optimised the 25% sand content to balance stability and fluidity well [45]. Zhang et al. also determined the best formulation of sand fog seal mortar and a method for predicting traffic open time based on image processing technology [46].

Figure 1. Hot pouring technology to heal the cracks.

Figure 2. Fog seal technology with operation.

4.3. Heating Technologies

Bituminous material itself is a self-healing material capable of repairing cracks, but sufficient temperature and time are required. Mainly because the viscosity of bitumen is temperature-sensitive; the higher the temperature, the smaller the viscosity [47]. Heating the bitumen can reduce the viscosity of the asphalt, which not only reduces the surface energy of the crack but also makes the bitumen have better fluidity to flow into the crack and heal it [48]. And high temperatures help improve bitumen molecular diffusion to heal the cracks. Based on the theories, heating asphalt concrete technologies were proposed to heal the crack that occurred in the service process due to ageing, traffic loading, or fatigue. Induction heating and microwave heating are efficient and non-contact heating methods that are suitable for heating asphalt pavement [49]. They just take dozens of seconds to heat up to asphalt's self-healing temperature.

4.3.1. Induction Heating

The basic principles of induction heating technology are electromagnetic induction and joule heating. During the test process, when the material is placed in the induced magnetic field, its interior will experience an electro-motive force according to Faraday's law. Then the eddy currents are generated to heat the materials by Joule's law. Besides, magnetic domain rotation will also produce hysteresis heating when applied to magnetic materials.Bituminous materials themselves cannot be heated directly by induction; some electrically conductive materials (like steel fibres, steel wool, steel slag, etc.) are considered to be added to asphalt mixtures [50,51]. After the conductive material heats up under an induction field, it can be conducted to the bitumen to heat up and heal the cracks [52]. The basic principle is shown in Figure 3. In Garcia et al.'s study, steel wool fibres were added to dense asphalt mixtures. The results show that a higher volume of steel wool fibres in the mixture may increase the air void content of asphalt concrete and affect its thermal conductivity [53]. When Liu et al. incorporated steel fibres, steel wool, and steel slag into porous asphalt concrete, it was found that the conductivity of samples with longer fibres with a smaller diameter was better than that of samples with shorter fibres with a larger diameter [54]. And the steel fibres and steel wool were more beneficial in increasing temperature than steel slag; they also improved the flexural strength of asphalt concrete [55]. 8% steel wool is considered the optimal content and increases the indirect tensile strength, resilient stiffness, and fatigue resistance of porous asphalt concrete [56]. An appropriate amount of steel fibres can increase the basic mechanical properties of asphalt concrete while also increasing its thermal properties.

Induction crack healing technology is mainly used to increase the temperature of asphalt concrete and reduce the viscosity of asphalt to promote crack healing. Temperature is the main index used to determine the crack healing rate [57]. Liu et al. believed that 85 °C was the optimal surface temperature for crack healing through a three-point bending test and that the optimal strength recovery rate could reach 78.8% [58]. Liu et al. designed the four-point blending test to investigate the fatigue life extension of asphalt concrete with steel fibres. Micro-strain amplitudes would affect the size of cracks between samples of the test. Higher micro-strain amplitudes and larger cracks were generated in the fatigue testing, which is hard to heal. Liu et al. found that the fatigue life extension ratio during different micro-strains and temperatures for hot mix asphalt and warm asphalt shows that induction heating technology can expand over 70% of the life by healing the crack [36,59]. Another advantage of induction heating technology is that the asphalt pavement can be heated multiple times during its service life. The strength recovery rate and fatigue life extension of asphalt concrete containing steel fibres are still unchanged after 5 cycles of induction heating [60,61]. Yang et al. also studied the induction heating crack healing level of asphalt concrete containing reclaimed asphalt pavement (RAP) and steel slag. The strength healing rate of RAP containing 40% can still reach 57.9%. At the same time, the crack healing rate will decrease by 10% after four cycles [62,63]. In December 2010 in the Netherlands, the first induction-heating asphalt pavement was paved [61], and it has been applied until now and remained well. In June 2014, this trial section received the first induction heating treatment, and it showed good healing ratios and ravelling resistance [64]. In 2018, in the Guangdong Province of China, a 400-metre induction healing pavement test section was also paved [4]. According to estimates, if all roads in the Netherlands were replaced with induction-heated pavements, it could save approximately 90 million euros every year, and the life span of roads would also extend by 50%. By the same calculation, China will save a maintenance expense of 1000 billion RMB if only 10% of the roads are replaced by induction healing pavemeng [56]. However, induction heating technology cannot prevent the ageing of asphalt pavement. And the pavement will be more and more prone to cracks, and the healing temperature will be higher than ever during the service process. The total mixing time should reach 5 min to get a homogeneous mix with minimum steel wool clusters. It is six times more than when normal asphalt pavement is applied [56]. And the heating efficiency is also limited; one hour can only heat 5 km since it takes 26.4 s for the temperature of the road surface to increase from 5 to 85 °C [65]. Large-scale induction equipment also requires further study in order to guarantee heating rates and maintenance times.

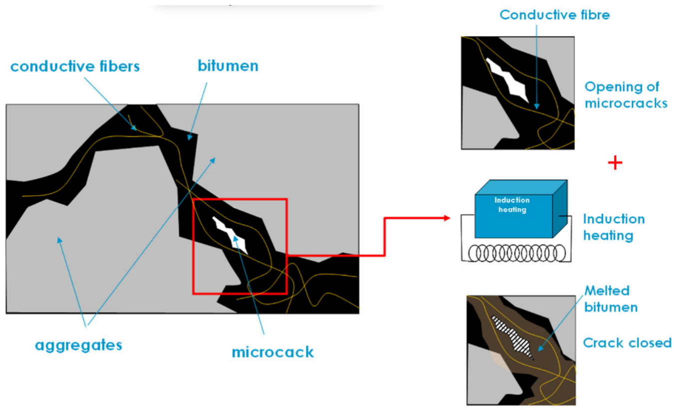

Figure 3. Induction heating scheme.

4.3.2. Microwave Heating

Microwave heating is also a good non-contact heating method used in road surface heating. The basic principle is that the direction of the electric polarity molecules in the object will vibrate with the oscillating electric field, and the inherent electromagnetic field of a molecule is changed and affects the adjacent molecules, so the vibration of the molecule is in the molecule passed between under the action of the electromagnetic field oscillated by microwave high frequency. Molecular vibration is internal energy, and increasing internal energy is like heating an object [66]. Microwaves cannot heat non-polar molecules. Bitumen contains a large number of polar molecules. And Lou et al. reported that microwave heating rarely aged asphalt, referring to the ageing index [67]. The mechanism of crack healing is the same as induction heating after the mixture is heated [68]. Researchers found that the incorporation of some additives can improve microwave heating effectiveness. Gallego et al. reported that 0.2% steel wool can significantly improve microwave heating potential, whereas only 1/10 dosage for induction heating can reach the same heat rate [69]. Li et al. found that nanometer microwave-absorber materials (like SiC, CNTs, and graphene) can also improve the microwave heating rate and healing properties of asphalt [70,71]. Sun et al. studied the heating and healing properties of a mixture incorporating steel slag and steel fibres using both induction and microwave technologies [72]. Lou et al. used three kinds of steel slag (hot braised, hot pour, and iron slag) to replace the coarse aggregates in the asphalt mixture and found that the microwave heating rate could improve. And 60% replacement is the most effective dosage [73]. Lou et al. also used ferrite fillers to replace limestone fillers in a mixture that incorporated steel slag, and the microwave heating rate was further improved [74]. Metallic powder and fly ash can also improve the microwave heating potential of asphalt [75,76]. In the Jahanbakhsh et al. study, carbon black increased the heating rate of asphalt pavement made of limestone and siliceous types of aggregate by 47% and 25%, respectively [77]. Wang et al. also found that pyrolysis carbon black (PCB) had good microwave absorbing performance for asphalt pavement. And the addition of 15% PCB increased the self-healing rate of bitumen by 3.59 times [78]. At present, the microwave heating cracking technology in the laboratory mainly relies on microwave ovens. The heating time and temperature are the biggest factors affecting the crack healing rate of asphalt concrete. Jose et al. comparatively studied the microwave and induction heating, the microwave healing rate of dense asphalt mixtures was superior to the induction healing rate through three-point bending test, the strength recover rate reached 93% for microwave healing, while 75% for induction heating. This is mainly because microwave heating is a holistic heating, while induction heating has a temperature gradient from top to bottom, and the bottom crack does not reach the optimal level of healing [13]. Zhu et al. investigated healing level of asphalt concrete with base bitumen and SBS modified bitumen in different temperature by semicircular bending test, it was found that the strength recover ratio could reach 85% in 80 °C [79]. The microwave heating healing ratios of asphalt mixtures with different structure (semi-dense, porous, and gap-graded) were investigated in Franesqui et al. study. It was found that top-down cracks (<4–5 mm)can be completely healed by microwave heating [75]. Crack healing level of asphalt concrete containing RAP was also investigated by microwave heating, the RAP content adversely affected the microwave healing [80]. Nevertheless, there are obvious disadvantages to microwave heating technology. It is challenging to control the microwave's reflection from the flat surfaces. And the human body can also absorb microwave energy, which can heat exposed tissues and cause thermal damage [81]. Therefore, further extensive research needs to be conducted to enhance the efficiency of microwave healing on asphalt pavements while ensuring safety is not compromised.In heating technology, conductive materials (steel fibres and steel slag) or absorbing microwave materials (ferrite, SiC, CNTs, graphene, fly ash, and carbon black) that are added to asphalt concrete basically belong to the waste products of other industries. Specifically, steel fibres and ferrite come from waste from the steel cutting and forging industries. Steel slag is a waste product after steelmaking [82]. Reusing asphalt concrete can turn waste into treasure, make full use of resources, reduce the capture of new resources, and be more sustainable.

4.4. Agents Encapsulated Technology

The agent-encapsulated technology solves the shortcomings of the spraying rejuvenator, such as difficult penetration and uneven distribution. Rejuvenating aged asphalt pavement when the aging starts to result in cracking is the optimal solution. This will be the most effective way to prolong the life of the road. It is crucial to avoid prematurely releasing the rejuvenator before the bitumen has been aged, which will reduce the permanent deformation resistance of the road [83].

4.4.1. Saturated Porous Aggregates Encapsulate Rejuvenators

Garcia et al. first proposed the asphalt self-healing technology with capsules by applying self-healing capsules to cementitious materials [84]. The porous sand is used as the core material, and its internal porous structure can effectively store the rejuvenator. Then, the surface is coated with epoxy resin and cement as a shell. The capsules of various sizes (with diameters ranging from 1.6 to 7.1 mm and shell thicknesses ranging from 0.1 to 0.35 mm) were produced by the same procedure. It is found that larger capsule cores contain more oil, and their force resistance is over 10 N in capsule compression tests [85,86]. The saturated porous aggregate capsules were added to porous asphalt concrete and could resist high temperatures (up to 180 °C) and tension during the mixing and compaction of the asphalt mixture [86]. It was found that the capsules inside the porous concrete could break and the oil could flow out and diffuse into bitumen after the indirect tensile test, and the crack could be effectively healed, as shown in Figure 4 [87]. However, the capsules were unevenly distributed in the asphalt mixture. They tended to accumulate at a certain depth in the test sample. The capsules decrease the indirect tensile strength of asphalt concrete. This happened because its strength is lower than normal aggregates [87]. Oil in the capsule is also extremely limited owing to the fact that most holes in the porous aggregates are closed. This kind of capsule is not particularly suitable for asphalt concrete to improve its self-healing ability.

Figure 4. Characterization and healing process of saturated porous aggregates encapsulate rejuvenators [87].

4.4.2. Core-Shell Polymeric Microcapsules

Core-shell polymeric microcapsules involve two primary components: the core material (rejuvenators) and the shell materials [88]. These capsules are categorised based on their size as nano-capsules (1 m), micro-capsules (1 m < D < 1000 m), and macro-capsules (>1000 m) [89]. The section focuses mainly on the application of microcapsules in asphalt crack healing. The core material may be surrounded by one or two layers of shell materials. There are two types of core-shell capsules: (1) single-shell capsules [90] and (2) double-shell capsules [91]. Through in-situ polymerization and two-step coacervation processes, a type of core-shell microcapsule was created, which significantly reduced the size of encapsulated rejuvenators and improved their incorporation into bituminous materials [92]. These microcapsules consist of a rejuvenator core surrounded by a protective shell, which can be ruptured by propagating crack fronts, allowing for the release of the healing agent through capillary action. TGA tests have indicated that these microcapsules can withstand the storage and mixing temperatures of bitumen [93]. Sun et al. have demonstrated that they can resist mechanical agitation at high temperatures while still being able to release the rejuvenator during loading, thereby enhancing the healing capacity of aged bitumen [94]. Furthermore, fatigue-rest-fatigue tests have shown that the inclusion of microcapsules containing rejuvenator can enhance the fatigue resistance of aged asphalt binder, with a 1 wt% concentration resulting in a 45.68% increase in fatigue life compared to non-aged neat bitumen [90]. At the same time, a commercial prepolymer of melamine-formaldehyde modified by methanol (MMF) was also developed as the shell material of microcapsules [91,92,95,96]. Its SEM images are shown in Figure 5. Thermal tests showed that the microcapsules survived in 200 °C bitumen and could improve the self-healing ability of bitumen with the capsules [97]. Moreover, nano-$CaCO_3$ powder was added to MMF as the shell to enhance adhesion with bitumen and thermal stability; these nano-$CaCO_3$/polymer microcapsules survived in bitumen for a long service time under radical conditions without damage because of their good thermal stability [96].

However, the capsule does have its limitations. Its preparation efficiency in the laboratory is relatively low, and the quantity of each preparation is limited, making it challenging to use on a large scale in road engineering. Additionally, there have been no experiments conducted on adding it to the asphalt mixtures; it is only added to binders. It is difficult to prove that it can also keep itself whole without breaking during mixing and compression. As the capsule has a single core, once it ruptures, all the rejuvenators inside are released completely, which could potentially reduce the asphalt concrete's resistance to permanent deformation.

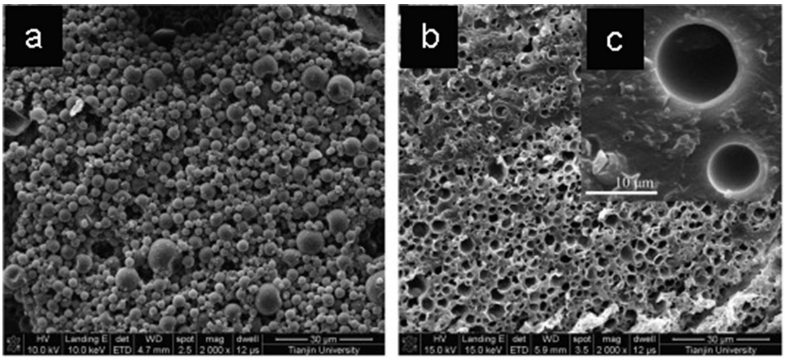

Figure 5. SEM images of core–shell microcapsules: (**a**) external aspect, and (**b**,**c**) cross section of the microcapsules [91].

4.4.3. Ca-Alginate Capsule

Calcium alginate capsules are prepared by dripping the emulsion containing sodium alginate, surfactant, and regenerant into calcium chloride solution. The shell material of the capsule is to fix the chain alginate ions into a three-dimensional network of calcium alginate material by the method of ion replacement. Therefore, the rejuvenator can be stored in the gaps of the network structure [98]. Rao et al. also innovated the experimental apparatus and successfully fabricated the capsules with industrial raw materials on a large scale in the laboratory [99]. The size of capsules is typically 1.5–3 mm, and the capsule is incorporated into the asphalt concrete as an aggregate. Its internal structure is a multi-chamber structure [100], which enables multiple releases of the internal rejuvenator for long-term crack healing, as shown in Figure 6.

This capsule healing technology uses an internal rejuvenator to soften the asphalt on the crack interface, reduce its surface energy, increase the flow activation energy of the asphalt, and promote crack healing. It is generally believed that there are two release mechanisms for the rejuvenator inside the calcium alginate capsule. The first one is the same as the core-shell capsule. The crack or loading induces the capsule to rupture and releases the rejuvenator inside, which can effectively heal the crack. Because the damaged capsules embedded in asphalt mixtures can be found by CT scan [101,102], as shown in Figure 7, The other is elastic contraction and expansion. Since the chambers inside the capsule are not all closed, under the action of the load, the capsules are deformed by pressure, the internal rejuvenator will flow out, and the capsule does not rupture. The release method could rejuvenate aged bitumen and improve its own self-healing capability [103]. The researchers studied the mechanical and thermal properties of the capsule itself. The uniaxial compression test to make capsules break is usually used to measure the mechanical strength of capsules. It was proved that the capsules could resist the pressure during mixing and compressive forces when the strength was higher than 10 N [84,104]. Zhang et al., Wan et al., Xu et al., Micaelo et al., Al-Mansoori et al., and Norambuena-Contreras et al. tested the strength of this capsule at different temperatures; the results ranged from 12–33 N [101,105–108]. By thermal gravimetric analysis (TGA), the capsules had a mass loss of 2.9–4% at 200 °C and 3.8–5.5% at 160 °C [101,105–108]. The rejuvenator content of the capsule weight could also be calculated by the thermogravimetric curve; it ranged from 52–80% [101,105–108]. It can be seen that the capsule can fully survive the mixing and compression of asphalt concrete.

Norambuena-Contreras et al. Incorporating 0.25–1% capsules into dense asphalt concrete (AC 13), 0.5% capsule content has basically no effect on the basic road performance (scattering, indirect tensile strength, Marshall stability, and freeze-thaw cycles) of asphalt concrete and only slightly reduces its resistance to permanent deformation [100]. Al-Mansoori et al. added the capsules to AC20 asphalt concrete and got similar results.

When the capsules were added to SMA asphalt concrete, its stiffness and deformation resistance decreased and had no influence on fatigue resistance [109]. Xu et al. found the capsules could reinforce the stiffness modulus of porous asphalt concrete.

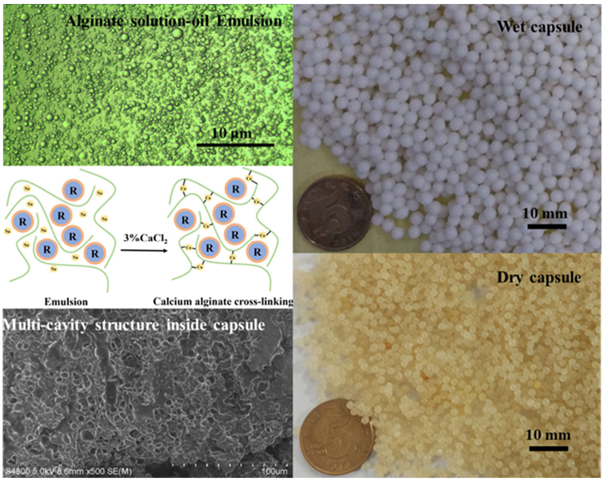

Figure 6. Morphological characterization of calcium alginate capsules.

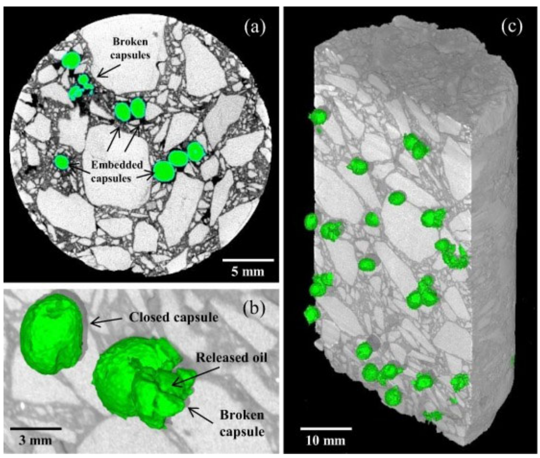

Figure 7. CT-Scans reconstructions of the asphalt mixture with capsules, (**a**) sectional view, (**b**) broken capsules in mixtures, (**c**) 3D image [104].

More importantly, this capsule can effectively increase the crack healing ability of asphalt concrete in low temperature. Al-Mansoori et al. found that the capsules can effect the healing levels of samples when the healing temperature below 40 °C, asphalt samples with and without capsules owned same healing levels when temperature was over 40 °C by fracture- rest-healing-refracture test [106]. Zhang et al. found that the strength recovery ratio and fracture energy recovery ratio of asphalt with capsules could reach 92.7% and 180.2% respectively, while the reference samples are 61% and 31.5%, shown in Figure 8. The capsule also significantly improve the healing capability of porous asphalt concrete by semi-circular bending (SCB) test by Xu et al. [110]. The self-healing property of reflective crack of asphalt mixtures with capsules was investigated in Garcia-Hernández et al. study. It was found that the capsules had the best self-healing efficiency in porous asphalt concrete, then stone mastic asphalt mixture, the last one dense asphalt mixture [111]. Jose et al. also used waste cooking oil as the rejuvenator to synthesis the alginate capsules, it was found that waste cooking oil capsules presented feasibility for self-healing applications for mechanical and thermal stability and physical-chemical properties. The capsules can diffuse in the aged bitumen, reducing its viscosity and promoting the self-healing of microcracks [112].

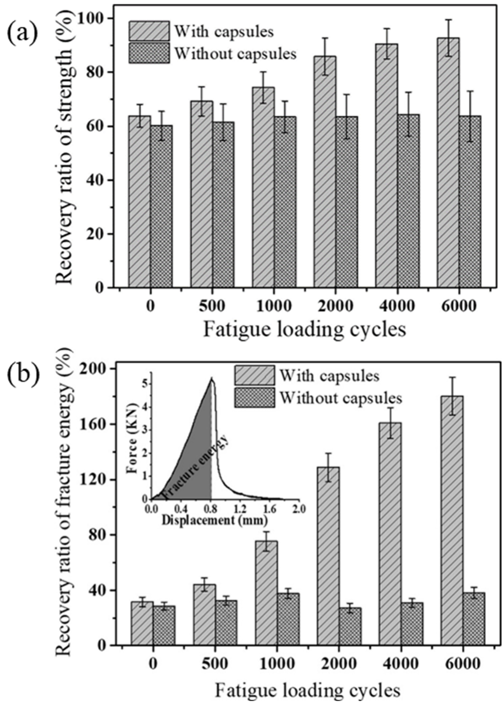

Figure 8. Recovery ratio of asphalt mixture with and without capsules: (**a**) strength, (**b**) fracture energy [98].

4.4.4. Hollow Fibers

Hollow fibres are used to provide a healing mechanism similar to that of encapsulated rejuvenators. Rejuvenators are encapsulated in the connected hollow pipe. And this method offers an advantage over capsule-based systems because the fibres increase the probability that rejuvenator will be released into cracks, which are more likely to pass through the fibre network [113]. Furthermore, the continuous pipe structure of the hollow system allows for the continuous supply of large volumes of rejuvenators, and the diameter of the fibres is usually 0.5–1.5 mm [114]. Zhang et al. prepared polyvinylidene fluoride resin (PVDF) hollow fibres by a one-step wet-spinning technology; the process is shown in Figure 9. They are distributed evenly in the bitumen base material and aim to reverse the ageing of bitumen and improve its crack repair capability [115]. The fibres were added to aged bitumen and still kept their integrality state by XCT test, proving they can resist the thermal actions of temperature changes in bitumen. Hollow fibres can survive in bitumen safely without debonding [114]. Guo et al. tested the self-healing ability and efficiency of bitumen ductility specimens with fibres and found that the self-healing rate reached 64% in the sample, which was larger than the pure bitumen sample. But an intersection angle between the tensile direction and the fibre hinders the flow of rejuvenator into the crack, which results in a poor self-healing effect [116].

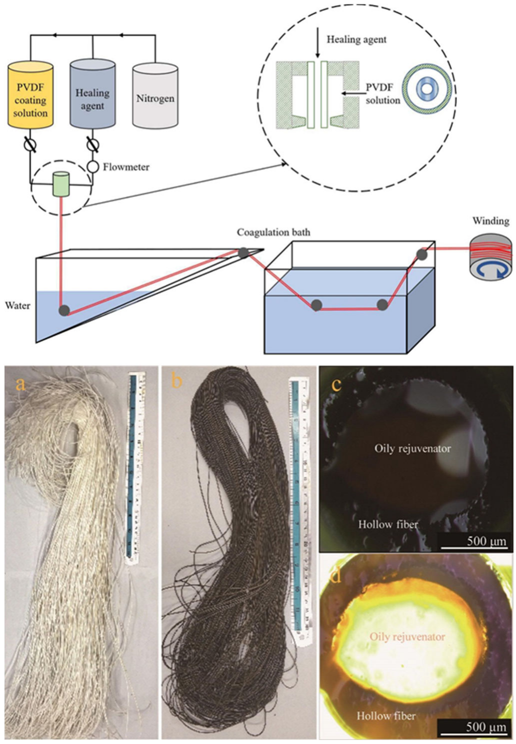

Figure 9. Schematic representation of the preparation of vascular hollow fibers and finished product: (**a**) fiber without rejuvenator, (**b**) fiber with rejuvenator, (**c**,**d**) cross-sectional of fiber with and without rejuvenator [114].

4.4.5. Compartment Fibers

Compartment fibres have their own advantages over hollow fibres. It does not allow the full release of the internal rejuvenator at one point of fracture, causing excessive local softening. Because the internal rejuvenator is separated into small droplets in the fibre. Its self-healing mechanism can be viewed as a merger of capsules and fibres.Tabakovi et al. used the physico-mechanical technique of wet-spinning to prepare the calcium alginate compartment fibres. The fibres have good thermal and mechanical properties because they still maintain their integrity after heating and mixing with bitumen [117]. These fibres present the rejuvenator distributed as individual droplets along their axis. The results demonstrated that the mechanical strength of mastic asphalt with fibres can increase by 36% compared to the reference, and the local micro-crack healing ability of samples with fibre also increases.After that, a microfluidic device was used to produce compartmented fibres with a commercial rejuvenator as a core and a sodium-alginate solution as a shell in Shu et al.'s study; the process is shown in Figure 10. The shell of fibres has excellent thermal stability and mechanical properties. The fibres were still intact after mixing and compacting with asphalt. The self-healing ratio of asphalt mix containing fibres increased by nearly 32% compared to asphalt mix without fibres. The system worked and enhanced the self-healing properties of the asphalt mixture [118,119]. In agent-encapsulated technologies, although the shell materials (epoxy resin, MF, MMF, Ca-alginate, and PVDF) used are all organic matter, they are basically non-toxic and will not flow into the environment and cause pollution when mixed into the asphalt. The core materials (commercial rejuvenator, sunflower oil, and waste oil) used are non-toxic and environment-friendly and will be part of bitumen, which can be recycled. This further advances the sustainability of asphalt pavement.

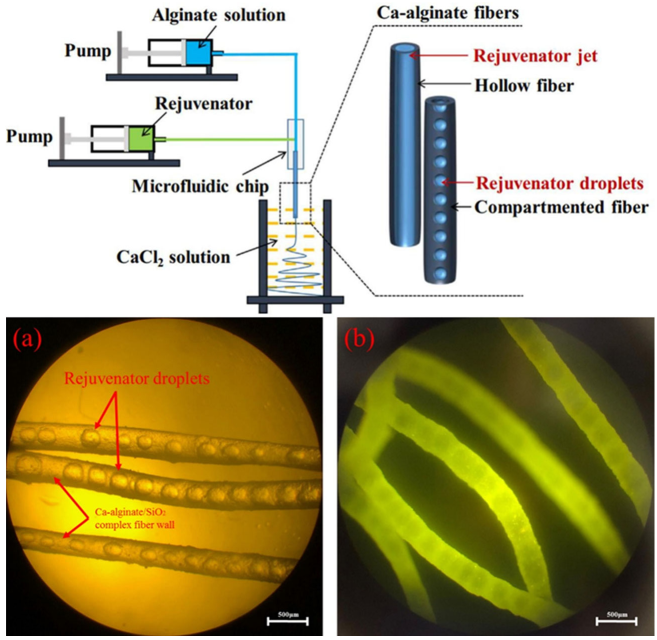

Figure 10. Microfluid synthetics compartment fibers and its morphology image, (**a**) optical microscope, (**b**) fluorescence microscope [118].

4.5. Other Technologies

There are also other technologies under study to help repair cracks in asphalt pavement. The comprehensive application of heating technology and rejuvenator supply technology is considered to overcome the shortcomings of their separate use. Xu et al. added both steel fibres and calcium alginate capsules to porous asphalt mixtures. The induction heating not only repairs cracks but also accelerates the outflow of the rejuvenators in the capsule and the diffusion in the bitumen [120]. Wan et al. design novel Ca-alginate capsules containing Fe_3O_4 powder, which can be induced to be heated to damage the shell of the capsules, leading to the rejuvenator's release by the low-frequency (2.45 GHz) microwave. So the capsule can achieve an artificially controlled release time [108,121,122]. Electrically conductive asphalt pavements are also designed to heal cracks in asphalt pavements by adding nanostructured conductive polymers, although asphalt is not electrically conductive [123]. At the crack, the resistance of the conductive asphalt will increase, and the temperature will also increase to heal cracks, according to Joule's law [124]. Three-dimensional printing technologies can also be applied for the maintenance of asphalt pavement cracks. Firstly, building 3D digital models of cracks by an advanced pavement distress detection system, then printing the crack directly in situ with prepared printing materials and equipment, and finally, checking printing quality by ultrasonic testing [125]. Jackson et al. realise bitumen can be directly used as a printing material to print into the cracks in the road surface to repair cracks at high temperatures to prolong the life of asphalt pavement [126]. Bitumen modified by polymer (SBS, Gilsonite, HDPE and crumb rubber in Lv et al. [127], SBS, HDPE and crumb rubber in Zhou et al. [128] crumb rubber, PPA, PE and gilsonite in Huang et al. [129]), nanomaterials (organoclay in Tabatabaee et al. [130], nano-silica in Ganjei et al. [131]), ionomers [132] and shape memory materials [133] to increasing the self-healing properties of bitumen itself can also improve the crack healing ability of the asphalt pavement.

5. Conclusions

Crack-healing technology can effectively control pavement distress at an early stage, which can effectively extend the service life of asphalt pavement, reduce emissions, and save costs. This review introduces crack healing theories and evaluation methods and focuses on several crack healing techniques that are currently being applied and researched.The healing theories (the molecular diffusion healing model, phase field healing theory, surface energy healing theory, and capillary flow healing theory) cited by the researchers can explain the corresponding crack healing. However, in the actual healing process, crack healing is formed by the coupling of multiple healing models. Therefore, more attention should be paid to the advancement of the crack healing theory in the following research so that it can assist quantitative calculations and promote the application of crack healing technology.Hot pouring and fog sealing are relatively well studied and are the crack-healing techniques currently used in practical engineering. They mainly fill cracks from the outside, which can effectively prevent further damage to the asphalt pavement. However, when they are used, the cracks have generally developed into the middle and late stages, and their extension of the life of the asphalt pavement is relatively limited.Induction and microwave heating technologies have demonstrated significant efficacy in enhancing the crack healing capability of asphalt pavement, particularly in addressing microcracks. Extensive laboratory testing and some field test sections have been conducted, and they are now awaiting industry endorsement for promotion.The agents encapsulated in the technology not only heal cracks but also rejuvenate the aged asphalt pavement. Various encapsulation methods (saturated porous aggregates that encapsulate rejuvenators, core-shell polymeric microcapsules, ca-alginate capsules, hollow fibres, and compartment fibres) have been investigated in the laboratory. In order to promote the industrial application, more field test sections and large industrial mixing and compaction equipment applications need to be implemented. The comprehensive application of heating technology and rejuvenator supply technology, electrical conductivity asphalt pavements, 3D printing technologies, modified bitumen, and so on were also designed to repair cracks in asphalt pavement.

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Appendix B - Paper II

Fusong Wang, **Lei Zhang**, Boxiang Yan, Dezhi Kong, Yuanyuan Li, Shaopeng Wu.

Diffusion mechanism of rejuvenator and its effects on the physical and rheological performance of aged asphalt binder.

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Diffusion Mechanism of Rejuvenator and Its Effects on the Physical and Rheological Performance of Aged Asphalt Binder

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Abstract: Using rejuvenator to improve the asphalt pavement service state has become an increasing concern in recent years. This study mainly focuses on the diffusion analysis between rejuvenator and aged asphalt, and further rheological influences by addition of rejuvenators. First, two rejuvenators, oil rejuvenator (OR) and penetrative rejuvenator (PR), were prepared in the laboratory. Afterward, the diffused performance of rejuvenators was investigated by viscosity, contact angle, and three self-designed feasible test indexes, which were sinking time test, softening rate test, and gravitational collapsing test. Beside the comparison in physical properties tests of aged and rejuvenated asphalt, their rheological performances were also evaluated by dynamic shear rheometer (DSR) and bending beam rheometer (BBR) respectively. The results indicated that three proposed indexes can comparatively analyze the diffusion rate of different rejuvenators on aged asphalt effectively. Furthermore, all adopted test indexes signaled that PR has a faster diffusion rate and better penetrative efficiency. Comparatively, exceeding rejuvenator dosage would increase the rutting possibility. Nevertheless, 2.5 wt% addition dosage for both OR and PR into aged asphalt can promote appropriate improvement in physical properties and crack resistance. The study would supply a significant reference for penetrative rejuvenator preparation and its diffusing evaluation.

Keywords: aged asphalt binder; rejuvenator; rheological property; diffusion; emulsified asphalt

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Highlights

- Two rejuvenators were prepared with waste cooking oil and emulsified asphalt;
- Three self-designed tests were used to study the diffusion efficiency of the rejuvenators;
- Dosages of rejuvenators were optimized based on the rheological property of asphalt;
- Two rejuvenators improved the crack resistance of aged asphalt;
- Penetrative rejuvenator has a better permeability to penetrate in aged asphalt.

1. Introduction

With the palpable trend of environmental sustainability development in the field of asphalt pavement [1,2], the preventive maintenance technology has been given increasing emphasis which has proved as a promising approach for alleviating pavement distresses and prolonging service life [3]. Preventive maintenance technology can make a significant difference by using some preliminary methods to control the pavement distresses before deterioration occurs [4,5]. Otherwise, greater consumption of material resources will be required for pavement reconstruction.

Preventive maintenance methods which included micro-surfacing, slurry seal, fog seal, and chip seal have been used to protect asphalt pavement in the recent years [6,7]. Nevertheless, the fog seal method attracted the most attention with its convenience in the application process and short construction period [8]. It means that spraying fluid material, such as rejuvenator, emulsified asphalt, and modified asphalt, creating a protective film on the pavement which fills the road cracks, stabilizes loose aggregates and results in an extended life of the aged asphalt [9–11]. Hence, the fluid material is the key point of fog seal method to achieve efficient results.

Not only in the field of preventive maintenance, rejuvenators were also warmly discussed in remixing with reclaimed asphalt pavement to deal with solid waste and meet road performance again [12–15]. Martins [16] integrated 10 optional places of asphalt plant to add rejuvenator (distilled tall oil) for better rejuvenation effects, and conveyor belt of cold reclaimed asphalt pavement (RAP) was recommended to obtain the improvement in asphalt fatigue and crack propagation resistance. Ali [17] claimed that using rejuvenator (date seed oil) could lead to better fatigue life of RAP. Similarly, with high RAP contained, Lu [18] investigated commercial rejuvenators' application in warm mix asphalt mixture, whose result showed that rejuvenators performed better than Evotherm in fatigue cracking resistance. Additionally, bio-oil from sawdust [19], pyrolyzed tire [20], cyclogen [21], petroleum derivatives [22], and waste cooking oil (WCO) [12] were utilized as rejuvenators in many researches.

In relation to the fog seal, Zhang [23] analyzed the application of rejuvenator in porous asphalt pavement, and found it can improve the bending stiffness and raveling resistance. Cui [24] explored the feasibility for using silicone resin polymer in fog seal maintenance. Feng [25] tested the practical application possibility by mixing various contents of sand with modified bio-oil. Wan [26] investigated the chemical structure and rheological properties of aged styrene-butadiene-styrene modified asphalt with two kinds of rejuvenator materials, and thought that high maltene content could significantly soften the aged binder. Utilizing a commercial rejuvenator, O'Connell [27] evaluated the guidelines and procedures of recycling asphalt with seal maintenances, as there was no standard available in South Africa then. Moreover, two patents associated with fog seal rejuvenation from the United States [28,29] were published in the same year.

However, good permeability is the important precondition for the high efficiency of the rejuvenator; the permeability and diffusivity of rejuvenator has been seldom researched before [30]. After spraying on the asphalt pavement, the maintenance effectiveness of rejuvenator mainly depends on the permeable depth and diffused area in asphalt mixture. Meanwhile, the experimental methods in assessing and quantifying rejuvenator's permeability and diffusivity to asphalt binder also has not been comprehensively researched, which strongly restrict the further application of rejuvenator in the preventive maintenance field.

In addition, biomass energy is a renewable energy which has the characteristics of large reserves, wide distribution, and environmental protection. WCO, belonging to current biomass energy, has been researched to produce biodiesel and functional chemicals [31]. In this study, the WCO was added to the emulsified asphalt to prepare the oil rejuvenator (OR). Because, when the dosage of WCO is 7%, the penetration, softening point, and ductility of rejuvenated asphalts can be restored to more than 90% of the original asphalt. WCO can be used as the rejuvenator and make a difference [32].

The objective of this study is to develop a kind of penetrative rejuvenator (PR) in laboratory, and evaluate the effects of its application in aged asphalt. First, the emulsified asphalt, WCO, and mixed penetrants were processed as OR and PR. Then the regenerating performance of OR and PR were investigated, including physical properties (penetration test, ductility test, and softening point test) of asphalt, high temperature shearing, and low temperature creeping. Besides that, viscosity and contact angle were measured, three concise and feasible test indexes were proposed assessing the permeability and diffusivity of rejuvenators which were sinking time test, softening rate test, and gravitational collapsing test. From this study, the rejuvenating properties and permeability of the rejuvenators were evaluated, and three feasible test indexes were proposed which can make a good reference in later penetrative rejuvenators' research.

2. Materials and Experiments

2.1. Raw Materials

The 90-grade heavy traffic asphalt binder was used as the raw material. Its fundamental properties are shown in Table 1. Lignin amine, which was synthesized via the Mannich reaction, was used as the cationic emulsifier to produce emulsified asphalt [33]. It was an effective approach to recycle the biopolymer and reduce pollution of black liquor [34]. WCO was use as the light component supplemental resource for rejuvenators in this study, and Table 2 presents its properties. In order to obtain the PR, composite penetrants which were produced by fatty alcohol polyoxymethylene ether and ethylan 1005 (nonionic surfactant based on a synthetic primary alcohol) were mixed with OR to decrease the interfacial tension [35].

Table 1. Fundamental properties of AH 90 asphalt binder.

Items	Parameter	Results
Physical properties	25 °C Penetration (0.1 mm)	80.5
	10 °C Ductility (cm)	>100
	Softening point [°C]	41.3
	135 °C Viscosity (Pa·s)	0.533
Chemical compositions	Saturates (%)	15.7
	Aromatics (%)	31.3
	Resins (%)	41.8
	Asphaltenes (%)	11.2

Table 2. Fundamental properties of waste cooking oil (WCO).

Items	Parameter	Results
Physical properties	pH values	4.2
	Density (g/mL)	0.920
	25 °C Viscosity (cP)	57.0
Chemical compositions	Saturates (%)	26.5
	Aromatics (%)	28.1
	Resins (%)	45.4
	Asphaltenes (%)	N/A

2.2. Experiments

This study prepared two kinds of rejuvenators (OR and PR) with WCO and emulsified asphalt in the laboratory. In order to evaluate their feasibility in rejuvenating aged asphalt, penetrative analysis was first conducted with five tests. After that, the comparison of physical and rheological performances for rejuvenated and aged asphalt was studied. Accordingly, Figure 1 depicts the schematic diagram for general research flow.

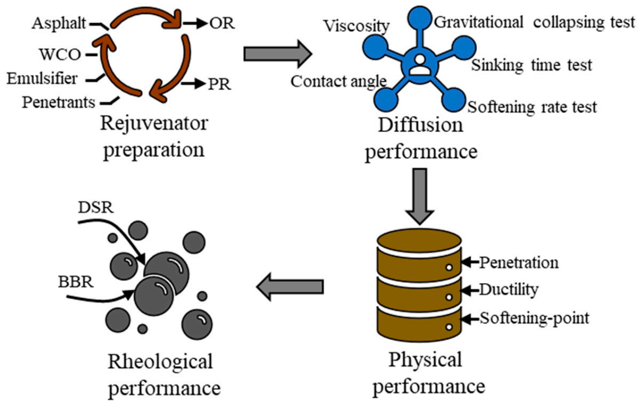


Figure 1. Schematic diagram for general research flow.

2.2.1. Preparation of Rejuvenators and Samples

Rejuvenators need to diffuse and penetrate into the aged asphalt mixtures during fog seal application, thereby refreshing the aged asphalt binder and repair micro cracks. Hence not only the regenerating components refreshing the aged binder is important, but the penetrative properties in the aged binder should be a point guaranteed [36]. Therefore, WCO was used as the regenerating components supplier, while emulsifier and penetrants were added to enhance the diffusivity and permeability [37,38]. First, a colloid mill (MIDE, Jiaxing, China) was used to prepare emulsified asphalt. Second, 40% mass ratio of WCO was added into the emulsified asphalt by a high speed shearing machine (5000 rpm, 120 min, ELE Mechanical & Electrical Equipment CO., LTD., Shanghai, China) to obtain OR. Third, 0.8% mass ratio of composite penetrants were introduced into the OR at 85 °C to produce PR (5000 rpm, 30 min). Figure 2 shows a brief preparation process of OR and PR.

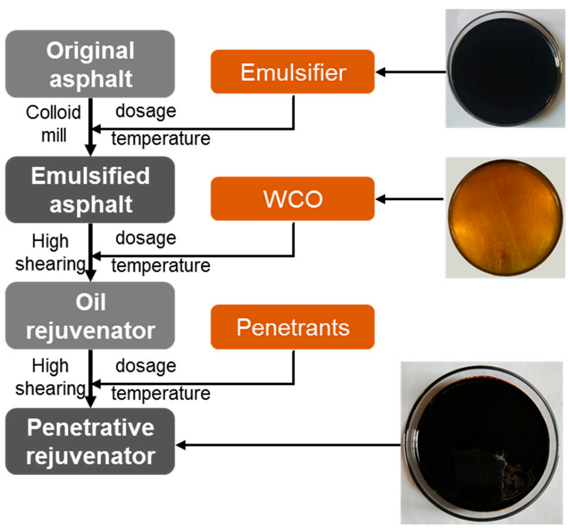


Figure 2. Flow chart for preparing oil rejuvenator (OR) and penetrative rejuvenator (PR).

Since fog seal maintenance was usually applied before the disease becomes evident, the study obtained the aged asphalt by treating with thin film oven test (TFOT, Huanan Experimental Instrument

Co., Ltd., Wuxi, China) to simulate the situation. In this research, dosages of rejuvenator with 2.5 wt%, 5 wt%, and 10 wt% were studied via comparison with their rheological and diffused influence on aged asphalt binder. Before dropping rejuvenator into asphalt, the aged asphalt was heated until fluid at 100 °C. Then different amount of rejuvenators were mixed with aged asphalt to ensure it is diffusing uniformly. Besides original asphalt (Original-A) and aged asphalt (Aged-A), six samples were analyzed which are listed in Table 3.

Table 3. Labels for rejuvenated binders.

Rejuvenators and Dosages	Oil Rejuvenator			Penetrative Rejuvenator		
	10%	**5%**	**2.5%**	**10%**	**5%**	**2.5%**
Labels	OA-10%	OA-5%	OA-2.5%	PA-10%	PA-5%	PA-2.5%

2.2.2. Diffused Performance Tests

Viscosity of the rejuvenators and the contact angle [39] between the aged binder and rejuvenators were first characterized. Then, three self-designed tests were proposed to evaluate the diffusion of the rejuvenator in aged asphalt binder, which were named as sinking time test, softening rate test, and gravitational collapsing test. These three tests provided a concise reference to characterize the diffusion of rejuvenators, by means of dissolving times.

(1) Sinking time test. The aged asphalt specimen was kept floating on the rejuvenator. Stirring magnetic rotor was used in the whole testing process to keep the temperature, at 40 °C, in the rejuvenator uniform. The aged asphalt specimen was designed in a special shape that can ensure floating on the liquid rejuvenator. During the test, substance exchange occurs under the effects of molecular motion between the aged asphalt and liquid rejuvenator, so that the specimen will become soft and finally sink to the bottom. Sinking time to reach the bottom can be used to characterize the diffusion of the rejuvenators. Figure 3 indicates the schematic diagram. Figure 4 shows the size of the aged asphalt binder in small sheet shape of 40 mm × 40 mm × 5.7 mm.

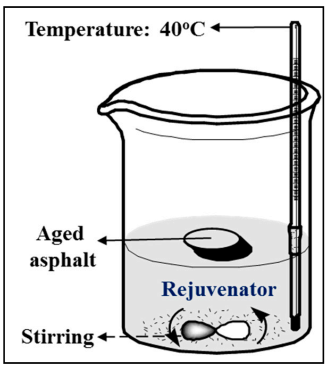


Figure 3. Schematic diagram of sinking time test.

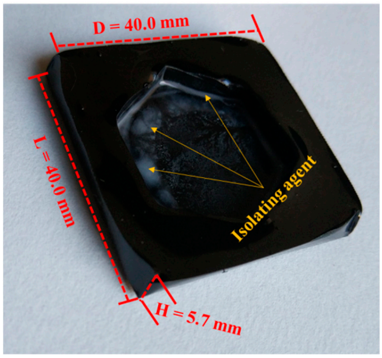


Figure 4. The size of aged asphalt in small sheet shape.

(2) Softening rate test. It is a kind of revised softening-point test. Rejuvenator replaced water and was kept at a constant temperature. The test principle is to measure the time for aged asphalt to completely soften and stretch to touch the bottom under the gravity of a fixed steel ball. First, two specimens of aged asphalt were made by the softening-point test mold, and then placed softening point balls onto the specimens individually. Second, the specimens were placed in a beaker with the height of rejuvenator being 30 mm. Moreover, stirring magnetic rotor and water bath heating were used to keep the system temperature uniform at 35 °C. The time was recorded as the aged asphalt specimens touches the bottom. The schematic diagram is depicted in Figure 5.

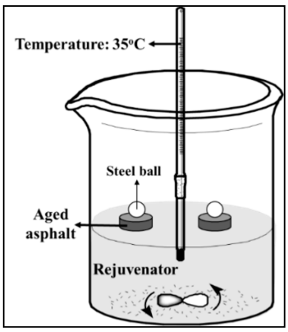


Figure 5. Schematic diagram of softening rate test.

(3) Gravitational collapsing test. It is designed to simulate the two phases diffusing rate at room temperature. The aged asphalt was dumped in a steel pipe whose another port is blocked up. Then rejuvenator was poured onto the solidified asphalt after it is cooled. At the two phases' interface, rejuvenator and aged asphalt will diffuse to each other until the aged asphalt fully softens and crushes down. In this way, the crushing time of the aged asphalt under gravity can be used to analyze the rejuvenator's diffusivity, as shown in Figure 6. The inner area of the mold is 4.23 cm^2, and the used rejuvenators' quality is 1.280 g. Hence, the pressure was 30.26 Pa on the diffusion interface. Moreover, the indoor temperature was 12 °C during the experiment.

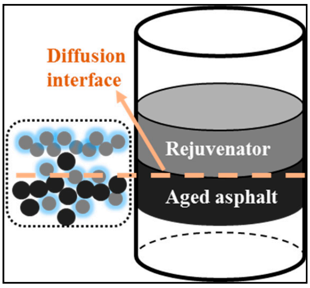


Figure 6. Schematic diagram of gravitational collapsing test.

2.2.3. Rheological Performance Tests

First, the penetration test at 25 °C, ductility test at 5 °C, and softening-point test were conducted to investigate the samples' physical properties. The rheological properties of aged asphalt always need to be considered with its brittleness at low temperature and rutting resistance at high temperature [40]. Then, dynamic shear rheometer (DSR, Anton Paar, Shanghai, China) and bending beam rheometer (BBR, Anton Paar, Shanghai, China) were used to evaluate the effect of two rejuvenators on the rheological properties of aged asphalt binder.

3. Results and Discussions

3.1. Diffusion Performance

Table 4 shows the results of diffusion tests for PR and OR, involved in viscosity, contact angle, and three self-proposed test methods. After the addition of penetrants, OR had an obvious decrease in viscosity, nearly 800 cP at room temperature. It reflected that the addition of composite penetrants allowed a smooth diffusion of the PR. Meanwhile, after dropping PR and OR onto the asphalt film samples, the results of the contact angle demonstrated that PR almost got a lesser contact angle than OR on both aged asphalt and original asphalt (approximate 20°). That illustrated that PR had a lower surface energy, which caused an obvious decrease in the interfacial tension between asphalt and rejuvenators. The addition of penetrants improved the efficiency in diffusion and permeability so that PR could spread out on the surface more easily. Compared to the original asphalt, the slight increase of contact angle for aged asphalt was explained as the aging process would increase the polarity, because nonpolar oil components are gradually transferred to polar resins and asphaltenes.

Table 4. The results of permeability tests for PR and OR.

Rejuvenators	25 °C Viscosity (Pa·s)	Contact Angle (°)		Sinking Time (s)	Softening Time (s)	Collapsing Time (s)
		Aged Asphalt	Original Asphalt			
OR	1.278	53.1	51.6	2660	1974	2873
PR	0.478	34.8	34.6	1557	1356	1926

In the sinking time test, the aged asphalt specimen would soften and deform because of the effects of molecular exchange and buoyancy, thus sinking to the bottom. From the results of sinking time in Table 4, it was known that PR took 1557 s to immerse the sample, while OR lasted 2660 s and 17 min more than PR to diffuse and penetrate into the sample completely. It indicated that both PR and OR had softened the aged asphalt and caused gradual deformation generally. Moreover, PR had a better permeability into the aged asphalt. Therefore, PR could improve the efficiency in fog seal applications.

Softening rate test aims to measure the time as aged asphalt specimen stretch to constant length under the constant pressure and temperature conditions. OR lasted 1974 s to soften and stretch the aged asphalt, while PR was more efficient by 10 min ahead of time under the same condition.

This means PR has a better permeability on the aged asphalt and diffuses to deeper parts for effective maintenance application.

As spraying on the asphalt pavement, the rejuvenator would contact and penetrate to the aged asphalt. Gravitational collapsing test simulated the penetration process of rejuvenator under normal conditions. With the effects of rejuvenators' gravity and penetrating, suspended specimen would fall down as it softens. It was 1926 s for PR to penetrate and soften the aged asphalt, which was 16 min ahead of time than OR. It was concluded that PR could penetrate and diffuse to deeper parts under same condition, hence PR had a better permeability compared to OR.

3.2. Diffusion Mechanisms

Diffusion for rejuvenator penetrating into asphalt can be interpreted as the result of random molecular movements, which is called Brownian motions. Cussler [41] concluded that the significant factors in influencing the rejuvenator diffusing rate mainly involved in the size, shape of molecules or agglomerations, intermolecular forces, temperature, and so forth.

3.2.1. Diffusion Theory

Fick's law [42,43] and Stoke–Einstein equation [44] have been used in modelling the diffusion process with a proper applicability, as shown in Equations (1) and (2) below. Focusing on the rejuvenating process with rejuvenator, diffusion coefficient could account a big part to enhance the penetration rate according to Equation (1). Meanwhile, Equation (2) explains the relative factors influencing the diffusion rate, which illustrates that a smaller viscosity and molecular size increases the diffusion coefficient generally. PR thereby engendered more efficient rate of penetration in aged asphalt because of a smaller viscosity, according to the previous analysis.

$$J = -D * \frac{\partial c}{\partial x}. \quad (1)$$

where, J is diffusion flux (mol/m^2·s), c is concentration (mol/m^3), x is the diffusion depth (m), and D is the diffusion coefficient.

$$\mathrm{D} = \frac{k_B T}{6\pi\mu(R)} \quad (2)$$

where, D is diffusion rate (m^2/s), R is the mean molecular radius, μ is dynamic viscosity (Pa·s), k_B is Boltzmann's constant (1.3807×10^{-23} J/K), and T is absolute temperature (K).

3.2.2. Penetration Principle for Interface

Adding mixed penetrants was an essential procedure to abate the molecular surface energy of rejuvenator as preparing PR, aiming to decrease the interface contact angle and then promote the penetration rate into aged asphalt [45].

Figure 7 depicts the mechanisms of improving PR penetration rate with mixed penetrants. Theoretically, aged asphalt is a highly polar polymer material and has a complex molecular composition, while rejuvenator is a non-polar oil component, so sufficient contact could be a precondition in efficient penetration for the rejuvenator. Because of mixed penetrants decreasing the contacting angle, more PR molecular can gather in the interface, diffuse and then rejuvenate the aged asphalt. The viscosity is defined as the resistance of fluid during flowing [46].

In Figure 7, PR had a smaller viscosity with the addition of penetrants than OR, which allowed to penetrate into the asphalt more quickly. Hence, the viscosity and contact angle in Table 4 demonstrated the more efficient penetrating rate of PR.

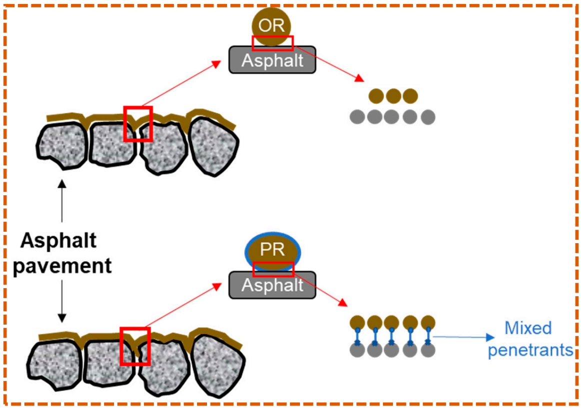


Figure 7. Improving penetration rate with mixed penetrants.

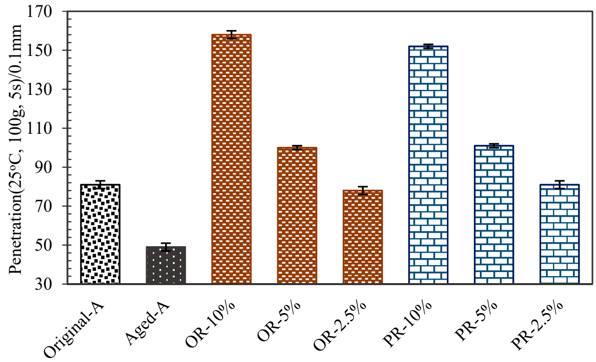
3.3. Physical and Rheological Performance

3.3.1. Physical Properties

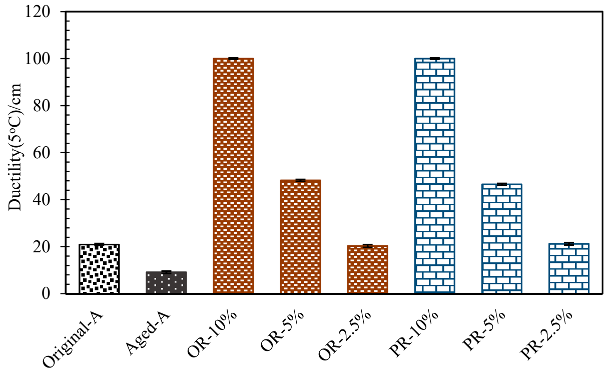
Asphalt and rejuvenators age to a certain extent during sample heating [47]. Consequently, Original-A was used as a benchmark to decide optimum dosage of rejuvenators. Figure 8 depicts the results of penetration test, ductility test, and softening-point test. It is obvious that both penetration and ductility testing data have increased, while softening point decreased in varying degrees, after PR or OR is added to the aged asphalt.

Meanwhile, OA-2.5% and PA-2.5% have a similar value as Original-A in penetration and ductility, but a minimal increase in soften point. Compared to the aged asphalt sample, a higher data in ductility shows a good cracking resistance at low temperature, and penetration results indicates a good shear resistance because of the rejuvenators. It also demonstrated that the rejuvenators have a positive efficiency in softening the aged asphalt, but excessive dosage will lead to aged asphalt being too soft to handle stress. Moreover, the subtle differences of OA-2.5% and PA-2.5% softening points reflected a better stability than other dosages in high temperature environment. Comprehensively, it can be concluded that 2.5% weight of rejuvenator could result in the most effective regeneration performance on aged asphalt, according to these physical test results.

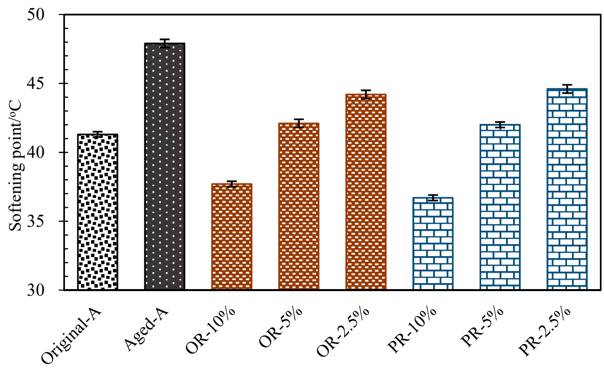
Figure 8 also shows that the same dosage of OA and PA had same effect on the physical properties of aged asphalt. This phenomenon indicated the penetrant had no effect on the physical properties of the aged asphalt, only accelerated the diffusion rate of the PA in the aged asphalt, when the rejuvenators were added to the aged asphalt by agitation.



(**a**)



(**b**)



(**c**)

Figure 8. The physical properties of samples: (**a**) penetration; (**b**) ductility; (**c**) softening point.

3.3.2. High-Temperature Rheological Properties

The changes of phase angles and composite shearing modulus because of rejuvenators are shown in Figure 9. Within 30–60 °C, the G^* value was found to decrease with higher temperature. Because the movement intensification of asphalt molecules resulted in molecular cross-linking and weak molecular force as the temperature increases. Aged-A had the highest G^*, then OA-2.5% and PA-2.5% had a similar *G** with Original-A in the temperature range, which illustrated that adding rejuvenators could recover the viscosity of aging asphalt partially. But excessive dosage of rejuvenator might cause worse stiffness modulus and more rutting possibility of asphalt pavements in summer. Phase angle of samples also indicated a similar trend that OA-2.5% and PA-2.5% were closer to Original-A, and the Aged-A had the smallest phase angle, which reflected that the aging program of asphalt would enhance its elasticity. The viscosity of aged asphalt can be partially recovered by both rejuvenators.

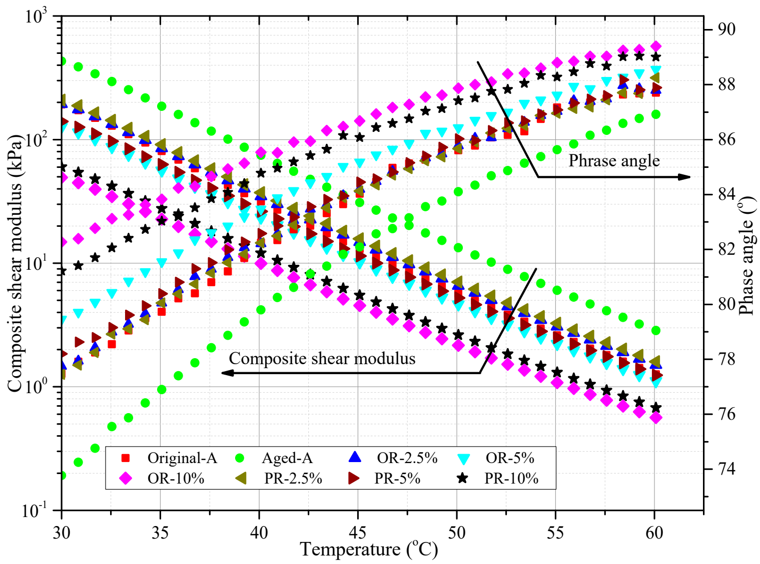


Figure 9. Changes in phase angles and composite shearing modulus because of rejuvenators.

Meanwhile, the regeneration effects on rutting factors are illustrated in Figure 10. Aged-A had the best rutting resistance for its small viscosity. It can be also found that lower rutting factor was obtained with increasing rejuvenators usage, such as PA-10% and OA-10%. Because of the rejuvenators added, aged asphalt became softened and easy to deform at high temperature resulting in rutting with multiple periodic loads, which corresponds to other research results such as reference [48]. Hence, 2.5% rejuvenators of mass percentage of asphalt should be the optimal dosage.

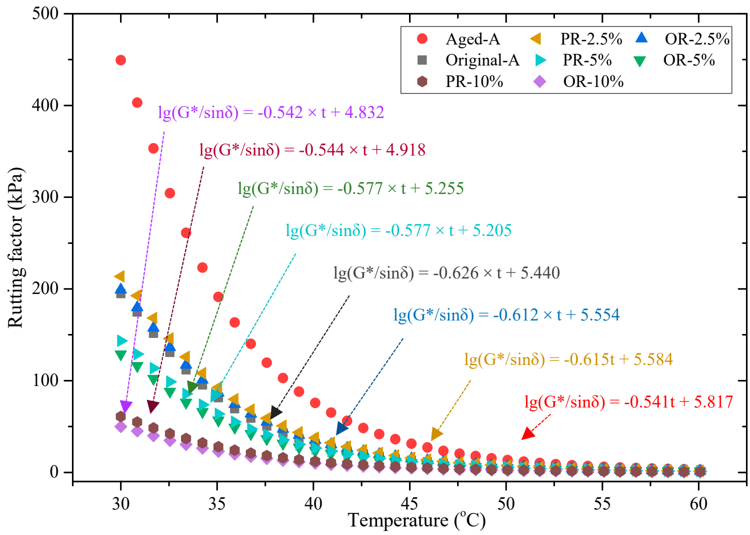


Figure 10. Regeneration effect on rutting factors.

DSR [49] tests composite shear modulus (G^*) and phase angle (δ) within 30–60 °C. Then the Equation (3), linear regression equation for the common logarithm of rutting factor (G^*/sinδ) and temperature, was used to calculate the absolute value of the slope, which was named modulus temperature susceptibility (GTS) [50]. Afterward, analyzing the GTS can obtain the deforming rate of asphalt during temperature rising. Generally, samples show stronger temperature sensitivity as GTS value increases [51].

$$\lg\frac{G^*}{\sin\delta} = -\mathrm{GTS}\cdot \mathrm{t} + \mathrm{K}_1 \quad (3)$$

where, G^*/sinδ is the rutting factor, kPa; t is temperature, °C; K_1 is regression constant; GTS is the absolute value of the slope.

Table 5 shows the GTS values, regression constant, and square of correlation coefficient in regression equation. The minimum GTS appeared at aged asphalt sample, while maximum at original asphalt sample. It reflected that temperature sensitivity of the asphalt became weaker after aging. Moreover, 10 wt% usage rejuvenators (both PR and OR) got similar GTS values with aged asphalt. It was explained that exceeding stiffness of aged asphalt obstructed its deformation. On the contrary, the addition of 10 wt% rejuvenator caused over softening and deformation of the samples evidently as the temperature changes. Therefore, excessive rejuvenator would lead to a worse stiffness modulus and more rutting possibility. However, 2.5 wt% samples had a close value with the original sample. It signaled that appropriate usage of rejuvenator can restore the temperature sensitivity of aged asphalt to a certain extent, resulting in the restoration of the pavement service performance gradually.

Table 5. The regression equation for modulus temperature susceptibility (GTS) value.

Samples	GTS	K_1	R^2
Original-A	0.626	5.440	0.998
Aged-A	0.541	5.817	0.999
OA-10%	0.542	4.832	0.998
OA-5%	0.577	5.255	0.998
OA-2.5%	0.612	5.554	0.998
PA-10%	0.544	4.918	0.998
PA-5%	0.577	5.205	0.998
PA-2.5%	0.615	5.584	0.998

3.3.3. Low-Temperature Rheological Properties

BBR [52] tests creep stiffness (S) and creep rate (m-value) of asphalt binder. Creep stiffness modulus indicates the ability of asphalt mixture to resist permanent deformation. Creep rate indicates the stress relaxation ability of asphalt at low temperature. Samples reflects a better low temperature crack resistance as S being smaller and m-value being higher. The asphalt beams were tested at −12 °C in this research.

According to the Strategic Highway Research Program, stiffness modulus of asphalt samples is ought to be smaller than 300 MPa at measuring temperature, besides whose creep rate should be greater than 0.300 [53,54]. Figures 11 and 12 showed the BBR test results. Since 10 wt% usage rejuvenators (OA-10% and PA-10%) caused over softening of the asphalt beams, the excess creep rate which was beyond the test range cannot be recorded then. From the creep stiffness data in Figure 11, it can be demonstrated that aged asphalt has the biggest S, nearly 192 MPa. After that, S decreased gradually with increasing rejuvenators dosages. That means that both OR and PR could increase the viscosity of the aged asphalt, improving the low temperature crack resistance effectively. The similar law is shown for m-value in Figure 12. Increasing the adding dosages got a bigger m-value which indicated that rejuvenators could soften and increase the creep rate of the aged asphalt. Moreover, the dosage of 2.5% rejuvenators in aged asphalt showed better crack resistance than original asphalt. Aged asphalt sample showed the smallest m-value, because low temperature obstructed its deformation, indicating its worse temperature sensitivity at cold condition.

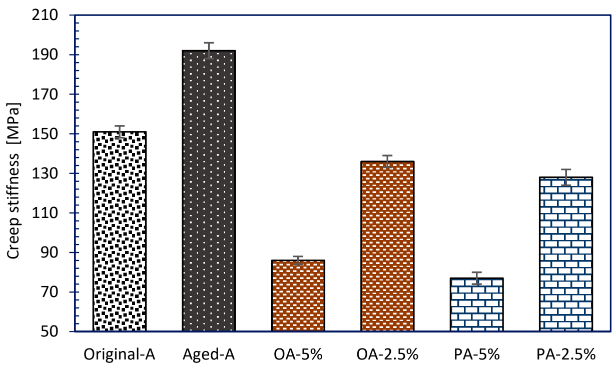


Figure 11. Creep stiffness (S) of asphalt binders with different rejuvenators.

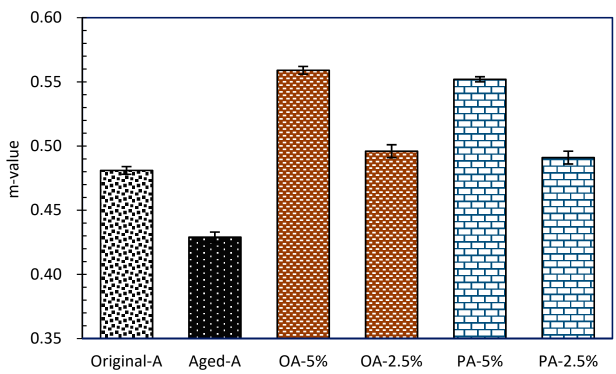


Figure 12. Creep rates (m-value) of asphalt binders with different rejuvenators.

4. Conclusions

This study proposed three test methods to evaluate the diffusion characteristics of rejuvenator in aged asphalt binder. A feasible rejuvenator with good permeability was designed as well by using emulsified asphalt and waste cooking oil. Both regenerative performance and permeability of OR and PR have been investigated. The following conclusions can be obtained.

(1) The applied penetrants can reduce the contact angle between the liquid rejuvenator and the aged asphalt binder, because of the diffusion mechanism and its interface information. It improved the efficiency of diffusion and permeability between rejuvenators and aged asphalt binder.
(2) The self-designed sinking time test, softening rate test, and gravitational collapsing test had been approved as effective ways to compare the diffusion efficiency between different rejuvenators. All these three tests agreed with each other quite well. PR has a better permeability into aged asphalt than that of OR. It has shorter sinking time, softening time, and collapsing time.
(3) Rejuvenators increased the penetration and ductility values, while decreased the softening point. The addition of 2.5 wt% rejuvenator could result in the most effective regeneration performance on aged asphalt, according to both physical and rheological tests results.
(4) Both modulus and phase angle indicated that adding rejuvenators can recover viscosity of aging asphalt partially. Moreover, BBR test demonstrated that the addition of rejuvenators can restore the rheology and temperature sensitivity of aged asphalt in cold condition. But excessive dosage of rejuvenator may cause a worse stiffness modulus, increasing the rutting possibility.

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Appendix C - Paper III

Lei Zhang, Inge Hoff, Xuemei Zhang, Chao Yang.

Investigation of the self-healing and rejuvenating properties of aged asphalt mixture containing multi-cavity Ca-alginate capsules.

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Investigation of the self-healing and rejuvenating properties of aged asphalt mixture containing multi-cavity Ca-alginate capsules

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Self-healing

ABSTRACT

Asphalt is one of the most widely used pavement materials, but is prone to ageing, creating cracks and further deterioration until failure. Self-healing capsules mixed into asphalt mixture can release agents to over time improve healing cracks and can effectively rejuvenate aged asphalt and extend the lifetime. In this paper, in order to explore the effect of Ca-alginate capsules on the self-healing and rejuvenating properties of aged asphalt concrete, and to clarify the mechanism of self-healing promotion, multi-cavity Ca-alginate self-healing capsules are mixed into dense asphalt concrete, and then exposed to thermal-oxidative accelerated ageing and ultraviolet ageing in laboratory. 3-point bending test and fracture-rest-refracture test are used to study the effect of self-healing capsules on mechanical properties and self-healing capability of aged asphalt mixture. The chemical component, rheological property and flow behavior of asphalt binders are used to demonstrate the rejuvenation of aged asphalt concrete. It is found that Calcium alginate capsules have little effect on the initial mechanical properties of the asphalt concrete, and ageing increases the stiffness of asphalt concrete with and without capsules and reduces their fracture energy. The capsules can effectively improve the strength healing rate and fracture energy healing rate of asphalt concrete. The aged asphalt concrete with capsules can also reach same self-healing level with ordinary virgin asphalt concrete without capsule. These are mainly because sunflower oil is released into the aged asphalt mortar after the capsules is broken, which increases the saturate and aromatic lost during the ageing process of the asphalt. It can effectively recover the rheological properties and flow property of aged asphalt binder, thereby improving the self-healing performance. Multi-cavity self-healing capsules enable in-situ rejuvenation of aged asphalt while healing cracks.

1. Introduction

Asphalt mixture is widely used for various roads because of its advantages, such as comfort, safety and low noise [1]. Ageing makes the asphalt harder and more prone to distress under the condition of fatigue loading and moisture erosion, resulting in cracks, unravelling, potholes etc [2]. Maintenance of asphalt road has become a great burden in terms of cost, ecology, energy use and health for worker. Most distress of asphalt pavement starts from cracks. If cracks were healed automatedly at earlier stage, Maintenance times and distress would decrease very much [3]. Self-healing technologies and aided rejuvenation system have been studied to delay the ageing process and extend life-span of asphalt roads [4,5].

There are three main ageing forms for asphalt, the volatilization of light asphalt binder components, oxidation reaction and steric hardening [6,7]. The chemical composition of aged asphalt will show a decrease in saturates and resins, and an increase in aromatics and asphaltenes [8], and all these molecular-scale changes result in an increase in stiffness of the pavement [9]. In terms of rheological properties, the aged asphalt also has a decrease in the complex modulus and its sensitivity to temperature, an increase in the phase angle [10,11]. These will cause the asphalt concrete to crack more easily, and the crack will grow to alligator cracking more easily [12]. In turn, the asphalt concrete pavement will be cracked, unraveled, potholes, until it loses its function. Effectively rejuvenating ageing asphalt and promoting crack closure at an early stage is one of the important methods to study long-life asphalt pavement [13]. Therefore, developing self-healing asphalt materials and technologies become a trend in long-life asphalt pavement research [13]. An on-site approach was proposed to apply by means of releasing encapsulated bitumen rejuvenating agents [14].

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The in-situ rejuvenation technology solves the shortcomings of difficult penetration and uneven rejuvenation compared with spraying rejuvenator on the surface [15]. The superior solution for rejuvenating aged asphalt pavement is to release the rejuvenator evenly in the materials when the ageing starts to result in cracking. This will help prolong the lifetime of the road better. It is important to prevent release of the rejuvenator too early before the asphalt has been aged since this would result in reduced resistance to permanent deformations and excessive rutting. Capsules start breaking when the asphalt material start to crack seems to be a very promising method. The rejuvenating agents are encapsulated and mixed into asphalt binder or mixture when the asphalt pavement is being paved. As the ageing progresses, the cracks induce the capsules to rupture, which can not only heal the cracks, but also rejuvenate the surrounding ageing asphalt binder to recover most of its initial performance [16,17]. Agents encapsulated technology not only heals asphalt cracks and effectively rejuvenates aged adhesives but requires no additional energy application. While other self-healing technologies (electromagnetic induction and microwave heating etc) need increase temperature by external energy giving. They increase healing time and cost [18,19].

There are different types of encapsulated rejuvenators that have been used, evolving from the saturated aggregates to the polymeric microcapsules, fibers and multi-cavity Ca-alginate capsules. Saturated porous aggregates encapsulate rejuvenators embedded in a hard matrix made of a porous stone, surrounded by a hard and impermeable shell made of cement and epoxy resin, developed in 2010 by Garcia et al. [20]. It has been proven that the capsules can resist high temperatures and compression, but it is hard for the oil to flow out. So it is limited promotion of self-healing of asphalt concrete [21,22]. But this is the first time that the capsule self-healing technology has been applied to asphalt concrete materials. The self-healing technology concept provides a pioneering idea for the subsequent development of capsule self-healing technologies. Self-healing capsules can be mixed as aggregate embedded in asphalt pavement, which is better than spraying rejuvenator on the surface. Su, Schlangen, Aguirrre and Sun et al., developed core–shell polymeric microcapsules, the size of which ranged from 35 to 350 µm [4,17,23–25]. They were manufactured by a combined method using chemical and physico-chemical methods (i.e. in-situ polymerization and twostep coacervation processes). Those capsules mainly are mixed into asphalt binder, which can resist mechanical agitation at high temperature, and that they can break and release the rejuvenator during loading. Meanwhile they also can heal broken asphalt binder and recover their fatigue life [26]. In order to increase the encapsulation rate of the rejuvenator, and optimize the production process, encapsulating fibers are developed by Tabakovic and Shu et al. [27–29]. Self-healing fibers conform vascular systems inside asphalt concrete, they can ensure to release the agents when crack pass though the fiber network. They can survive mixing and compaction processes in asphalt mixture, and release the rejuvenator to heal crack in laboratory test. They can be inserted into bituminous mastic and increase the strength of asphalt mixes by 36 % [30]. However, it is difficult to ensure that they are evenly distributed in the asphalt concrete after mixing in large machines and in a large number of applications. Multi-cavity Ca-alginate capsules which diameter range from 2 to 7 mm, are developed by Micaelo, Al-Mansoori, Norambuena-Contrerats, Xu and Zhang et al.[16,31–35]. The capsules contains the advantages of both saturated porous aggregates and core–shell polymeric microcapsules, they have little effect on the initial basic road performance of asphalt concrete when directly incorporated into asphalt concrete [34]. At the same time, its multi-cavity structural oil has many advantages: first, it provides a structural reinforcement for surviving during asphalt mixing and compression, and secondly, it will not release all oil once time, thus providing multiple crack-healing and long-term healing. The capsules can undertake high temperature at 180℃ and stress during compression. The strength and fracture energy recovery rate of asphalt mixture with capsules can reach 92.7 % and 180.2 %, respectively [35]. The capsules are continued and extended the application from binder to mixture, including mixture like Stone Matrix Asphalt (SMA) and Open-graded friction course (OGFC) Pavement [36,37]. This paper also researches the self-healing and rejuvenating properties of aged asphalt mixture containing multi-cavity Ca-alginate capsules.

Micro-mechanism of asphalt self-healing has been studied for several decades, and inspired by the theory of healing in polymers, which containing five stages: 1) surface rearrangement, 2) surface approach, 3) wetting, 4) diffusion and 5) randomization [38,39]. More macroscopically, some researcher believe that the self-healing ability of asphalt is mainly manifested in flow capability and the recovery of viscoelastic properties [40,41]. Asphalt binder can flow into crack by capillarity and heal the crack like a Newtonian fluid, but the flow capability of asphalt binder becomes weaker with ageing [42]. Asphalt binder extracted from the aged asphalt concrete containing capsules will be used to investigate the healing and rejuvenation of the aged asphalt concrete by the capsules. The flow behavior and the recovery of viscoelastic properties of binder are tested.

The paper aims to explore effect of multi-cavity Ca-alginate capsules on crack resistance, self-healing and rejuvenation of aged asphalt mixture. At the same time, the mechanism of in-situ rejuvenation and self-healing improvement were revealed by studying the effect of sunflower oil in capsules on chemical components change, the rheological properties and flow properties of aged asphalt binder.

Table 1
Technical information of bitumen binder.

Technical information	Results	Methods
Penetration (25℃, 100 g, 5 s)/0.1 mm	77.5	NS-EN 1426:2015
Softening point/℃	48.6	NS-EN 1427:2015
Ductility (50 mm/min, 15℃)/cm	>100	NS-EN 13589:2018
Kinematic viscosity (135℃)/Pa·s	0.46	NS-EN 12595:2014
Density (25℃)/(g/cm^3)	1.035	NS-EN 15326:2007 + A1

Table 2
Physical properties of multi-cavity Ca-alginate capsules.

Physical properties	Alginate solution (2.5 wt%): Oil	Radius /mm	Density /(g/cm^3)	Oil content /%	Mechanical strength /N
Result	10:1	0.95–1.05	1.056	62.50	11.9

2. Materials and experiments

2.1. Materials

The asphalt binder with 60/80 penetration grade was selected to prepare asphalt mixture and conduct different ageing processes, whose technical information of asphalt binder is shown in Table 1. Multi-cavity Ca-alginate capsule was also used to rejuvenate aged asphalt concrete in situ and improve its self-healing properties, which was synthesized with sodium alginate, sunflower oil, Tween80, deionized water and calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$) by ion exchange. Sunflower oil was selected among several common used rejuvenators as core material because of positive effect on asphalt rejuvenator, low cost and no extra treatment required [43]. The synthesis process of capsules has been introduced in Zhang's research [35]. In this study, optimal capsules with an alginate solution (2.5 wt%)-to-oil ratio of 10: 1 were selected because of its excellent physical and chemical properties surviving the asphalt concrete mixing and compaction [35].

2.2. Characterization of the capsules

Multi-cavity Ca-alginate capsules were added to asphalt mixture as

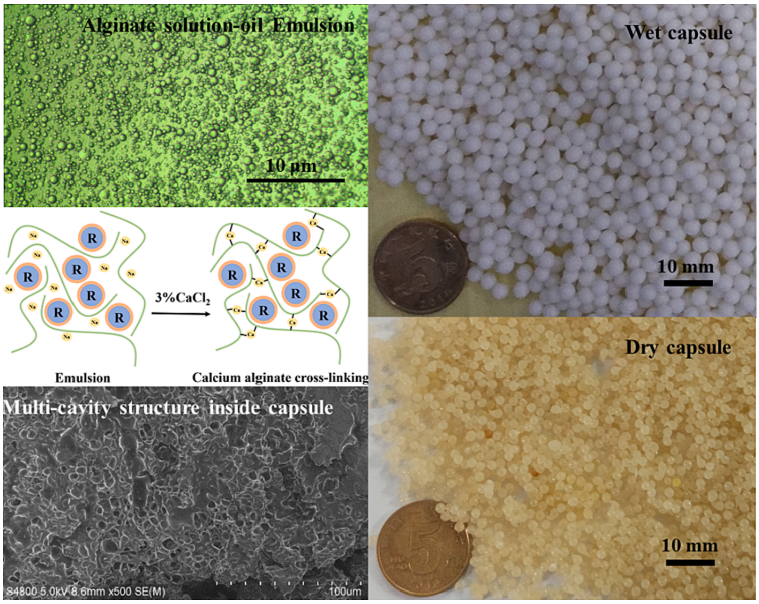

Fig. 1. Characterization of the multi-cavity Ca-alginate capsules.

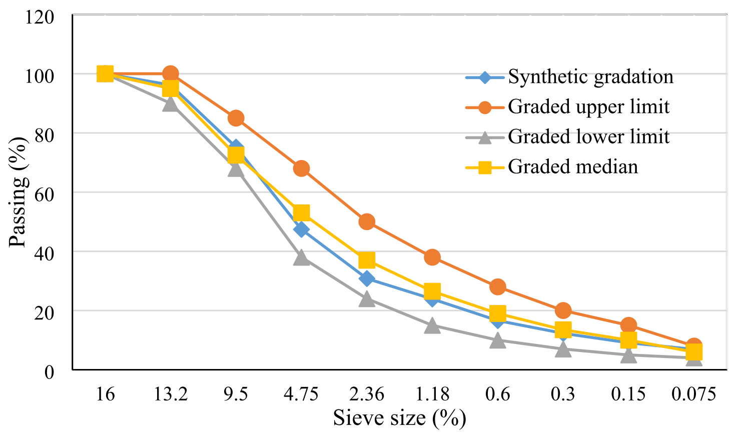

Fig. 2. The gradation curve of the AC11 asphalt mixture.

automatic in-situ rejuvenation systems and a supplier of self-healing capability, whose physical properties are shown in Table 2. The capsules with alginate solution (2.5 wt%)-oil ratio of 10/1 have similar density (1.056 g/cm^3) with asphalt binder and high oil content (62.5 %). Furthermore, its mechanical strength reaches 11.9 N, which can survive after HMA (hot mix asphalt) mixing and compressing [44].

Fig. 1 shows the morphological changes during capsules synthesis from emulsion to ready-made capsules, which were observed by Fluorescence microscope, SEM and camera respectively. A mixed solution of sodium alginate and sunflower oil forms an oil-in-water structure with the help of a surfactant and high shearing speed. And the structure was retained during the cross-linking process of Calcium ion. During the drying process, the water inside the capsules evaporates and the radius of the capsules decreases. Due to the different wall thickness and location of the cavity inside the capsules, the internal rejuvenator will be gradually released over time under the influence of traffic loads and environmental factors during the service process. If the asphalt ageing process matches the release rate of the rejuvenator, the aged asphalt pavement will be automatically rejuvenated in situ.

2.3. Preparation of asphalt mixture

A dense asphalt mixture AC11, which was widely used in the upper layers of highways of all levels, was used in this study. The aggregate gradation curve is shown in Fig. 2. Under the premise of unchanged aggregate degradation and binder content, 0.5 wt% capsules of the whole mix were added directly and mixed for 15 s at the end of the mixing process to make them evenly distributed in asphalt mixture.

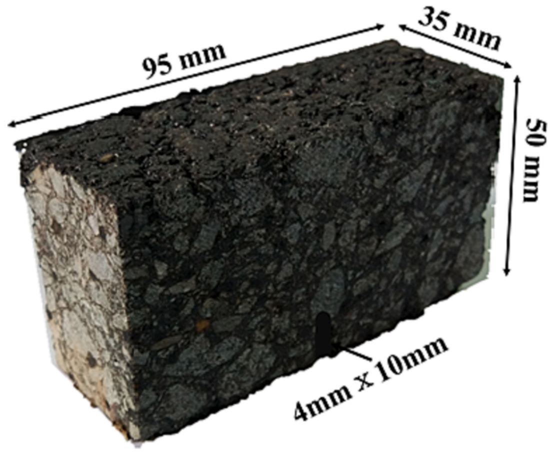

Fig. 3. Asphalt mixture beam used in the 3-point bending test.

Table 3
Physical properties of asphalt mixture with and without capsules.

Physical property	Value	
	Without capsules	With capsules
Binder content /%	4.7	4.7
Bulk density /(g/cm^3)	2.560	2.557
Theoretical density/ (g/cm^3)	2.681	2.673
Air voids (VV)/%	4.5	4.3
Voids in mineral aggregate (VMA)/%	15.8	15.9
Voids filled with bitumen (VFA) /%	71.5	73.0

Table 4
Ageing process of asphalt mixture.

Ageing types	Ageing condition	Ageing level
Not aged (UA)	–	–
Short term thermo-oxidative ageing (STA)	135℃ 4 h	Simulate to asphalt mixture ageing in construction process after mixing at construction site
Long term thermo-oxidative ageing (LTA)	135℃ 4 h + 85℃ 5d	Simulate the ageing process of asphalt pavement using 5–7 year service life
Long term UV-ageing (UVA)	135℃ 4 h + UV 14d (21 W/m^2, 40℃)	Simulate the ageing process of asphalt pavement in real service conditions

Before roller compaction, part of the asphalt mixtures with and without capsules were placed in a forced ventilation oven with 135℃ to perform short term thermo-oxidative ageing for 4 h and mixed each hour to simulate asphalt mixture ageing in construction process. The remaining mixture was directly rolled into a 300 mm × 300 mm × 50 mm rutting plate. Rutting plates were cut into 95 mm × 50 mm × 35 mm beams with a 10 mm × 4 mm notch (shown in Fig. 3) to perform next experiment. Table 3 shows the physical properties of asphalt mixture with and without capsules. The addition of capsules reduced the void ratio of asphalt concrete by 0.2 % points. A similar reduction was reported by Jose [45]. The other properties are similar and the two mixes are considered to be comparable.

Meanwhile, in order to evaluate the ageing effect on crack resistance and self-healing properties of aged asphalt mixture with capsules, the asphalt mixture was aged following 3 different types ageing programmer. The samples of long-term thermo-oxidative ageing (LTA) and long-term UV-ageing (UVA) underwent shot-term thermo-oxidative ageing.

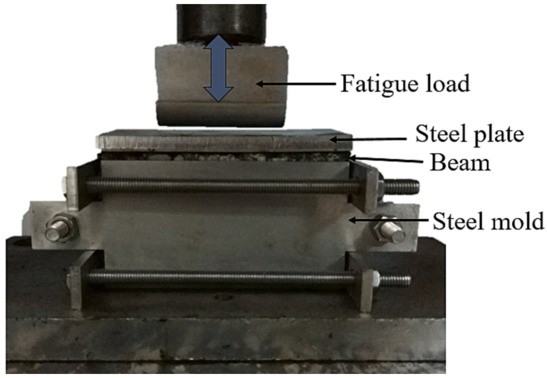

Fig. 4. The mold used in fatigue load test.

Table 4 shows the detailed ageing process of asphalt mixture.

2.4. Preparation of asphalt binders

Ageing, self-healing and rejuvenation of asphalt mixture refer to composition and performance changes of asphalt binder. This paper also uses the same ageing conditions as the mixture to simulate the ageing of the asphalt binder for comparison purposes. 50 g of original asphalt is aged to obtain aged binder in a disc with a diameter of 150 mm referring to TFOT as same as mixture (135℃ 4 h + 85℃ 5d). Referred for previous study of Zhang et al. [35], fatigue loads can promote oil release from capsules. When asphalt mixture was performed 4000 cycles fatigue loads, most of oil will be released and the content of sunflower oil in the asphalt binder was 5 %. So 5 % sunflower oil was added to the asphalt binder and aged together to obtain rejuvenated asphalt binder (named aged binder with oil). Meanwhile, separated sunflower oil also was aged for 5d at 85 ℃. Correspondingly, then they were mixed after being aged separately to obtain another rejuvenated asphalt binder (named aged binder and aged oil).

2.5. 3-point bending test

Crack is one of the most common distresses in asphalt concrete pavement, and often other large distresses such as potholes and unravelling starting from cracks. 3-point bending (3 PB) were used to evaluate effect of polymer capsules on crack resistance of virgin and aged asphalt mixture. Results of 3-PB also reflect the storage stability of capsules in aged asphalt concrete. Before testing, the asphalt mixture beams, with and without polymer capsules, with and without ageing, were conditioned at −10 ℃ for a minimum of 4 h. This temperature was chosen to avoid any creep deformation and to create a brittle fracture on the samples. This type of damage is mostly a problem in cold weather condition. Then a universal testing machine (UTM-25) was used to carry out 3 PB testing until the asphalt mixture beam was broken in two pieces. A deformation ratio of 0.5 mm/min was selected to ensure stable crack grown conditions [46]. And the force and vertical displacement were recorded automatically by the control system.

2.6. Fracture-rest-refracture test

The effects of capsules on the self-healing ability of different asphalt mixture beams were quantitatively analyzed by fracture-rest-refracture test. A definitive rest period (48 h, 20 ℃) between two 3BP fracture tests was set to promote self-healing of cracks generated during the first 3BP by the action of asphalt binder flow and gravity. At the beginning of the rest period, the fatigue loading of 4000 cycles was conducted via UTM-

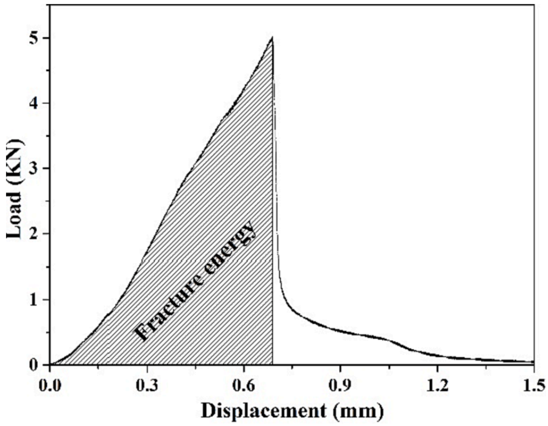

Fig. 5. Calculation of fracture energy.

25 to simulate the loading of vehicles on the road surface aiming to let the capsules release the oil and simulate the traffic load on the cracked road surface (see Fig. 4). The loading pressure was 2.1 MPa and the frequency was 1 Hz.

The strength recovery ratio (SHL) and energy recovery ratio (EHL) were used to quantify the self-healing level of asphalt mixture with or without capsules, aged or unaged.

The strength recovery ratio (SHL), which is defined as the ratio of the maximum load measured in the beam after the healing process, F_i, and the maximum load of the beam initially tested, F_a, following Eq (1).

$$SHL = \frac{F_i}{F_a} \tag{1}$$

The fracture energy recovery ratio (EHL), which is defined as the ratio of fracture energy measured in the beam after the healing process, E_i, and the fracture energy of the beam initially tested, E_a, following Eq (2).

$$\mathrm{EHL} = \frac{E_i}{E_a} \tag{2}$$

The fracture energy (E_f) is a good indicator of the cracking potential of the asphalt pavement and calculated according to Eq (3), and its schematic diagram is shown in Fig. 5.

$$E_f = \frac{W_f}{A_{lig}} \tag{3}$$

Ligament area (A_{lig}) is the area of the crack face evaluated according to Eq (4).

$$A_{lig} = (h-a)t \tag{4}$$

Where h, a and t are the specimen height (m), notch length (m) and specimen thickness, respectively. The work of fracture (W_f) is defined as the area under the force–displacement curve up to the maximum load according to Eq (5).

$$W_f = \int_0^b F du \tag{5}$$

Where b is the displacement when the force reaches the maximum. F and u are applied load and load line displacement respectively.

2.7. SARA analysis of asphalt binders

In order to clearly understand components change of asphalt binder in the mix, after different processes such as ageing and capsule releasing, SARA(saturate, romantic, resin and asphaltene) analysis was performed by The TLC-FID which has the advantage of faster detection speed (about 30 s) and higher sensitivity than traditional components analysis method. Bitumen samples were collected directly from the intermediate of asphalt mixture test specimens with a hot knife [31], then were dissolved in dichloromethane (2 % mass/volume ratio). 1 μL prepared solution was dropped at origin point of a silica gel chromatography bar by five times. Then, the prepared silica gel chromatography bars were put into three expansion slots for expansion. The expansion solvents were *n*-heptane, heptane/toluene mixture (volume ratio 1:4) and toluene/ethanol mixture (volume ratio 11:9) respectively. After each expansion process, the expanded silica gel chromatograph was placed in an oven at 70℃ for 1 min to completely evaporate the solvent. Finally, the prepared silica gel chromatography bars were placed into TLC-FID to analyze the components of asphalt binders.

2.8. DSR test

In order to explore the improvement mechanism of sunflower oil on asphalt flow and self-healing performance after the capsules is broken, a dynamic shear rheometer (DSR) was applied to perform temperature sweep test and frequency sweep test which apply a shear stress on a thin asphalt specimen sandwiched between two parallel oscillatory plates (diameter of 25 mm) with a gap of 1 mm.

2.8.1. Temperature sweep

The temperature sweep test was performed at a constant strain of 0.5 % and a constant frequency of 10 rad/s with temperature ranging 30–80℃ (heating rate of 2 ℃/min). Three indicators, complex modulus (G*), phase angle (δ) and fatigue factor (|G*|·sin δ), were automatically calculated, respectively.

2.8.2. Frequency sweep

The frequency sweep test was conducted for each bitumen in nine different temperatures (increasing from 30℃ to 70℃ with an interval of 5℃). The test frequency ranged from 0.1 Hz to 100 Hz and the constant strain was 0.5 %. Complex modulus(G*), phase angle (δ) and complex viscosity (η*) were recorded as frequency increases at each temperature point. The main curves of different binders were constructed by Williams–Landel–Ferry (WLF) Time-Temperature Superposition principle (see in Eq. (6)) based on the frequency sweep analysis results in order to study rheological properties over a wide frequency rang.

$$\log\alpha_T = \frac{-C_1(T-T_0)}{C_2+(T-T_0)} \tag{6}$$

where α_T is the horizon shift factor, T is actual measured temperature, C_1 and C_2 are constants, and T_0 is reference temperature.

During construction, 30℃ was selected as the reference temperature. The formula for calculating replaced frequency (f_R), complex modulus (G*) and phase angle (δ) were shown in Eq. (7), Eq. (8) and Eq. (9), respectively [47].

$$f_R = f \times \alpha_T \tag{7}$$

$$G^* = G_{min} + (G_{max} - G_{min}) \times (1 - \exp(-\left(\frac{f_R}{\beta_G}\right)^{\gamma_G}) \tag{8}$$

$$\delta^* = \delta_{min} + (\delta_{max} - \delta_{min}) \times (1 - \exp(-\left(\frac{f_R}{\beta_\delta}\right)^{\gamma_\delta}) \tag{9}$$

where f is testing frequency in DSR apparatus, G* is the complex modulus in master curves, G_{min} and G_{max} are the complex modulus when f_R is 0 and infinity, δ* is the phase angle in master curves, δ_{min} and δ_{max} are the phase angles when f_R is infinity and 0, β_G β_δ γ_G γ_δ are the curve parameters.

The flow behavior index (n) of different binder could be obtained in each tested temperature by fitting a power-law model (Ostwald-De

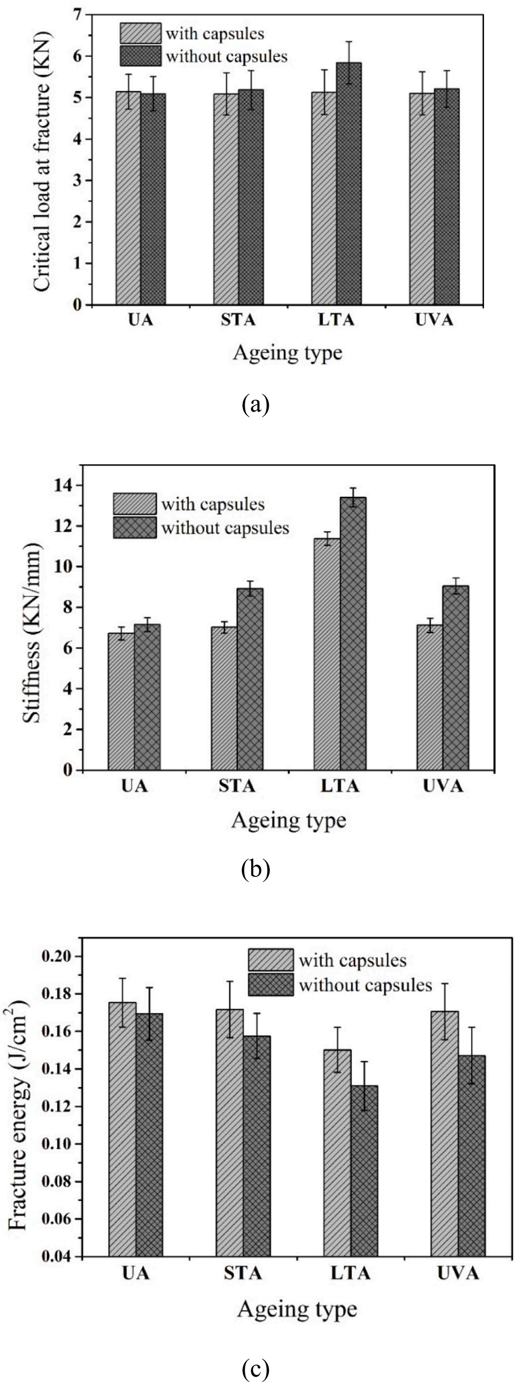

Fig. 6. Mechanical properties of asphalt mixtures with different ageing types: (a) critical load at fracture; (b) stiffness; (c) fracture energy.

Waele model) according to Eq. (10) [48,49].

$$\eta^{*} = m\cdot f^{n-1} \quad (10)$$

where η* is the complex viscosity (Pa·s), f is the testing frequency (Hz), m and n are the fitting parameters.

3. Result and discussion

3.1. Effect of ageing on the fracture behavior of asphalt mixtures

In order to investigate the effect of ageing on the fracture behavior of asphalt mixtures with/without capsules, at least 6 beams for each sample were tested and the average values of the results were recorded in Fig. 6. For reference asphalt mixture beams, it can be seen from Fig. 6 (a) that the critical load at fracture the increases with the increase of thermal oxygen ageing degree. The critical load is 5.09KN, 5.18KN and 5.84KN for UA, STA and LTA, respectively. At the same time, with the increase of thermal oxidative ageing, their stiffness also increases and the fracture energy decreases, which is shown in Fig. 6(b) and (c). In addition, the difference value between LTA and STA (0.66KN, 4.5KN/mm and 0.0267 J/cm^2) is much greater than that between STA and UA (0.11KN, 1.8KN/mm and 0.0118 J/cm^2). This could indicate that the long-term ageing procedure as specified in AASHTO R30 has a very significant effect on the mixtures. The above phenomenon is mainly due to the hardening effect of ageing on bitumen. Thus, the aged mixture has the highest load at fracture, but once the crack begins, it propagates rapidly within the fracture zone. The high crack propagation rate reduces the fracture energy in Fig. 6(c). The trend of hardening also increases with ageing, but short-term ageing has minor changes. The STA samples have closer stiffness to UA samples, while the stiffness of LTA samples increases significantly. However, it also indicates that the critical load, stiffness and fracture energy of UVA samples are basically unchanged from STA samples. This is mainly because UV ageing can only act on the surface, but not on the inside of asphalt mixture beams. It is no effect for UV ageing on 3 PB behavior of asphalt mixtures. According to review of Li et al., UV light can only act on the micron depth of the asphalt surface. It is difficult for dense asphalt mixture to apply UV light to the interior of asphalt concrete [50]. From the discussion of section 3.3.1, the components of bitumen inside UV aged specimens have no obvious changes by surface ageing with UV light. At the same time, comparison of the above physical parameters of the encapsulated asphalt concrete with the reference beams on different ageing degree, it can be found from Fig. 6 that the influence law of different ageing on the critical load, stiffness and fracture energy of mixtures containing capsules are similar to the reference group. With the deepening of ageing, the critical load and stiffness increase, while the fracture energy decreases.

It can be seen that the calcium alginate capsule has almost slight effect on the initial mechanical properties of the asphalt concrete. As for different ageing asphalt beams with and without capsules, it can be found that the critical load and stiffness of all beams with capsules are slightly smaller than their corresponding reference groups, and the fracture energy is slightly larger. The difference is caused by the one-time release of the oil, making the bitumen containing the capsules relatively softer. Comparing LTA and STA samples, it is also found that the increase in critical load and stiffness and decrease in fracture energy of the beams with capsules are smaller than reference beams. It is highly likely that the 135 ℃ and 85 ℃ during the ageing process caused some of the oil in the capsule to escape. However, the pavement temperature cannot reach 85 ℃ during the actual service, thus the laboratory accelerated mixture ageing process could be not fully applied to the ageing process of asphalt mixture containing calcium alginate capsules. And the more serious the ageing, the greater the difference between beams with capsules and without capsules. It indicates that self-healing capsules has remarkable effect on crack resistance of asphalt mixture,

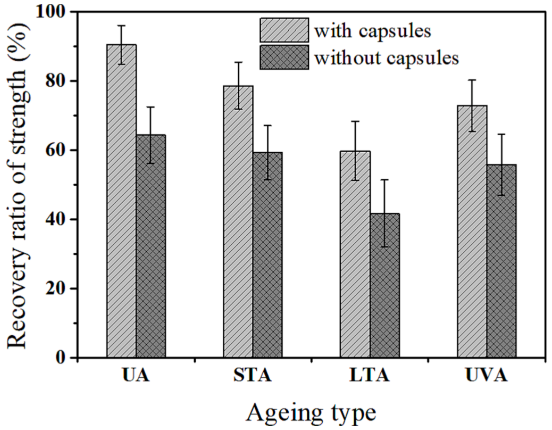

Fig. 7. Recovery ratio of strength for asphalt mixture beams of different ageing type after 4000 fatigue loads.

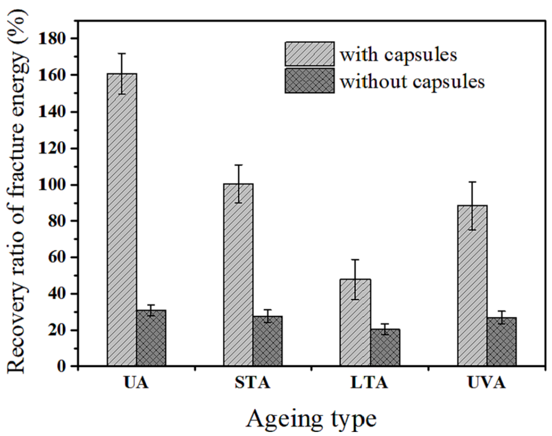

Fig. 8. Recovery ratio of fracture energy for asphalt mixture beams of different ageing type after 4000 fatigue loads.

especially in aged asphalt mixture.

3.2. Self-healing properties of ageing asphalt mixture containing capsules

The self-healing behavior of the aged asphalt mixtures with capsules was also investigated by fracture-healing-refracture test. After the first fracture, the aged beams were subjected to a fatigue load of 4000 cycles and a second fracture was performed after 48 h of self-healing at 20℃ [35]. The strength recovery ratio and energy recovery ratio are shown in Fig. 7and Fig. 8. With the deepening of thermal-oxygen ageing, the strength recovery ratio and fracture energy recovery ratio of asphalt beams with/without capsules decrease significantly. This is mainly because ageing reduces the self-healing ability of the asphalt itself. The main reason is that ageing makes the fluidity of asphalt mortar in asphalt concrete worse and cannot achieve the healing level of virgin asphalt under the same conditions. The specific reasons will be analyzed in the following mechanism study, shown in the section 3.4.

It can be seen that the strength recovery ratio of the beams containing capsules is obviously improved after the sunflower oil inside the capsules is released, and the LTA is increased from 41.7 % to 59.8 % and

Table 5
Four components (SARA) percentage of different asphalt binders.

Samples		Saturate (%)	Aromatic (%)	Resin (%)	Asphaltene (%)	C_{II}
UA-0	Without capsules	15.46	39.94	30.7	13.9	0.416
STA-0		14.72	38.32	29.75	17.21	0.469
LTA-0		13.4	35.04	26.89	24.67	**0.617**
UVA-0		14.35	38.38	28.99	18.28	0.484
UA-1	With capsules	15.34	40.01	29.98	14.67	0.429
STA-1		15.01	38.87	28.85	17.27	0.477
LTA-1		13.02	36.59	27.05	23.34	0.571
UVA-1		14.76	38.56	28.58	18.1	0.489
UA-2	With capsules and 4000 cycles fatigue loads	17.01	43.2	30.07	9.72	0.365
STA-2		16.45	42.04	29.16	12.35	0.405
LTA-2		14.34	40.21	27.03	18.42	**0.487**
UVA-2		16.2	42.1	27.14	14.56	0.444

returns to the state with the STA. It indicates that the fracture energy recovery ratio of aged and unaged beams containing capsules is also larger than that of the asphalt mixtures without capsules. The energy healing rate of asphalt concrete containing capsules is as high as 162.1 %, which is mainly due to the softening of asphalt after the release of sunflower oil into binder, which increases the viscosity of asphalt mastic at room temperature. With the ageing deepening, the difference between the energy recovery rate of the beams with and without capsule decreases. This is because sunflower oil in the capsules will also be aged during the ageing process, reducing the enhancement of asphalt self-healing performance [33].

3.3. Self-healing improvement mechanism

3.3.1. Chemical component

In order to clearly understand components change of asphalt binder in the mix, after going through different processes such as ageing and capsules releasing, Table 5 shows four components (SARA) contents of asphalt binder extracted from different asphalt mixture. As the ageing increase, the content of saturates in the asphalt will continue to decrease and the asphaltene will increase significantly, but the aromatics and resins will only have minor change. This phenomenon might be caused by the fact that the aromatics were condensed to resins and the resins were condensed to asphaltene, which led to the increase of asphaltene during the ageing process [51]. The "Colloidal Instability Index" (C_{II}) is also used to describe the bitumen using the dispersed polar fluid model, which calculates by Eq11. Smaller values of the index indicate a higher stability and better dispersion of the micelle fractions in the bitumen [52]. Thermal oxidative ageing also exacerbated the colloidal instability of asphalt from type-0 results. Comparing different asphalt binders extracted from concrete with capsules and without capsules (data type-0 and type-1 group), the SARA component and C_{II} are similar, which shows that the capsules is basically not released during the concrete mixing, compacting and ageing process, and has certain weather resistance and long-term storage ability.

When the sunflower oil in the capsules flows into the asphalt binder after the 4000 cycles fatigue load, which oil accounts for about 5 % of binders now [35], it can be seen that the saturates and the aromatics are increased, and the aged asphalt binder is rejuvenated.

The self-healing ability of STA-2, LTA-2 and UVA-2 is significantly increasing compared to STA-0, LTA-0 and UVA-0, the asphaltene content after rejuvenation did not decrease much, but the lightweight

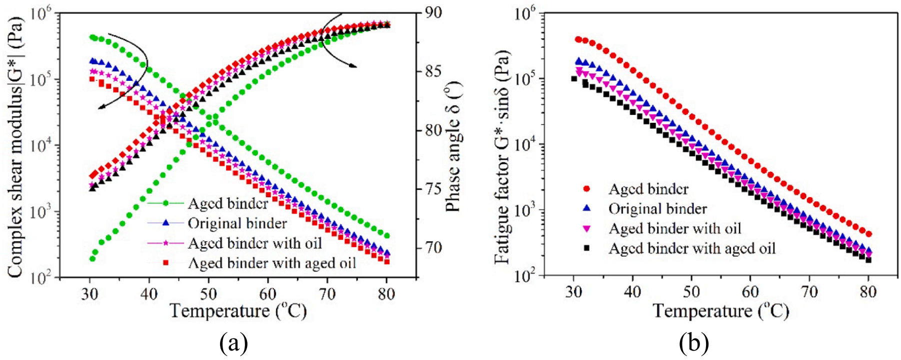

Fig. 9. Results of temperature sweep test: (a) Complex shear modulus and Phase angle; (b) Fatigue factor.

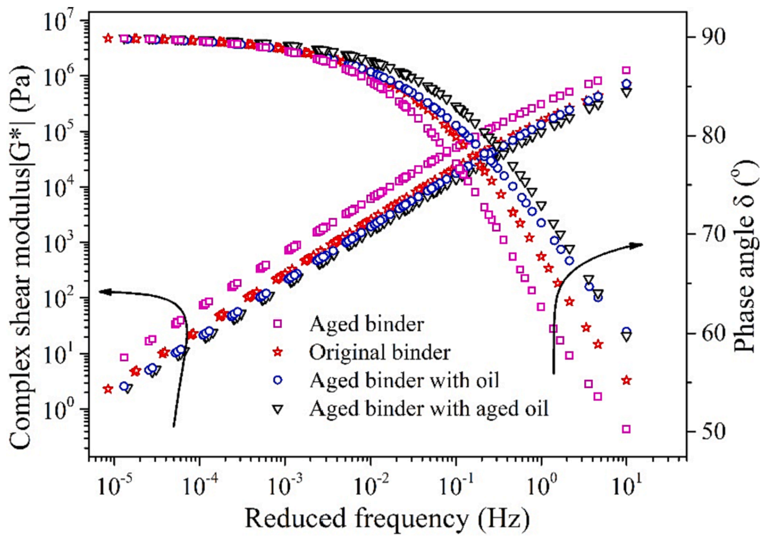

Fig. 10. Master curves of complex modulus and phase angle of different asphalt binders.

asphalt increased. It can be found that the improvement of the self-healing ability of the asphalt binder mainly depends on the light-weight components. Therefore, the sunflower oil in the calcium alginate capsules can significantly improve the self-healing and rejuvenation ability of the aged asphalt mixture.

$$C_{II} = (Saturate + Asphaltness)/(Aromatic + Resin) \quad (11)$$

3.3.2. Rheological property

The change of the chemical composition of asphalt binder will definitely affect the rheological properties of asphalt. In order to analyze the mechanism of self-healing improvement from a rheological property point of view, Fig. 9 and Fig. 10 show the temperature sweep results and frequency sweep results of different asphalt mortars, respectively. At the same time, in order to add extra comparison, a set of reference groups was added in the design process of the experiment. After the sunflower oil of the capsules core material was aged under same conditions as asphalt binder, it was added to the aged asphalt in the same proportion. It can be seen from the temperature sweep results in Fig. 9, the difference in complex shear viscosity, phase angle and fatigue factor of different types of asphalt binder samples at low temperature is much larger than that at high temperature, which are caused by the basic properties of asphalt. While the asphalt concrete pavement with capsules is more paved under relatively low temperature conditions, the difference and recovery of the property should be further studied at low temperature. At the same time, the rheological properties of the aged bitumen samples are worse than those of the other three types of samples, and aged binder with oil and aged binder with aged oil both can recover the rheological properties to the level of virgin bitumen. It can be seen that when the sunflower oil is released from the capsules and physically penetrated with the aged asphalt, which can effectively restore its rheological properties, and then rejuvenate the aged asphalt concrete pavement. Furthermore, its self-healing performance has been effectively improved in function.

The results also show that the sample aged binder with aged oil and the sample aged binder with oil basically make no difference to the rejuvenation of the rheological properties of the aged asphalt concrete. It can be seen from the curve that the rheological properties indexes of aged binder with aged oil are slightly better than that of aged binder with oil, which may be due to the fact that the directly aged sunflower oil volatilizes the ultra-light components with very little internal

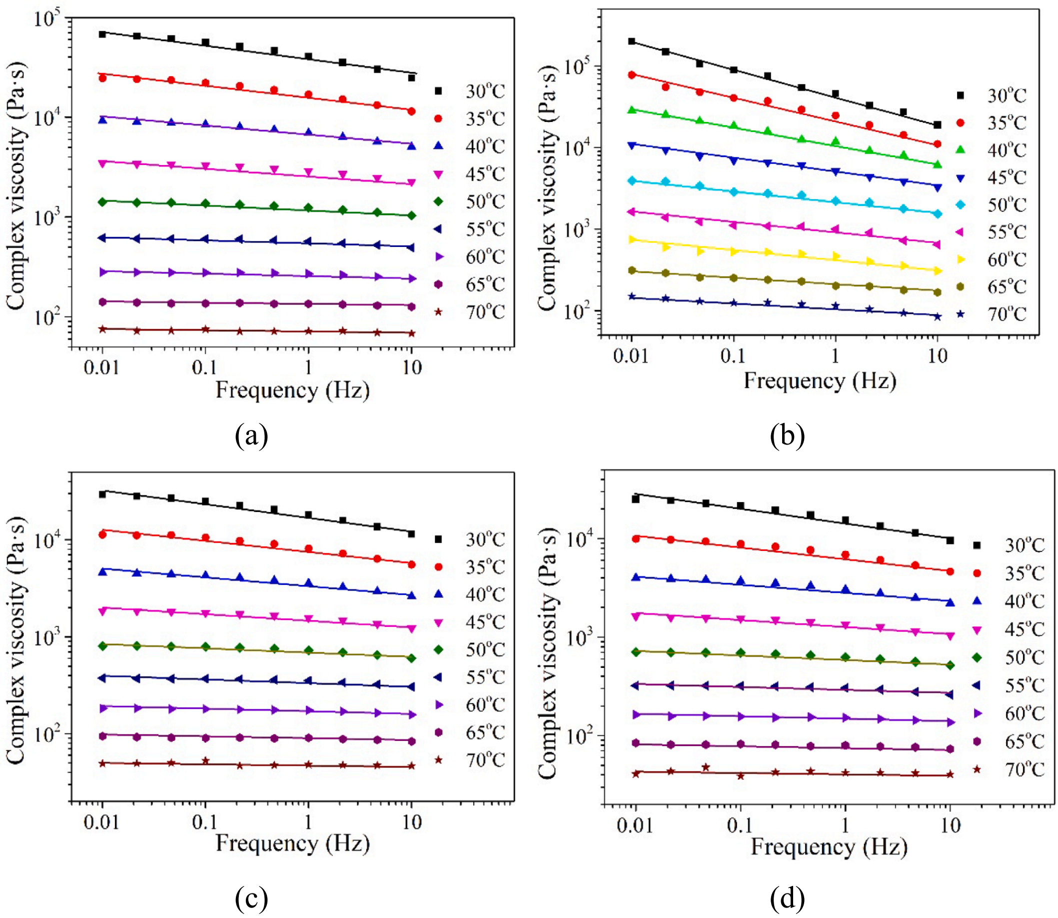

Fig. 11. Complex viscosity-frequency curves of different asphalt binders: (a) Original binder; (b) Aged binder; (c) Aged binder with oil; (d) Aged binder with aged oil.

content, so the effective proportion of adding aged oil is slightly higher than that of simultaneously ageing oil and asphalt in the same proportion.

The main curve in Fig. 10 also shows that the results are basically consistent with the temperature sweep. The reference temperature for constructing the master curves is 30℃. In the whole frequency range, the complex shear modulus of the aged asphalt binder are about 5 times higher than that of the other three samples at same frequency. And the phase angle is also lower than other three samples. It indicates that ageing reduces the complex shear modulus of the bitumen and increases the sensitivity of the phase angle, and that the bitumen becomes harder. At the same time, the addition of oil from capsules makes the modulus recover more than the results before being aged, and the sensitivity of the phase angle is more obvious. That is because that the light components supplemented by the oil are still more than those lost during ageing, and the light components have a relatively significance to the phase angle. Sunflower oil can effectively restore the complex shear modulus and phase angle of the aged asphalt concrete over the full frequency sweep range. Aged bitumen can be rejuvenated and softened to improve their self-healing capability.

3.3.3. *Flow behavior*

In the frequency sweep results, the frequency-complex viscosity curves of the four binder samples are listed separately as shown in Fig. 11. The sensitivity of the complex viscosity to frequency is different at different temperatures, which can be fitted by Equation (10), the slope of which represents an indicator of the prevailing behavior of bitumen. Table 6 and Fig. 12 show the fitting results. It is found that the values of R^2 are high, which shows complex viscosity and sweep frequency have a good exponential fit in all temperature ranges. The parameter “n” is the slope of the viscosity-frequency curve, which is usually used to present flow behavior index of Newtonian fluids. Its value is between 0 and 1, a value of 0 indicates that the material is a solid, and a value of 1 indicates that the material is an absolute fluid [42].

It can be found that the flow behavior index of several asphalt binders increases with temperature from Fig. 12, which is determined by the temperature sensitivity of asphalt. It is difficult for asphalt pavements to reach very high temperatures during practical application, especially in the north. In order to improve self-healing properties, increasing flow capability is better method at low temperatures. Fig. 12 shows that aged asphalt binder has worse flow capability than virgin binder during all test temperature range, which means that ageing has severely reduced self-healing capability of asphalt. However, the flow capability has been recovered to reference level for oil encapsulated entering aged asphalt binder after the capsules breaking. It can be summited that the healing mechanism of the calcium-alginate capsules:

Table 6
Fitting results of flow behavior index of different asphalt binders at different temperature.

Binder	Temperature (℃)	Fitting formula ($y = a{\cdot}x^b$)	R^2	Flow behavior index
Original binder	30	$y = 38614x^{-0.144}$	0.9622	0.856
	35	$y = 16195x^{-0.112}$	0.946	0.888
	40	$y = 6673.6x^{-0.085}$	0.9425	0.915
	45	$y = 2788x^{-0.061}$	0.9139	0.939
	50	$y = 1205x^{-0.044}$	0.9054	0.956
	55	$y = 554.13x^{-0.03}$	0.8493	0.97
	60	$y = 263.5x^{-0.019}$	0.8825	0.981
	65	$y = 132.84x^{-0.013}$	0.9344	0.987
	70	$y = 71.158x^{-0.01}$	0.8865	0.99
Aged binder	30	$y = 42996x^{-0.325}$	0.9941	0.675
	35	$y = 22434x^{-0.263}$	0.9845	0.737
	40	$y = 10868x^{-0.218}$	0.8915	0.782
	45	$y = 4991.1x^{-0.164}$	0.9881	0.836
	50	$y = 2218.1x^{-0.133}$	0.9793	0.867
	55	$y = 913.26x^{-0.117}$	0.939	0.883
	60	$y = 426.07x^{-0.106}$	0.9255	0.894
	65	$y = 206.82x^{-0.086}$	0.8839	0.914
	70	$y = 107.69x^{-0.075}$	0.9375	0.925
Aged binder with oil	30	$y = 16651x^{-0.14}$	0.9585	0.86
	35	$y = 7543.8x^{-0.111}$	0.946	0.889
	40	$y = 3226.6x^{-0.084}$	0.9282	0.916
	45	$y = 1496.8x^{-0.062}$	0.9065	0.938
	50	$y = 707.7x^{-0.043}$	0.8812	0.957
	55	$y = 343.89x^{-0.028}$	0.9072	0.972
	60	$y = 168.06x^{-0.021}$	0.866	0.979
	65	$y = 87.707x^{-0.016}$	0.8423	0.984
	70	$y = 46.849x^{-0.006}$	0.8628	0.994
Aged binder with aged oil	30	$y = 15383x^{-0.135}$	0.9593	0.865
	35	$y = 6782.4x^{-0.105}$	0.925	0.895
	40	$y = 3021.9x^{-0.08}$	0.9307	0.92
	45	$y = 1413.9x^{-0.057}$	0.9046	0.943
	50	$y = 602.52x^{-0.04}$	0.8695	0.96
	55	$y = 311.33x^{-0.027}$	0.9246	0.973
	60	$y = 150.42x^{-0.02}$	0.8416	0.98
	65	$y = 78.161x^{-0.014}$	0.9322	0.986
	70	$y = 45.852x^{-0.011}$	0.8983	0.989

in the local microenvironment of the crack, the cracks in the asphalt mixture pass through the asphalt binder, affecting the capsules; compressive forces and make the rejuvenator flow out of the capsules in small volumes, reducing the viscosity of bitumen around them; finally, bitumen flows to the crack, sealing it. And then with the further diffusion of the rejuvenator, the rheological properties of the aged asphalt will also be restored.

4. Conclusions

In this paper, 3 PB test and fracture-rest-refracture test are used to study the effect of multi-cavity Ca-alginate capsules on mechanical properties and self-healing capability of aged asphalt mixture. Meanwhile, the chemical component, rheological property and flow behavior of asphalt binders are used to demonstrate the rejuvenation of aged asphalt concrete by capsules and to explain its healing improvement mechanism. The following conclusions were drawn:

1. Calcium alginate capsules have almost no effect on the initial mechanical properties of the asphalt concrete. Thermo-oxidative ageing increases the stiffness of asphalt concrete with and without capsules and reduces their fracture energy. UV ageing has little effect on 3 PB behavior of asphalt mixtures by only ageing the surface of asphalt mixture.
2. After some capsules broken after 4000 cycles of fatigue load, the content of sunflower oil in the asphalt binder was 5 %, the capsules can effectively improve the strength healing rate and fracture energy healing rate of asphalt concrete, which is mainly caused by the oil in the capsules flowing into the asphalt to soften the asphalt. The strength recovery rate and fracture energy recovery rate of the aged asphalt concrete with capsules can also reach the level of ordinary virgin asphalt concrete without capsules.
3. Aged asphalt binder softening is mainly caused by the sunflower oil penetrating into the aged asphalt mortar after the capsules broken, which increases the saturate and aromatic lost during the ageing process of the asphalt. It can effectively recover the rheological properties and flow property of ageing asphalt binder, thereby improving the self-healing performance.

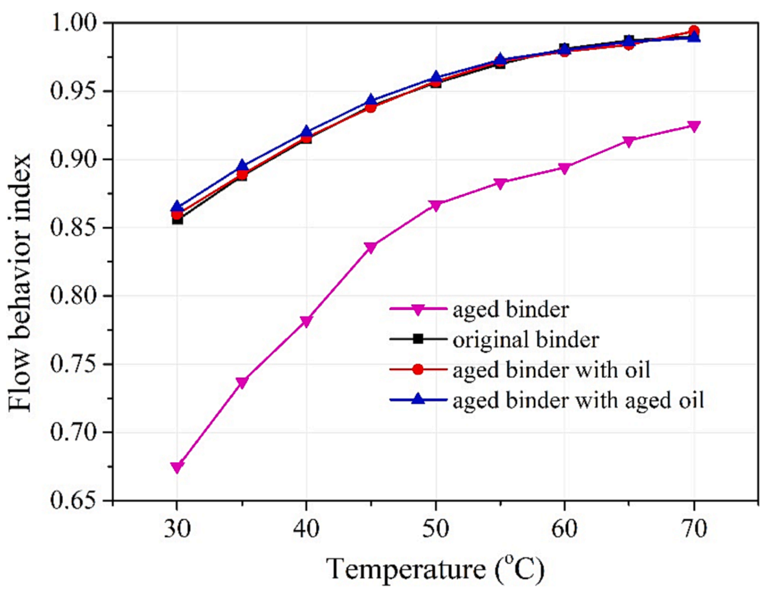

Fig. 12. Flow behavior index of different asphalt binders.

4. Aged asphalt has poorer fluidity and self-healing properties than virgin asphalt. The self-healing improving mechanism of asphalt concrete with capsules is that sunflower oil released from capsules rejuvenate aged asphalt by supplemental components saturate and aromatic, and improve the fluidity of asphalt mortar.

CRediT authorship contribution statement

Lei Zhang: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing. **Inge Hoff:** Conceptualization, Writing – review & editing , Supervision. **Xuemei Zhang:** Conceptualization, Methodology, Supervision, Writing - review & editing. **Chao Yang:** Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix D - Paper IV

Lei Zhang; Chao Yang; Inge Hoff; Xuemei Zhang; Hao Chen; Fusong Wang;

A self-healing asphalt pavement with both RAP and Ca-alginate capsules

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