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Review Article

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Properties of Microcapsules Used in Self-healing of Asphalt Pavement: A Review

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Abstract

Ageing and cracking are the main failure forms of the distresses in asphalt pavements. These issues occur due to the impact of factors such as heavy traffic and weather. Asphalt pavement is a self-healing material that can fix itself because it has the ability to restore its properties by closing micro-cracks. To make asphalt roads better at fixing themselves, numerous successful technologies are investigated. One of these techniques is called microencapsulation which represents nowadays a promising approach that could help make asphalt pavement last longer. In general, self-healing microcapsules will be incorporated into asphalt pavements before they are activated to release the rejuvenator, requiring them to be stable for years. Thereby, excessive thermal and mechanical properties in terms of asphalt pavements are necessary, because of how they are mixed and compacted. This paper aims to present an overview of new research on microencapsulation technologies, focusing on the durability of microcapsules embedded in asphalt pavement. Furthermore, some recommendations of future solutions to improve the mechanical stability of microcapsules will be proposed.

Keywords

Microcapsules, Asphalt pavements, Self-healing, Stability, Durability

Introduction

Asphalt is a common type of pavement used in the world for its excellent road performance, and comfortable driving conditions [1]. Asphalt pavement is a composite material, generally prepared by mixing petroleum refined bitumen, mineral aggregates and filler at high temperature in a specific proportion [2]. Bitumen works as a binder of asphalt, forming a thin layer of about 20 - 50 μm [3], also it must be resistant to its environment and traffic loads. The major problem concerning the use of bitumen in asphalt pavement is the ageing process during the storage, transport, mixing and paving, as well as in service life. Under the effect of the natural environment (Oxygen, rainwater, moisture, ultraviolet radiation, and temperature) and the impact of heavy traffic [4], the adhesion between the compounds of asphalt pavement decrease [5], and the cracks will be created. Then, the performances of asphalt pavement deteriorate. There are two types of aging, the first characterizes the chemical changes in the binder, and it is irre-

versible. The second type attributes to the molecular structure, known as physical hardening and is a reversible process [6]. Bitumen consists of four components: saturated hydrocarbons, aromatics, resins and asphaltenes [7]. During the aging process, saturated and aromatic components are easily volatilized at room temperature. The amount of asphaltenes in bitumen increases, making the asphalt binder more brittle and cracking [8]. Micro-cracks will not negatively affect the asphalt pavement [9], but under the continuous action of varying loads, micro-cracks progressively transform into macro-cracks, and then develop into potholes, losing the performance of the pavement.

Asphalt pavements have an inherent self-healing ability; it is a typical temperature-sensitive viscoelastic material that can recover its properties by closing micro-cracks autonomously. However, the asphalt intrinsic self-healing is not enough and is limited, because it depends on several conditions as the damage degree [10], chemical compounds [11] and rest periods [12]. For this reason, researchers suggest various methods related to the supplement of energy and substance, including induction heating, nanoparticles, and encapsulated rejuvenator. Induction heating is one of the technologies that have been proposed to accelerate the healing process [12]. Scientists have proven that temperature is the main factor that influences the self-healing properties of asphalt. The principle of this method is to heat a conductive or microwave-absorbing material in asphalt pavement by electromagnetic field or microwave radiation [13]. Thus, changing heat from the outside to the asphalt pavement and improving the mobility of bitumen molecules. The induction heating in asphalt pavement was introduced by Minsk [14], he investigates the use of graphite as a conductor material in asphalt pavement to melt snow and ice on road surfaces by induction heating. In 2011, Liu et al. [15], prove that cracks can be repaired via induction heating. They examine the electrical conductivity and induction heating of asphalt concrete containing steel wool and steel fibers as conductive fillers. Metal shavings with a density of 7.980 g/cm^3 are used to replace steel wool fibers. Adding steel shaving to the asphalt mixture was investigated by Gonzalez et al. [16] , it is concluded that this additive has the potential to facilitate the healing of mixture by microwaves radiation.

Adding nanoparticles presents a significant scientific interest, with a dimension less than 100 nm. Nanoparticles have the possibility to modify the asphalt mixture at the molecular level, with a high self-healing capacity [17-20]. Self-healing by nanoparticles has been described by stretching and extending of the polymer chains near to the nanoparticles [21]. To understand the properties of nanoparticles in asphalt pavement, scientists incorporate nanomaterials in deferent applications, to improve rheological, fatigue and aging performances of asphalt. Sun et al. [22], investigate the use of seven types of inorganic-nanoparticles as a modifier of base asphalt used in the asphalt pavement to increase its performance. They found that silicon dioxide (SiO_2) is the suitable one, due to its ability to improve the water and thermal stability of base asphalt pavement. The study of Mubaraki et al. [23], was conducted to evaluate and to characterize the properties of asphalt binder exposed to high temperature and modified by Acrylate Styrene Acrylonhrtilrei polymer and Nano-aluminum oxide (Al_2O_3). The result demonstrate that the additives impact the rheological properties of asphalt with the preference to the Al_2O_3 nanoparticles. Al-Mansob et al. [24], examine the performances of Epoxidized Natural Rubber modified asphalt using nano-Al_2O_3 as Additive. Which enhances the stiffness, the compatibility, the elastic behavior, and the viscosity of the binder.

It is well-known that the healing ability of asphalt pavements decreases when bitumen is aged. To overcome this issue, rejuvenating the bitumen to repair asphalt pavement will be a promising approach. Rejuvenator is an oil with high number of light components, used to improve the rheological and engineering properties of aged or hard binder, by restoring its colloidal structure. Rejuvenators decrease softening point, rutting factor and viscosity, reduce the stiffness, increase the penetration grade, phase angle (δ) and ductility [25]. There are three methods to rejuvenate the aged asphalt pavement: by spraying, by blending with the recycled asphalt pavement, or by microencapsulation. Zargar et al. [26], reported that the use of waste cooking oil as a rejuvenator for aged bitumen aided to restore the properties of asphalt pavement, especially the maltenes to asphaltenes balance. The problem with this technology is that the rejuvenator cannot penetrate the asphalt pavement deeply, which means that the deeply aged bitumen cannot be restored. Shen et al. [27], investigate the use of three rejuvenators and found that none could penetrate more than 2 cm into the asphalt concrete. The penetration capacity is considered a critical factor because it directly influences the rejuvenation process and determines the effectiveness of the rejuvenator in revitalizing the aged bitumen. In order to overcome these problems, encapsulated rejuvenators have been considered as a potential solution to improve the self-healing ability of asphalt pavement. The principle of this approach is that when micro-cracks appear, the microcapsules containing rejuvenator will be broken, and the healing agent will be released and flows into the micro-cracks under the capillarity and diffusion action [28]. Then the rejuvenator and asphalt binder will be mixed in order to close the micro-cracks. Self-healing bituminous composites based on microcapsules have become a research hotspot in the field of self-healing of asphalt, thanks to their unique advantages such as controlled the release of rejuvenator materiel and it's targeted in specific areas [29]. The purpose of this method is liberating the healing agent encapsulated by a wall material under the effect of cracking. Microcapsule defined as an active material embedded with another material called the shell, synthesized via several methods like *in situ* polymerization, coacervation and interfacial polymerization. The type of microcapsules results in differences in microcapsule properties such as size, morphology, compatibility with bitumen, high thermal stability, survival under mixing and construction conditions [17]. Thus, it is very important to learn about these properties of the microcapsule.

The objective of this paper is to provide an overview of the literature that addresses the durability of microcapsules incorporated in asphalt pavements. In addition, some suggestions for potential future solutions to improve the properties of microcapsules are provided.

Self-healing Mechanism of the Core Material in the Asphalt Pavements

Bitumen's self-healing properties can be improved by adding rejuvenators. These rejuvenators typically contain additives that can soften the aged binder, improve its elasticity, and reduce the brittleness caused by oxidation, by increasing the resin and aromatic contents of the maltene phase, and decreasing the asphaltenes content, which in turn can lead to a sol-gel type asphalt (Restoring asphaltenes to maltenes ratio). The impact of ageing and rejuvenation on the colloidal structure of bituminous binders are described in figure 1. Rejuvenation promotes self-healing and increases the lifespan of asphalt pavements.

The microcapsules can be incorporated directly into the asphalt binder or mixed with the aggregate. The mechanism of microcapsules performance in asphalt pavements requires a controlled release of the core materials in response to certain triggers, such as ageing, traffic loads, or temperature changes. When asphalt pavement is subjected to stresses such as heavy traffic or weather, microcapsules can break. This rupture results in the release of the encapsulated substances, then interact with the bitumen binder, enhancing its properties. This healing mechanism can be illustrated in figure 2.

It is well-known, that the mechanism of rejuvenation depends on the type of rejuvenator used and its chemical composition. In 2016, the effect of waste cooking oil (WCO) on the rheological properties of aged bitumen was investigated by Sun et al. [22]. They revealed that there was no chemical reaction between WCO and asphalt binder. The research of Chen et al. [31] and Cai et al. [32] supports the notion that the rejuvenation mechanism is the result of physical interaction that does not affect the microstructure of aged binders. Table 1 summarizes the effect of rejuvenators on the properties of bitumen.

Table 1: The effect of rejuvenators on bitumen.

Property	Testing method	Effects	Ref.
Chemical composition	SARA™	The chemical composition of the rejuvenated binder depends on the type and dosage of rejuvenating agent and the chemical composition of the aged bituminous binder.	[34]
High temperature properties	Dynamic shear rheometer Penetration grade test Ring and ball softening point	Reduced stiffness Increased penetration grade Decreased softening point Decreased viscosity Decreased rutting factor Decreased shear complex modulus (|G* |) Increased phase angle (δ) Increased ductility	[35, 36]
Low temperature properties	Bending beam rheometer	Reduced stiffness	[37]
Oxidation kinetics	Fourier transform infrared spectroscopy	Decreased carbonyl (C=O) index Decreased sulfoxide (S=O) index	[38]

Microcapsules Containing Rejuvenator Used in Asphalt

Generally, microcapsules defined as the composite material with core-shell structure, it refers to the synthesis of particles with microscopic dimension. They have been employed in different fields of industry. The core material can be a solid, liquid or gas, it is called core, cargo, nucleus, active agent, or inner phase. The protective film of the microcapsule, the membrane, the wall material, the external phase, or the shell is used to protect the core material from the external factors. Table 2 summarizes some materials design of microcapsules.

At present, encapsulation rejuvenator has become a great approach that provides a new solution to increase the healing capacity of asphalt pavement, in the field of asphalt self-healing. Much research shows the success of the application of microcapsules in asphalt pavement. In 2010, García et al. [48], developed a method to encapsulate rejuvenator in porous sand by epoxy resin and cement. They obtained a self-healing capsule

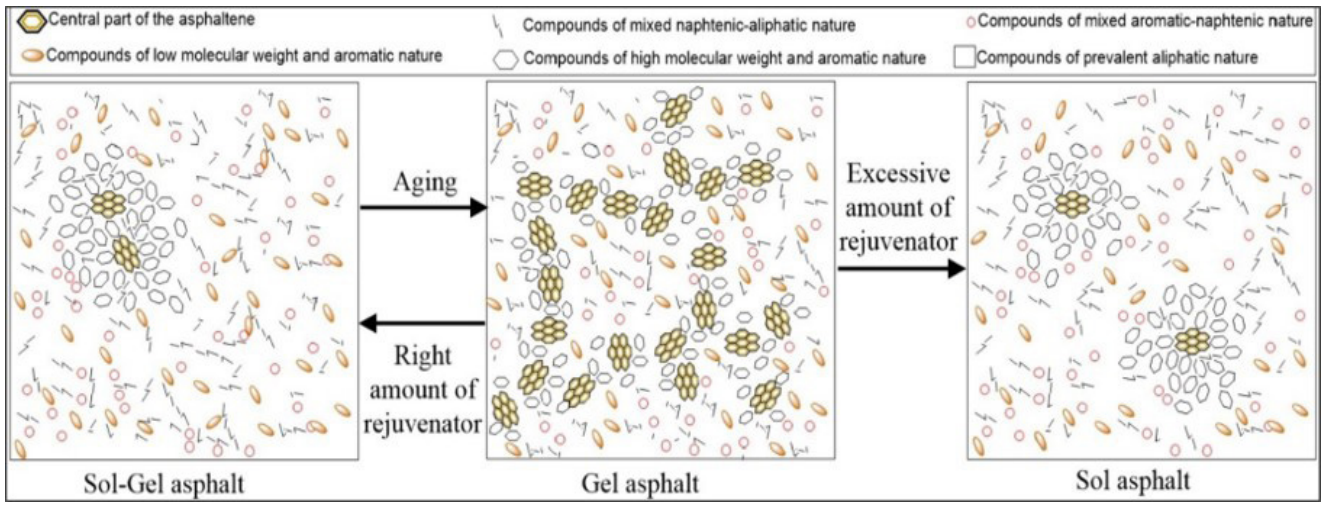

Figure 1: The effects of ageing and rejuvenation on the colloidal structure of bitumen (Reproduced from [30]).

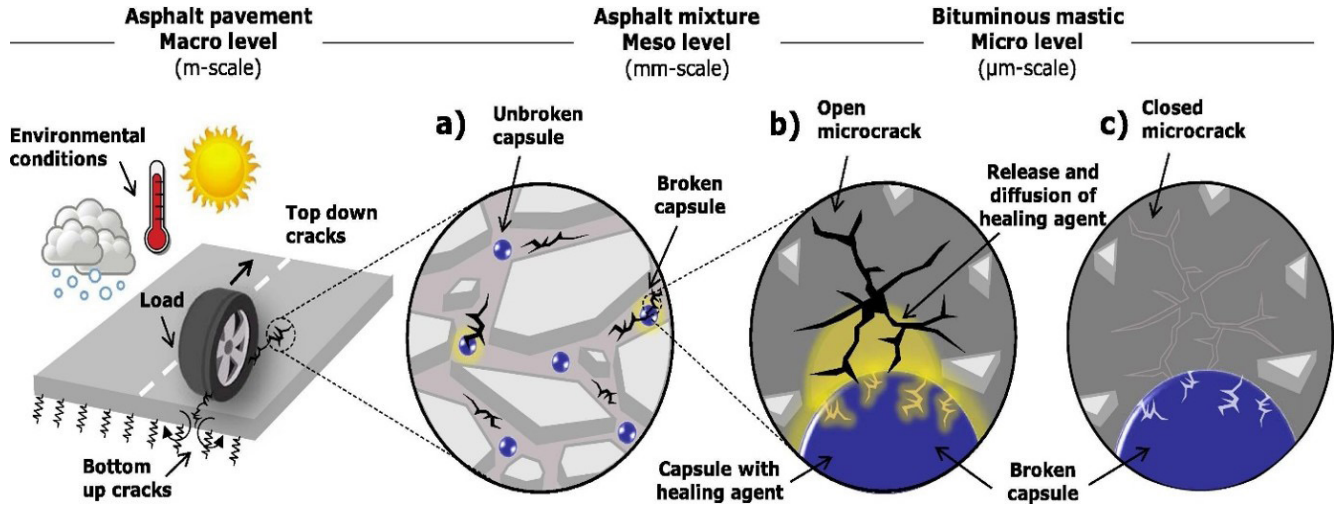

Figure 2: Crack-healing mechanism of bituminous materials with encapsulated rejuvenators [33].

with good strength, heat resistance and size is mainly concentrated in 1.0 to 1.7 mm. The issue of this technic summarized in the limited rejuvenator content and its release. For overcoming that, the chemical synthetize process using polymer as external phase can be applied to prepare a self-healing capsule. These microcapsules were manufactured using amino resin such as shell (urea-formaldehyde (UF) resin, melamine-formaldehyde (MF) resin, melamine-urea-formaldehyde (MUF) resin, and methanol modified melamine-formaldehyde (MMF)), by different technics like *in situ* polymerization, interfacial polymerization and coacervation. Zhang et al. [43], prepared microcapsules with UF resin as the wall and asphalt rejuvenator as the core by *in situ* polymerization. The results show that UF microcapsules have been successfully manufactured, and the rheological properties and self-healing ability of asphalt had been improved. In 2017, Al-Mansoori et al. [46], prepared calcium (Ca)-alginate microcapsules containing sunflower oil, and investigated the effect of Ca-alginate capsules on the mechanical performance and self-healing properties of asphalt mixture. They found that Ca-alginate capsules can recover 52.9% of initial strength of cracked asphalt at 20 °C compared with 14.0% of asphalt mixture without capsules. Micaelo et al. [49], encapsulated sunflower oil and Ca-alginate with a hard wall prepared by epoxy resin and cement composite to studied the self-healing capacity of asphalt mixtures. Microcapsules containing rejuvenator for asphalt pavement were synthesized via interfacial polymerization by Ji et al. [42]. The mean size of microcapsules was 14.26 µm, the thickness of microcapsules shell was 2 - 3 µm. Also, these particles had good thermal, mechanical, and chemical stability.

Table 2: Materials used for the synthesis of microcapsules.

Shell	Core	Method	Ref.
MUF	Rejuvenator	*In situ* polymerization	[39]
MMF	Rejuvenator	*In situ* polymerization + two-step coacervation	[40]
Ca-alginate	Sunflower cooking oil	Inverse gelation	[41]
Isophorone di-isocyanate	Rejuvenator	Interfacial polymerization	[42]
UF	Rejuvenator	*In situ* polymerization	[43]
UF	Green bio-oil product	*In situ* polymerization	[44]
MMF	Dense aromatic oil	*In situ* polymerization + two-step coacervation	[40]
MMF	Diphenyl silane	*In situ* polymerization + two-step coacervation	[45]
Ca-alginate	Sunflower oil	Ionic gelation	[46]
PVDF	Commercial rejuvenator	Dry-wet spinning	[47]

However, the microcapsules applied in asphalt pavements are quite different from those used in other fields, this application should have some requirements:

- The reaction between the core and shell materials should be inert.
- Microcapsules should have enough chemical, thermal, and mechanical stability to decomposition and deform under the conditions of production, transportation, paving and compaction process.
- The shell and the core materials should be friendly to the environment, easy to obtain and not expensive.

Different Properties of Microcapsules

Physicochemical properties

Controlling microencapsulation process is crucial to obtain optimum physicochemical properties, which affect the thermal and mechanical stability of microcapsules. The physical properties of microcapsules containing asphalt rejuvenator (Like particle size distribution, micro-morphology, and shell thickness) are primarily influenced by the emulsification process, especially the reaction temperature, emulsion speed, the emulsifier concentration and core/shell ratio [50].

The shell thickness of microcapsule is an important factor, because it is related to the mechanical strength. It can be measured using optical microscope or scanning electron microscopy images of cross-section of ruptured microcapsules. The optimization of the ratio of the core to the wall material is necessary to achieve a stable microcapsule shell structure. For

example, the excess of the shell material conducts to reduce the relative content of the rejuvenator in the microcapsule. However, the insufficient dosage of the wall material involves the formation of a thin layer, which decreases the mechanical properties, as reported by Ji et al. [42]. Furthermore, the core/shell ratio has another effect on the morphology. A higher amount of rejuvenator leads to a spherical shape, and a large diameter [51]. Reaction temperature has an important effect on the morphology and in the formation of shells. When the reaction temperature is low, the reaction time is long, and slow shell formation. Thus, the shell becomes thin. In contradiction, a high reaction temperature leads to a fast reaction rate, then shell rupture and the adhesion between microcapsules. In 2021, Ji et al. [42], studied the effect of temperature on the morphology of microcapsule as shown in figure 3, and they selected 60 - 70 °C as the optimum reaction temperature range for the synthesis of microcapsules. The emulsion speed affects the droplet size in the emulsion solution. Increasing the stirring rate leads to a decrease in particle size [52].

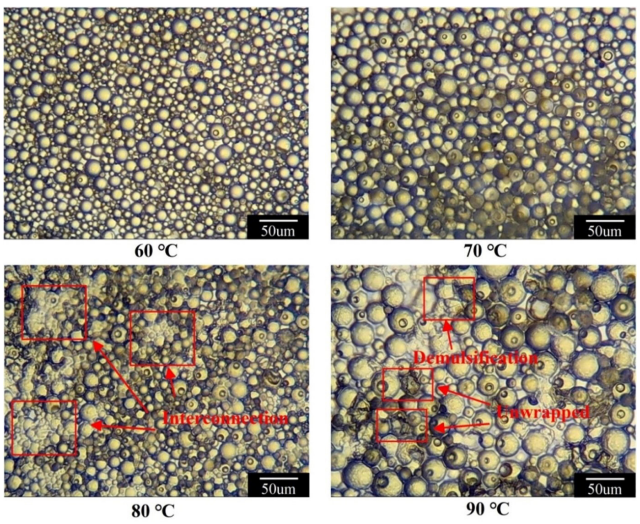

Figure 3: Microcapsules prepared at different temperatures [42].

Thermal properties

Thermal stability of microcapsules is the most important property in studying the performance of microcapsules. The microcapsules used in asphalt pavement are different from those used in other fields. To survive the mixing process, the microcapsules must resist the high temperature of the melting bitumen, which means that their thermal decomposition temperature of microcapsules should be higher than 180 °C. The thermal stability of the microcapsules was performed on a thermogravimetric analysis (TGA) by calculating the mass loss due to evaporation of their compounds at high temperatures.

Garcia et al. [48], embedded rejuvenator in a hard matrix made of a porous sand using cement-epoxy resin as the shell material. The TGA curve indicates that the mass loss of the capsules is 0.8% and 1.3%, between 160 °C and 180 °C, respectively, which are the asphalt mixing temperatures. These losses correspond to the evaporation of pore water from the porous sand, not from the rejuvenator. Microcapsules with polymeric shells like MMF, MUF, and UF seem to have good thermal stability. Li et al. [52], found that the thermal stability temperature of the UF-microcapsule was 250 °C, which is higher than the melting temperature of bitumen. Also, Su et al. [53], indicated that the MMF microcapsules still maintained the globe shape and smooth surface as original state under 180 °C and 200 °C. Thus, they will not decompose thermally during the process of mixing. In 2016, Micaelo et al. [49], investigated the thermal stability of Ca-alginate capsules with cement-epoxy resin like a hard composite shell. These capsules had a mass loss percentage of 4% at 200 °C, caused by the dehydration of water from the capsules and the degradation of Ca-alginate. Al-Mansoori et al. [54], used TGA analysis to evaluate the thermal property of Ca-alginate capsules, indicating that the capsule containing a large amount of oil resists the increase in temperature, with only about 2% loss in mass at 200 °C. The effect of nano-clay on thermal stability was studied by Jagtap et al. [55], they found that the fraction of nano-clay can enhance the thermal property of microcapsules, with the onset of degradation at approximately 290 °C. The TGA curves of thermal stabilities of different capsules extracted from literature had been evaluated by Li and Zhang [56], as observed in figure 4.

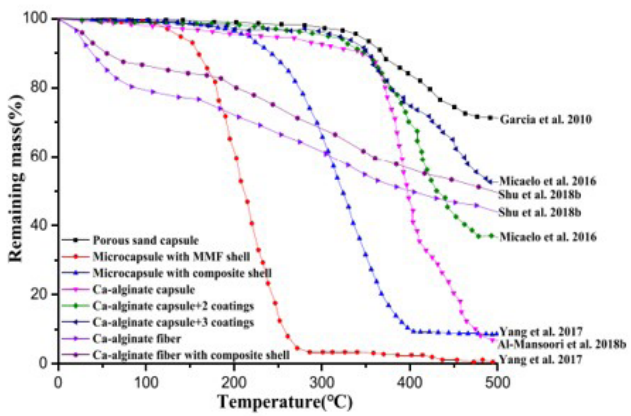

Figure 4: TGA curves of capsules prepared by different methods [56].

Mechanical properties

Mechanical stability is crucial for the microcapsules containing the rejuvenator to resist during the construction process of asphalt pavement, because they will be affected by the impact of the mineral aggregates. The maximum strength of microcapsules should be higher than the stress due to the heavy traffic. Mechanical properties of microcapsules are related by their physical properties such as the shell thickness, the particle size, and the core/shell ratio. Garcia et al. [2], designed five capsules on porous sand with 5 different diameters, and investigated the effect of capsules size on their compressive strength, as shown in figure 5. The capsules with a smaller diameter had high compressive strength, the reason for this was that the capsule's size increased with the core/shell ratio, causing the decrease of the thickness of the shell.

Different mechanical testing technologies are performed to characterize the mechanical properties like elastic modulus and hardness of micro-sized capsules, such as nano-indentation test, compressive strength test, two-plate micromanipulation, and micro tensile testing. The mechanical characteristics are reported in table 3. Li et al. [57], applied the

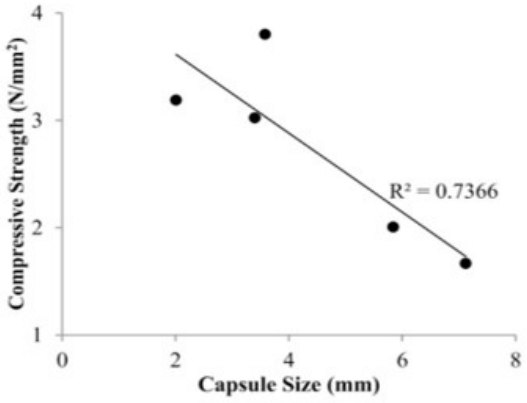

Figure 5: Compressive strength against capsule size [2].

nano-indentation to test the Young's modulus and hardness of MUF microcapsules. The results showed that the hardness ranges from 0.26 to 0.31 GPa, while the elastic modulus was in the range of 2.28 to 2.68 GPa. The force-displacement curve of MMF microcapsules performed by Su et al. [58], indicates that they have the possibility to deform elastically and return to their original state after removing the applied stress. Modifying the polymeric shell with inorganic materials such as nano-$CaCO_3$ particles, can be a good approach to enhance the mechanical properties of microcapsules as reported by Wang et al. [59].

Table 3: Mechanical properties of different microcapsules.

Capsule type	Test	Young's modulus	Ref.
MUF	Nanoindentation	2.50 GPa	[57]
IPDI	Nanoindentation	466.86 MPa	[42]
MMF	Nanoindentation	1.5 - 2.7 GPa	[58]
MMF/nano-$CaCO_3$	Nanoindentation	2.75 - 3.46 GPa	[60]

Functional properties

The release mechanism of rejuvenator embedded in microcapsules is based on the micro-cracks stress or external stress. However, this release mode is passive, because it is unable to guarantee the timely release of the asphalt rejuvenator at the appropriate time. Moreover, the modified shell structure can provide the adjustment and the management of core release, via the detection of the environmental variations and the control of its permeability. In these terms, advance strategies have been developed to enhance the matching degree between the self-healing ability and the cracking of asphalt pavement.

Relying on the self-healing by induction heating [61], incorporating magnetic nanoparticles or microwaves absorbing substances in the shell or in the core, can be a promising approach to control the releasing mode of asphalt rejuvenator. This method is based not only on the action of stress, but on the action of electromagnetic or microwave fields. Ca-alginate/nano-Fe_3O_4 composite capsule with an average diameter range from 1.6 to 1.8 mm was prepared by Wan et al. [62], this capsule could release the sunflower oil under short time of low frequency microwave field (2.45 GHz). Graphene is a two-dimensional carbon material that is attracting worldwide interest thanks to its unique physical characteristics. The addition of graphene to the polymeric wall materials in the microcapsules can improve their physicochemical properties, as proved by Guo et al. [63] and Wang et al. [64]. In addition, modifying the shell with inorganic nanoparticle compounds like nano-$CaCO_3$, nano-Al_2O_3, and nano-SiO_2 were own a good thermal stability, hardness, and compactness to the microcapsules [60].

Conclusions

Microencapsulated asphalt rejuvenator technology has aroused a great interest and a large application in terms of developing a smart asphalt pavement. This technology involves incorporating active agents into a tiny capsule to protect and release them effectively. They are generally designed to restore the properties of bitumen, with a healing efficiency of approximately 90%. Based on a comprehensive literature study, this review highlights the rejuvenation mechanism, the microcapsule properties, and the impact of synthesis method on them. The main conclusions are as follows:

- Rejuvenators can enhance the self-healing properties of bitumen in asphalt pavements. By incorporating additives that soften the aged binder, improve elasticity, and reduce brittleness, rejuvenators increase the resin and aromatic contents of the maltene phase while decreasing the asphaltenes content. This leads to a sol-gel type asphalt, restoring the desired ratio of asphaltenes to maltenes and promoting self-healing.
- The mechanism of rejuvenation depends on the type and chemical composition of the rejuvenator used. Research has shown that certain rejuvenators, such as WCO, do not undergo chemical reactions with the asphalt binder but rather exhibit physical interactions.
- Microcapsules used in asphalt pavements require specific properties and characteristics. They should have inert reactions between the core and shell materials, as well as sufficient chemical, thermal, and mechanical stability during production, transportation, paving, and compaction processes. Additionally, the materials used for the shell and core should be environmentally friendly, easily accessible, and cost-effective.
- The synthesis of microcapsules for asphalt pavements involves different shell and core materials, such as MUF, MMF, Ca-alginate, isophorone di-isocyanate, UF, and PVDF. These materials are combined with rejuvenators, including sunflower cooking oil, green bio-oil product, and commercial rejuvenator, using methods such as *in situ* polymerization, two-step coacervation, inverse gelation, interfacial polymerization, and dry-wet spinning.
- Incorporating microcapsules containing rejuvenators in asphalt pavements improve the rheological properties, self-healing ability, and mechanical performance of asphalt mixtures.
- The size, thickness, and stability of the microcapsules play important roles in their performance. Microcapsules with sizes around 14.26 μm and shell thickness of 2 - 3 μm

have been reported, exhibiting good thermal, mechanical, and chemical stability.

- Thermal stability is a crucial property for microcapsules used in asphalt pavements. The microcapsules must withstand high temperatures during the mixing process, with a thermal decomposition temperature higher than 180 °C. Different shell materials, such as MMF, MUF and UF, exhibit good thermal stability. TGA analysis is commonly used to evaluate the thermal properties of microcapsules.
- Mechanical stability is essential for microcapsules to withstand the construction process of asphalt pavement, including the impact of mineral aggregates. The maximum strength of microcapsules should be higher than the stress caused by heavy traffic. Mechanical properties are influenced by factors such as shell thickness, particle size, and core/shell ratio. Testing methods such as nano-indentation, compressive strength tests, and micromanipulation are employed to characterize the mechanical properties of microcapsules.
- Adding magnetic nanoparticles, microwaves absorbing substances, or graphene to the microcapsule shell or core can enhance their functional properties and control the release of asphalt rejuvenators. Modifying the shell with inorganic nanoparticle compounds like nano-$CaCO_3$, nano-Al_2O_3, and nano-SiO_2 can improve thermal stability, hardness, and compactness.

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Conflict of Interest

None.

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