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Encapsulated Healing Agents for Asphalt Self-Healing

By

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To my family

Abstract

Service life of asphalt roads could be extended by enhancing the natural self-healing ability of asphalt mixtures with encapsulated rejuvenators. When crack damage appears, the capsules release healing agents, which dissolve bitumen to flow into cracks. In this research, a new type of capsules was developed. These capsules contain sunflower oil as a rejuvenating agent. The size, morphology, mechanical strength and thermal stability of these capsules were investigated. The composition of the capsules, which nominally divides these capsules into different types based on their oil content, epoxy-cement shell and polymer amount, and its effect on capsule characteristics were also studied. In addition, the effect of the capsules on the chemical composition of bitumen with time of exposure to broken capsules was evaluated by the FTIR test. Results show that the characteristics of the capsules and their effect on chemical composition allow them to be incorporated in asphalt mixtures for further investigations for their effect on asphalt mechanical performance and self-healing.

The mechanical performance of aged asphalt mixtures is investigated by using three nominally different types of capsules. Two of these were protected with a hard shell made of epoxy-cement composite; two coats with 1.0 o/w (oil-to-water), three coats with 1.0 o/w and without the hard shell with 0.5 o/w. The optimum amount of capsules used in all mixtures was 0.5% of total mass of asphalt mixture. Tests started by investigating the effect of mixing and compaction processes on these capsules. Results show that the hard shell (epoxy-cement) was not necessary for the capsules to survive mixing and compaction processes. Capsules deformed and broke with cyclic loading, releasing oil that diffused in the bitumen in less than 24h. Healing of cracks in aged asphalt mixtures led to an increase of stiffness under cyclic loading. However, asphalt specimens with capsules had lower deformation

resistance. Computer tomography scanning of specimens showed large reductions in cracks around the capsules, after resting 4 days (96h) at 20°C.

The mechanical properties of asphalt mixture containing capsules have been evaluated. Including water sensitivity, particle loss, stiffness and permanent deformation. One type of capsule (0.1 o/w) with three different capsule contents by mass of asphalt mixture were used, 0.1%, 0.25% and 0.5% with oil-to-bitumen ratio 1.1, 2.8 and 5.5, respectively. Capsules were strongly bonded to the asphalt mixture and results showed improved or at least similar mechanical properties to that of asphalt mixtures without capsules. This shows that capsules for asphalt self-healing can be safely used in the road, without affecting its quality. Asphalt containing capsules had slightly lower stiffness (no rest period), which can be easily solved by reducing the size of the capsules in the future.

Furthermore, a new method for testing asphalt self-healing by the action of capsules was designed and tested. This method was based on a 3-point bending test (3PB) to break samples and measure their flexural strength. The test was implemented by comparing the strength recovery of the broken beams after healing to their original flexural strength. The test was first applied to asphalt mastic beams, which are asphalt mixtures with higher bitumen content and fine aggregate and filler. Five different types of capsules used, based on their o/w ratios. These were 0.05, 0.1, 0.2, 0.5 and 1.0 o/w ratios with different amounts depending on their oil content so that they can provide a 7.2% of rejuvenator (sunflower oil) to the asphalt mastic beams. The effect of capsule content on self-healing was investigated by the 3PB on samples containing all those five capsule types (different contents) at one healing temperature, namely 20°C and different healing times. Effect of temperature on healing was investigated as well by 3PB test applied to mastic beams containing one type of capsules with 0.5 o/w ratio at four different temperatures, namely 5°C, 10°C, 15°C and 20°C. The

main results showed that the capsules can break inside the asphalt mastic releasing the encapsulated oil to bitumen. Healing levels in the asphalt mastic samples with capsules were greater than samples without capsules, and the healing level of asphalt samples with, and without, capsules increased with the healing time. Additionally, the healing level given by the capsules inside the cracked asphalt mastic depended on the oil/water content of the capsule and on the temperature at which the healing process occurs. Finally, a correlation factor was developed between the healing level of asphalt mastic with and without capsules, independent of the temperature and time evaluated.

Self-healing of real asphalt mixture was also investigated by same method of 3PB at different healing times and different temperatures. One type of capsules, namely 0.1 o/w with three different capsule contents, 0.10%, 0.25% and 0.50% by total weight of the mixture, were mixed with the asphalt. Eight different healing temperatures were used in this test, namely - 5°C, 5°C, 10°C, 15°C, 20°C, 30°C, 40°C and 50°C. It was proven that the capsules can resist the mixing and compaction processes and break inside the asphalt mixture as a result of applying external mechanical loads, releasing the encapsulated oil. The capsules content in asphalt mixture has a significant influence on the healing level, where a higher capsule content led to higher healing levels. It was found that cracked asphalt mixture with capsules recovered 52.9% of initial strength at 20°C versus 14.0% of asphalt mixture without capsules.

Likewise, asphalt with, and without, capsules presents an increase of the healing level when the temperature increases. Finally, it was proved that healing temperature over 40°C has significant influence on the healing levels of the asphalt beams.

Keywords: Encapsulated rejuvenator; Aged asphalt; Mechanical performance; Self-healing.

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Declaration

The research described in this thesis was conducted at the Nottingham Transportation Engineering Centre, the University of Nottingham between October 2014 and April 2018. I declare that the work is my own and has not been submitted for a degree at another university.

Tariq Al-Mansoori

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Chapter 1: Introduction

1.1 Background

According to NAPA (2011), the highway industry uses 110 million tons of bitumen annually around the world. This indicates the importance of this material for construction and development of asphalt pavements. Bitumen binder has a direct interface with oxygen, and over time, the effect of oxygen on bitumen increases, resulting in changes to its chemical composition that directly affect its rheological and mechanical properties. This change is known as ageing, which results in higher stiffness of the pavement. Ageing reduces the strain level to failure and stress relaxation behaviour, which may increase sensitivity to fretting and cracking (Hagos, 2008). In addition, it may result in reflective cracking and ravelling in asphalt pavements.

The ageing effect on the pavements has huge implications on the economy, for example, in England the government spent about £4bn on road maintenance in 2009/2010. In 2014/2015 the spending dropped to £1.91bn because of 72 unfunded projects reported (Road User's Alliance, 2016). The consequences of pavement damage due to ageing and the related maintenance requirements highlight the need for new and improved pavement materials. Recycling can be cost-effective pavement repair technique, although there is still the important issue of dealing with large quantities of aged bitumen (Su et al., 2015). Most countries use large proportions of reclaimed asphalt materials, recycling and incorporating them into new pavement layers. These recycled asphalt materials are mixed with virgin binder, additives and aggregates in order to obtain the desired quality for use in roads.

Additives can be softening agents or rejuvenating agents that can modify the chemical composition of the aged binder, recovering the lost components that caused the increase of the asphalt viscosity (Sun et al., 2016, Yang and Lee, 2016). The ideal maintenance would be that asphalt layers are rehabilitated in-situ without milling or scarifying interventions. The self-healing nature of bitumen promotes this technique. This idea of self-healing in asphalt pavements has been existed and studied for many years (Qiu, 2008) and it is expected to replace the normal asphalt maintenance, to some extent, in future. Pavement self-healing has the interest of highway agencies as it has the potential to remove the necessity for pavement maintenance or at least to defer it by extending the service life of roads. Reducing the need for current maintenance strategies, self-healed pavements could reduce the environmental effect of gas emissions associated with maintenance, improve traffic flow by avoiding interruptions and enhance road user experience and safety.

Naturally, bitumen is a self-healing material with the ability to close microcracks and restore its strength and stiffness. The viscosity of bitumen is highly related to temperature and, when the temperature is above a value in the range 30°C to 70°C, which is different for every type of bitumen, the binder can flow through the cracks in the material, causing potential healing. Microcracks occur as a result of cyclic loading; the rest periods after loading help healing to take place when stresses relax due to the viscoelastic property of the bitumen (Qiu et al., 2012a). The process of self-healing is defined as the ability of the material to repair itself when subjected to mechanically or thermally induced damage, and it can be activated naturally or by external stimuli such as heat (Chen et al., 2002, Chen et al., 2003, García et al., 2009, García et al., 2011c). Little and Bhasin (2007) summarise the process as the wetting of the two faces of the microcracks, then diffusion of molecules from one side of a microcrack to another and the randomisation of diffused molecules. This process is, however, very slow; therefore it is only able to heal microcracks. As a result, researchers have investigated possible ways to accelerate the process. Surface technologies, such softening agents and rejuvenating agents, have been used extensively in the USA.

Karlsson and Isacson (2003) distinguish between softening agents and rejuvenating agents. Softening agents such as asphalt flux oil, lube stock (The distilled fraction of crude oil) and slurry oil are used to reduce the viscosity of the aged bitumen. Rejuvenating agents have the ability to reverse the ageing effects of bitumen by restoring its chemical composition to the original properties. They consist of lubricating and extender oils that may have a high

proportion of maltene constituents, which can replace those lost in bitumen due to ageing. Generally, rejuvenators must be highly aromatic so that both hardening and temperature susceptibility can be improved (Peterson et al., 1994). Rejuvenators used are supposed to increase the peptizing ability of the maltene phase; therefore, they should be composed in a way that allows them to perform this requirement (Venable et al., 1983). However, rejuvenators may have several disadvantages for the following reasons: they are surface treatments, which means they are only effective on the pavement surface or few centimetres below; they might reduce pavement skid resistance and they could have negative effects on the environment.

One of the promising techniques to overcome the shortcomings of using the rejuvenators, which can trigger the healing and increase its speed, is encapsulating the rejuvenators and adding them to the asphalt during the mixing process. The idea is that these capsules will remain inactive in the asphalt road for several years until an external factor, e.g. an excessive loading, triggers their breakage and the rejuvenators dissolve the bitumen around the capsules (García et al., 2010b). As a consequence, the binder can easily flow into the cracks and self-healing is accelerated.

1.2 Problem Statement

The wearing course of roads is very sensitive to ravelling, which results from the normal deterioration process whenever the bitumen ages. Due to ravelling, moisture can move through into the lower pavement layers creating surface roughness, potholes, degradation and eventually structural failure. This will result in an uncomfortable ride and a high noise level. Occasionally, when the deterioration signs are visible, a surface treatment or thin overlay is applied to prevent or deter further deterioration before further rehabilitation or reconstruction is required.

The accumulating traffic loads not only increase road deterioration but also restrict the opportunity for maintenance of these roads. Less time is available for implementing maintenance in order to keep traffic delay at a tolerable minimum level. In addition, maintenance may cost highway agencies large sums of money, consume the finite resources available and can cause significant gas emissions. Therefore, on the one hand methods are needed to slow down the damage of ageing and on the other hand, quick, efficient and cheap repairs are required to any damaged portions of the wearing course.

Bitumen naturally has the ability to self-heal, although the process takes a long time and it cannot repair all pavement failures. The original properties of aged bitumen can be restored by using rejuvenators, which can, as well, accelerate the self-healing process of pavements. Technically, bitumen can be described as a dense oil; when cracked, it could close by itself, although this could work faster if the viscosity of that oil decreased. This can be done by either increasing its temperature, which is not practical in roads or by mixing with a less dense oil. On the other hand, chemicals in the rejuvenators might be unsafe and have the potential to contaminate the environment as well as reducing the friction of the pavement surface, which can directly affect the safety of road users. An encapsulated rejuvenator technique is used in this research as an alternative to traditional pavement maintenance and a replacement for the rejuvenator spreading method. These have showed promising self-healing rates in asphalt pavement at ambient temperatures without affecting the durability and other mechanical properties of the asphalt mixture.

1.3 Aim and Objectives

The work was a combination of the following aims. The first is to propose a new type of capsule containing rejuvenators to enhance the healing ability of the asphalt. These capsules should have more oil and be easier to manufacture than capsules proposed by other researchers. The second is to investigate the effect of these capsules on the mechanical properties of the asphalt mixtures by incorporating them into asphalt samples and applying standard mechanical tests, then comparing the behaviour of these samples with and without capsules. The third is to develop an asphalt mixture that can heal at room temperature through the use of the encapsulated healing agents provided by the produced capsules.

To accomplish these aims, the following research objectives are introduced:

- (1) Develop an encapsulation method based on other methods found in the literature; a protocol for the production of capsules with different characteristics is presented.
- (2) Characterise the different capsules in terms of the geometry, the temperature susceptibility, the mechanical resistance and the morphology.
- (3) Evaluate the effect of the capsules in the asphalt production process (mixing and compaction), namely, the survival rate under mixing/compaction stresses and temperatures.

- (4) Assess the effect of the capsules on asphalt mechanical behaviour. Standard testing protocols are applied to evaluate the most important properties, such as water sensitivity, particle loss, stiffness, rutting resistance and fatigue.
- (5) Introduce rest periods into the self-healing properties of asphalt mixture containing capsules. The self-healing is visualised using computer tomography scans. In addition, an extensive experimental program is planned and carried out with the objective of investigating asphalt crack healing mechanically by measuring the strength of the asphalt samples before and after healing in the presence of the capsules. The test is repeated with samples without capsules for comparison purposes. Then, use the range of temperatures and rest periods to combine the effect of capsules-temperature on asphalt self-healing and the optimum time and temperature that can achieve the maximum healing level.

1.4 Research Methodology

To accomplish the aforementioned objectives, the research methodology will be divided into the following phases:

Phase 1: Capsule manufacture and characterisation. The phase of manufacturing the capsules starts with writing a protocol for the capsule production technique. Afterwards, the acquisition of equipment is planned, e.g. purchasing utensils, droppers, and materials. Then, the protocol is implemented with different proportions of the material to produce different types of capsules. A simple test is made to assess the process, such as crushing by hand or using a hammer to roughly assess the capsule strength.

After producing the capsules, their characteristics are evaluated and analysed. This involves measuring the mechanical strength of the capsules, their size and thermal resistance to investigate whether they can survive the mixing temperature, which is about 160°C. The morphology of the capsules is studied by using Scanning Electron Microscopy (SEM) analysis to investigate the structural composition of the capsules. For example, the variation of the shell-core proportions with oil content used and the interaction between core and shell for some capsules.

Furthermore, this phase includes testing the capsules' ability to release oil inside bitumen by preparing small samples of bitumen with premeasured dimensions and inserting one capsule

in each sample then breaking the capsule gently without affecting the bitumen specimen. The oil is then allowed to diffuse into the sample. The change in the chemical composition of the sample due to the oil is measured at different times; the FTIR test is used to perform this process.

Phase 2: Asphalt mixture testing and incorporation of capsules. Capsules are added to the asphalt mixture with different percentages by total weight of the mix. Each type of capsule added to the mix is based on its mechanical strength characteristics, which explain its ability to survive the mixing temperature and break when cracks happen in the asphalt. Computer tomography (CT) scans are taken to evaluate the survival and distribution of the capsules inside asphalt samples. Then, asphalt samples are prepared to measure the mechanical effect of the capsules on the mixture. These samples are subjected to different loadings and rest periods to consider the time required for the oil to diffuse inside the asphalt. The first point of the laboratory testing in this phase is to investigate whether the capsules can reduce the stiffness of the bitumen, as this is the principal assumption for rejuvenating aged asphalt. The second step is to investigate the effect of the capsules on the mechanical properties of the asphalt mixture such as durability, rutting, fatigue, particle loss, moisture effect and permanent deformation. Cylindrical asphalt specimens are used in this phase, with and without capsules. Three different capsule contents are used, with oil-to-bitumen mass ratios 1.1%, 2.8% and 5.5%, respectively. Capsules are strongly bonded into the asphalt mixture and the mechanical performance of asphalt with and without capsules is evaluated. Asphalt samples containing capsules are compared with those without capsules to accurately assess the capsules' effect on asphalt. In a later step, the particle loss of specimens with capsules is investigated after self-healing to compare the effect of oil release on the mixture.

Phase 3: Self-healing investigation. Two stages are carried out to investigate the self-healing potential of the capsules used. The elementary stage starts by adding capsules to a high bitumen content mixture such as asphalt mastic. A healing test is applied to the asphalt mastic beams with and without capsules at four different temperatures. Five different types of capsules, in terms of size and oil content, are used in the mastic healing tests. The advanced stage is to apply the capsules into an asphalt mixture and test the healing in a real asphalt pavement. Asphalt beams with and without capsules are made in the laboratory and tested for healing. Eight different temperatures are applied to evaluate the healing at different rest periods. Three capsule contents with respect to oil-bitumen ratio are added to the asphalt

mixture and tested for healing in the asphalt beams. The dimensions of the mastic beams and the asphalt beams are non-standard, cast in workshop-made moulds to achieve the purpose of this stage, which is the self-healing.

The healing test starts by subjecting the mastic/asphalt samples to a static compressive loading to make cracks in the asphalt and to make sure that the capsules will be broken to allow the oil to spread out into the asphalt. Then, a specified time is given to the oil to diffuse and the crack self-healing is checked after a certain time. Figure 1.1 presents the sequence of this research methodology.

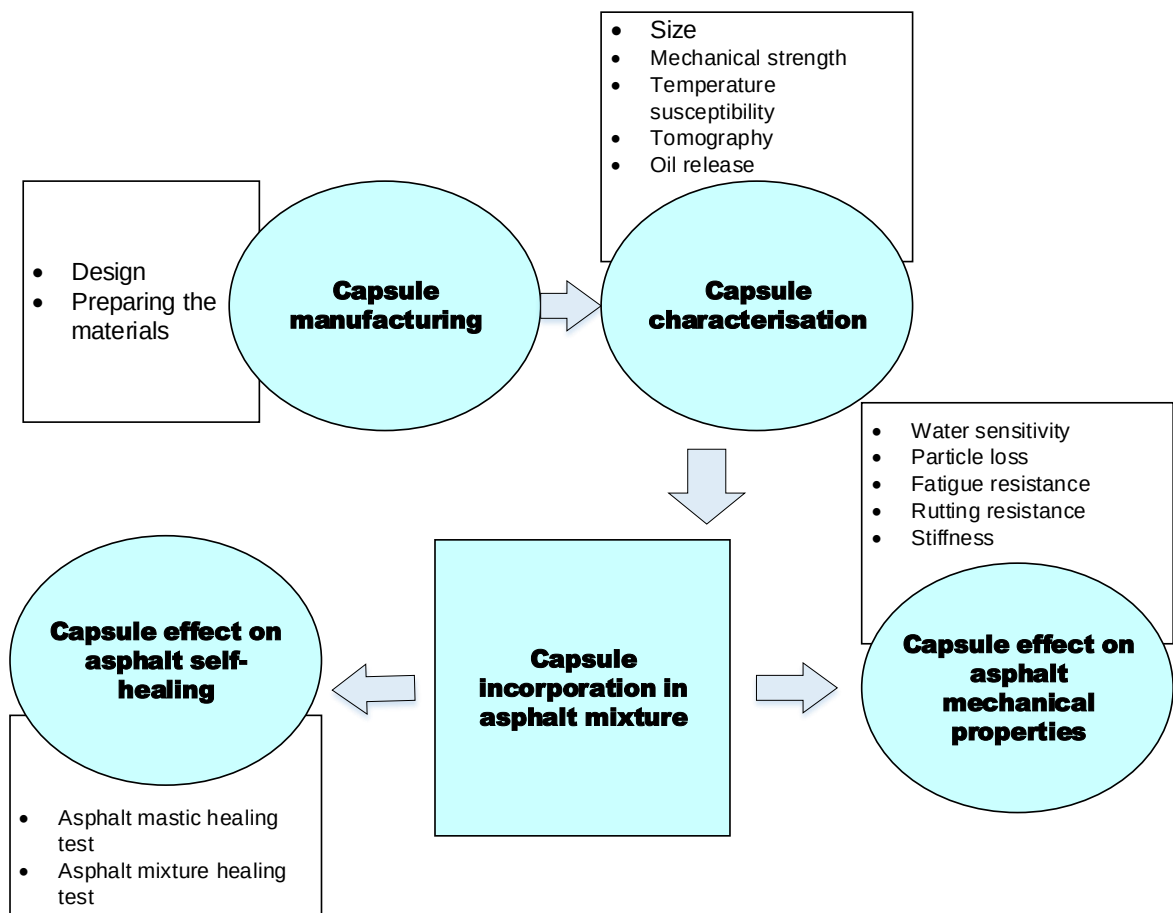


Figure 1.1: Elements of the research methodology.

1.5 Thesis Outline

Chapter	Description
Chapter 1	An overview and general background information about asphalt pavement maintenance, bitumen ageing and asphalt self-healing. This chapter also includes the problem statement, the aims and objectives as well as the research methodology.
Chapter 2	This chapter provides an overview, background of pavement types and materials in general, pavement defects and maintenance, self-healing materials, the general concept of encapsulated rejuvenators, diffusion of rejuvenators inside an asphalt pavement, asphalt self-healing by induction heating and asphalt self-healing by encapsulated rejuvenators.
Chapter 3	This chapter presents the materials and methods involved in capsule production, asphalt mixture preparation and types, types of asphalt samples used in the research, methods of incorporating the capsules into the asphalt mixtures, all testing methods performed in the research.
Chapter 4	In this chapter, all capsule properties are presented, including tomography, capsule structure, size of the capsules, thermal resistance, capsule strength, capsule oil content and capsule oil diffusion.
Chapter 5	In this chapter, the effect of capsules on asphalt behaviour is investigated. This includes standard and non-standard mechanical tests performed on the asphalt mixture to assess the effect of capsules on the asphalt stiffness, and on the asphalt durability.
Chapter 6	The investigation of crack healing with the proposed capsules is the main topic of this chapter. It includes the testing program, asphalt types used in the self-healing tests, visual and mechanical assessment of asphalt self-healing.
Chapter 7	In this chapter, the main conclusions and recommendations for future research are presented.

Chapter 2: Literature Review

2.1 Overview

Recently, engineers have begun to explore methods of alternative pavement maintenance for economic and environmental reasons. One of these methods is improving the self-healing property of bituminous materials. This property has been known about for more than four decades; but it is only recently that engineers have started to investigate methods of accelerating this natural healing in asphalt pavements. Self-healing pavements are expected to extend service life, most importantly reducing maintenance costs, and creating a sustainable means of road engineering. For more understanding of self-healing in asphalt pavements, it is essential to consider and investigate all the factors that contribute to it.

The aim of this chapter, therefore, is to provide a literature review that introduces the topic of self-healing in asphalt pavement in order to provide a suitable background into the subject. It describes the types of asphalt mixtures and the rheological and mechanical properties of asphalt materials, the behaviour of bitumen within an asphalt mixture, the factors affecting this behaviour and therefore bitumen ageing and in addition, the effect of ageing on the phenomenon of self-healing. Details of natural self-healing and how this been engineered to improve the self-healing of asphalt by using a variety of materials as healing agents, and assessing their strengths and weaknesses, are presented. Finally, the analysis is carried out on two different methods (heat induction and encapsulating rejuvenators) that have recently been researched and developed to increase levels of self-healing within asphalt, describing the different encapsulation methods that have been produced to date.

2.2 Asphalt mixture

Flexible or asphalt pavements is an asphalt mixture structure, which is manufactured at a very high temperature (about 160°C) and typically comprises a bituminous binder, graded aggregate and air voids. Huang (2004) defines a flexible pavement as a multi-layer structure with better quality material on top where the intensity of stresses is high and lower quality material at the bottom where the intensity is relatively low. The load intensity reduces as it is transferred through the pavement layers into the soil by spreading over an increasingly large area, which allows materials with less quality to be used as depth increases, minimising material costs (Brown et al., 2002). Figure 2.1 shows the load distribution through the pavement layers. The most widely used upper pavement material is hot mix asphalt (HMA), which must be sufficiently durable to resist temperature changes and environmental deterioration.

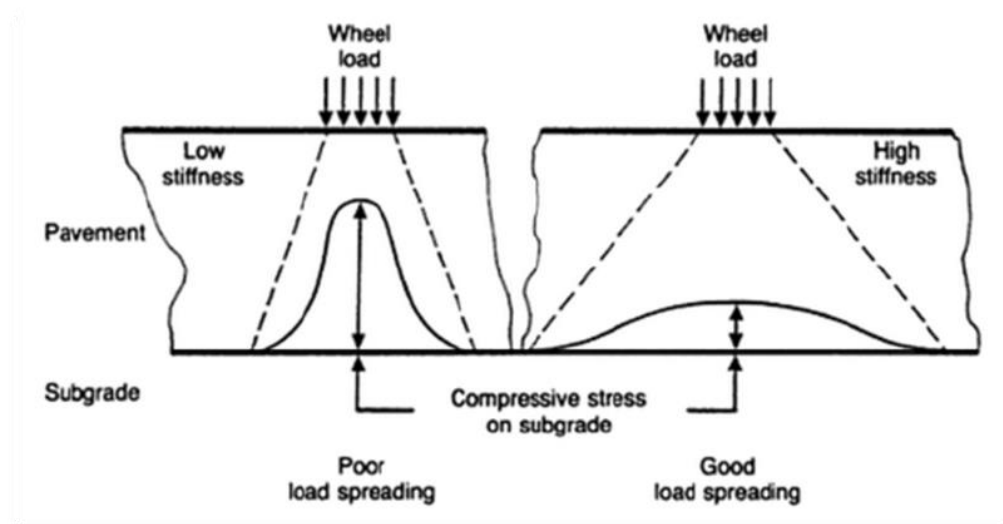


Figure 2.1: Load spread through asphalt pavement layers (Brown et al., 2002).

Hot mix asphalt (HMA) comes in many types depending on the way the classification is formulated, such as classification based on the method of production and mixing, or based on mixture composition of bitumen and aggregate (Pavement Interactive, 2010, Garber and Hoel, 2014, NCHRP, 2011). These different types of asphalt mixture are based mainly on maximum aggregate size, aggregate gradation and bitumen type and content. The three most general classifications are:

- Dense-graded HMA

These kinds of mixtures are normally impermeable and referred to by their maximum aggregate size. They can be subdivided into fine-graded and course graded mixes depending on their fine sized particles and the amount of sand in their composition. These mixtures are versatile and commonly used in pavement works. Garber and Hoel (2014) state the characteristics of these mixtures as: the amount of voids in mineral aggregate (VMA) are 11-17%, the air voids are 3-5% and the bitumen content ranges between 4.5-6% based on the pavement layer the mix is produced for. Figure 2.2 shows this type of mixture.

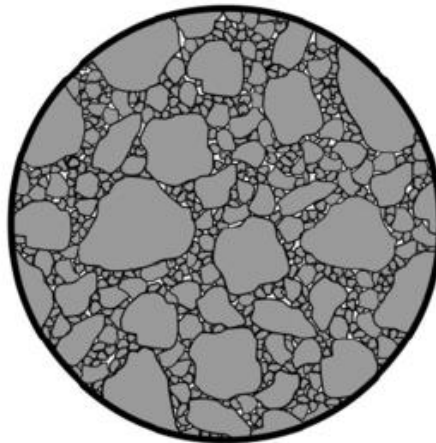


Figure 2.2: Dense-graded HMA (Pavement Interactive, 2010).

- Gap-graded HMA

This type of mixtures is intended to increase the durability of the pavement and improve the resistance to plastic deformation, which is known as permanent deformation or rutting. This strength or resistance relies on the aggregate properties rather than the bitumen type or content. The aggregate develops a stone on stone structure, which is why it is called stone matrix asphalt (SMA) as well.

This mixture requires more durable aggregate, high asphalt content, and for the most typical mixes, an additive to asphalt binder and fibres (Garber and Hoel, 2014). Fibres are used to stabilise the mixture during handling and placement. Therefore, it is more expensive than normal dense-graded HMA if not used in the right place where the improvement is required

to resist rutting and increase durability. The properties of this type of mixtures are: VMA is more than 17%, the bitumen content is higher than 6% and the air voids range from 3-5%. Figure 2.3 shows this type of asphalt mix.

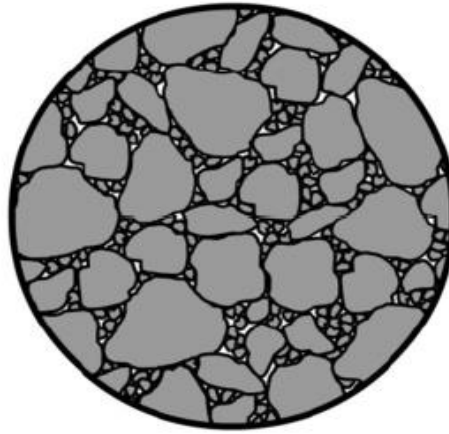


Figure 2.3: Gap-graded HMA (Pavement Interactive, 2010).

- Open-graded HMA

This type of mixture is usually designed for areas where high water permeability is required. It is generally a gap-graded HMA with high air void content. The advantages of this type of HMA mixture are: it minimises the potential for hydroplaning, improves friction in wet weather, reduces splash and spray, reduces glare and improves the visibility of pavement markings in wet weather. This type of asphalt mixture usually contains modified bitumen and fibres to increase the binder content and improve its durability. In addition, this mix costs more than dense-graded mixtures; they can be considered for wearing courses on high speed pavement sections when the traffic levels exceed 10,000,000 ESALs (NCHRP, 2011). The properties of this type of mix are: air voids 15-20%, VMA is generally 20-25% and the bitumen content ranges from 5-8%. Figure 2.4 shows this type of mixture.

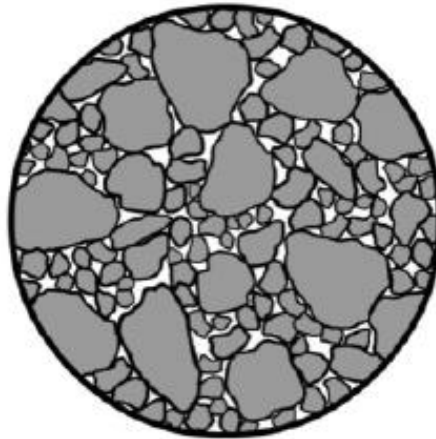


Figure 2.4: Open-graded HMA (Pavement Interactive, 2010).

2.3 The interaction between bitumen and aggregate

Asphalt mixture properties are highly dependent on the type of bitumen binder and the type and gradation of the aggregate used. Some mixtures include additives such as fillers, rubbers and plastics to improve the properties of the asphalt mix. These additives are different in their application depending on the type of the additive and its functional properties; they may be added by weight of bitumen, by weight of aggregate or by weight of the total mix (Lu and Isacsson, 1998).

The behaviour of asphalt pavement depends heavily on the bitumen used. It is supposed to provide a suitable surface for vehicle contact, resist cracking and provide resistance to the tensile and compressive stresses induced by repeated traffic loading and the environment (Thom, 2008). Asphalt pavement performance and response to traffic loading are highly related to its stiffness modulus, which depends on how well the binder restricts inter-particle movement in the asphalt mix. This inter-particle movement is affected by temperature, traffic loading and the asphalt constitution. Furthermore, the stiffness of an asphalt mix will increase as the bitumen ages, resulting in increasing viscosity that leads to a reduction in the inter-particle bond in the asphalt mix.

2.3.1 Bitumen

Bitumen is a complex, viscoelastic material formed by different components with various chemical structures; the leading components are carbon and hydrogen, known as hydrocarbons. Other components of elements such as oxygen, sulphur and nitrogen, are called heteroatom structures. Binders consist of different molecular compositions and structures depending on the petroleum source and refining procedure used to produce them (Wang, 2011).

The complex and diverse composition of these hydrocarbon and heteroatom molecules results in the unique balance of bitumen properties. This composition is usually subdivided into two major fractions, a solid fraction called asphaltenes and a liquid one called maltenes. The asphaltene content has a significant influence on the properties of the bitumen, including viscosity and stiffness. The maltene fraction can be further subdivided into three chemical groups; saturates, aromatics and resins, (Read and Whiteoak, 2003, García et al., 2011a). The complexity of bitumen can lead to a wide range of physical properties that can be tested through rheological and empirical tests. These properties, however, must meet the specification requirements of bitumen, such as European Standard BS EN12591: 2000.

Flexible pavements spread the traffic loads from bitumen bound layers to underlying unbound materials to decrease the stresses and prevent failure. The mechanical properties of the asphalt layer are highly dependent on the properties of bitumen, therefore; it is essential to understand and test the mechanical and rheological properties of the bitumen.

2.3.2 The rheological and mechanical properties of bitumen

Rheology is a very powerful tool for characterising and quantifying material properties. It has been well proved that the rheological properties of asphalt binder affect pavement performance. The necessity to study the phenomenon of ageing of asphalt mixture is due to the fact that the rheological properties of asphalt change with time from production and continue changing subsequently during service (Joshi et al., 2013). The first obvious change in bitumen rheology when hardening of asphalt takes place is in the mixing plant where heated aggregate is mixed with hot asphalt binder. Both air oxidation and loss of volatiles result in significant rheological changes such as a decrease in penetration and increase in the stiffness and viscosity of asphalt binder during the short mixing period.

As previously mentioned, bitumen is a complicated structure of molecules, predominantly hydrocarbons with minor contents of functional groups including atoms of sulphur, nitrogen and oxygen, besides traces of metals like nickel and magnesium (Tran et al., 2012). It is divided into two chemical fractions, asphaltenes and maltenes; maltenes are further subdivided into saturates, aromatics and resins. The asphaltenes are responsible for the rheological properties of bitumen; the higher the asphaltene content the harder and more viscous the bitumen (Read and Whiteoak, 2003). Resins and aromatics are peptisers or dispersing agents for asphaltenes, their proportion to asphaltenes is important in that it controls the structural nature of the bitumen.

Saturates are non-polar, viscous liquids that work on softening the bitumen. The structure of bitumen is considered as a colloidal system with a high molecular weight (Domone and Illston, 2010). The index of colloidal stability (CI), which means dispersing the asphaltene micelles in a lower molecular oil medium, is the ratio of asphaltenes and saturates to the ratio of aromatics and resins. This index is used to describe the stability of the colloidal structure; the lower the CI the more stable the colloidal structure (Domone and Illston, 2010). As a result, the constitution and structure of the bitumen defines its physical and mechanical properties.

Regarding bitumen structure, Read and Whiteoak (2003) further divide bitumen into two types; if the fraction of aromatic to resin exists in sufficient quantity in the bitumen, the asphaltenes become fully peptised and the resulting micelles can move easily within the bitumen. This type of bitumen is called 'SOL' bitumen. On the other hand, when the presence of aromatics and resins is not sufficient to peptise the micelles, the asphaltenes can connect to each other further. This type of bitumen is called 'GEL' bitumen, which has the irregular open packed structure of micelles with inconsistent distribution and movement within the bitumen. These two types are illustrated in Figure 2.5.

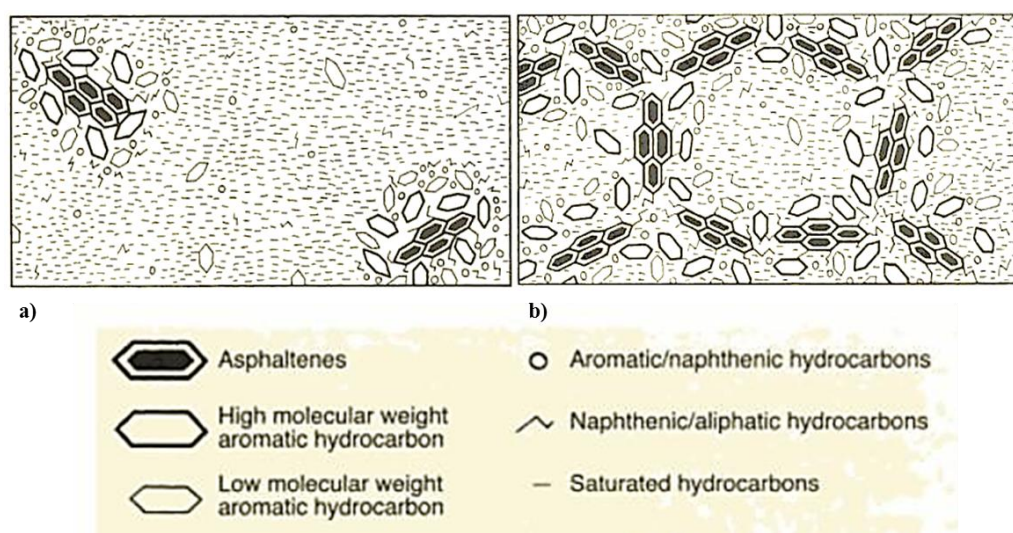


Figure 2.5: A schematic representation of a) SOL bitumen, and b) GEL bitumen (Read and Whiteoak, 2003).

Furthermore, bitumen is, as well, defined by its thermoplastic and viscoelastic properties. The thermoplastic properties directly affect the viscosity of the material, as it decreases when heated and increases when cooled, showing a solid behaviour at low temperatures ($<0^{\circ}\text{C}$) and a liquid behaviour at high temperatures ($>60^{\circ}\text{C}$) (Domone and Illston, 2010). At intermediate temperatures ($0-60^{\circ}\text{C}$), bitumen has viscoelastic characteristics. When a force is applied to the material its structure will deform and flow. Viscous deformation cannot be recovered, whereas elastic deformation is recoverable. The relative proportions of viscous to elastic response of bitumen when a force is applied are dependent on its constitution, the rate of loading and temperature (Hunter, 1994). Any material responds to stresses by two types of reaction; a recoverable reaction that is recorded as strain, and an irrecoverable reaction that is recorded as the rate of strain. Viscosity is the measure of a liquid's resistance to flow and it is defined as the ratio of shear stress to the corresponding rate of shear strain. The stiffness modulus is a parameter of solids that is defined as the ratio of applied stress to the corresponding strain. Although the physical behaviour of bitumen is complex, Airey (2003) demonstrated several empirical tests used to illustrate the physical properties of the bitumen in a simplified procedure according to the requirements of the European standard EN12591: 2000.

2.3.3 The ageing of bitumen

The ageing of bitumen is highly related to the climate, bitumen composition, aggregate, and pavement structure. The main ageing mechanisms of bitumen are oxidation and the loss of volatiles. Oxidation and loss of volatiles are external conditions to bitumen causing changes in chemical composition, which affect its rheological and mechanical properties. Aged bitumen has higher viscosity and is stiffer than fresh bitumen with noticeable changes in its composition. These changes can lead to the loss of adhesion in the presence of moisture and brittleness, where oxidation products have acidic characteristics and can be hydrolysed. In addition, they may cause surface ravelling and cracking as aged bitumen becomes more brittle (Lu and Isacsson, 1998, Holleran et al., 2006).

Nunn (1998) claims that ageing of bitumen could give an improvement to the structural performance of an asphalt pavement, as increasing the hardening (curing) of bitumen over time could result in a 200% increase in the elastic stiffness of dense bitumen macadam (DBM) in just a few years of service. Hagos (2008) on the other hand, explains that ageing of bitumen can be detrimental, reducing the pavement flexibility hence reducing the strain level to failure and its stress relaxation behaviour, as well as increasing sensitivity to fretting and cracking.

Bitumen oxidises with time if it is in direct contact with oxygen, the more permeable the asphalt the more susceptible to the oxidation process, which can be considered as a long-term ageing of the asphalt. During asphalt mix production, transportation and laying, bitumen loses a considerable amount of its mass due to loss of volatiles (at this stage it can be called short-term ageing). Nielsen (2007) used thin sections of asphalt pavement to investigate the micro-structure of the same field specimens with different ages, namely 1 and 12 years old specimens. The aim of the study was to evaluate the effect of ageing on ravelling process from a micro level of the bituminous material. Figure 2.6 indicates that the asphalt deterioration is related to adhesive and cohesive failures, which is considerably related to bitumen deterioration with time.

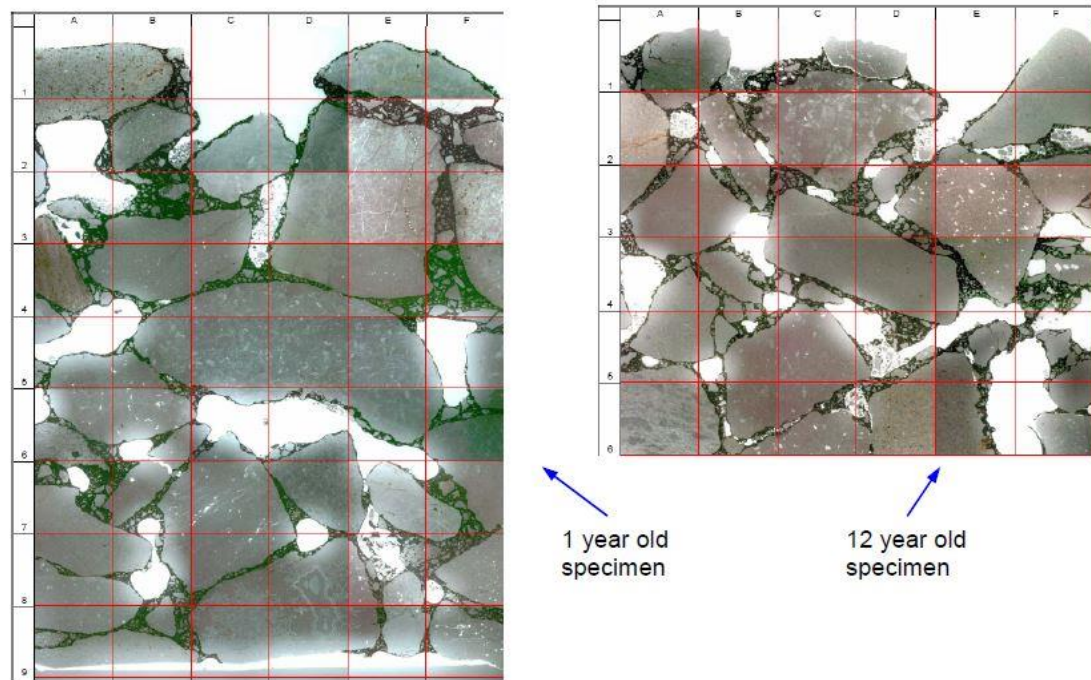


Figure 2.6: CT-scan images of field specimens of 1 and 12 years old asphalt pavement (Nielsen, 2007).

The particles of bitumen are constantly moving, leading to physical hardening taking place, although very slowly at ambient temperatures. This hardening occurs due to the reorientation of the molecules, which results from slowly crystallised waxes and hydrogen bonding. Eventually, with time of service, the movement of the molecules is considerably reduced, which results in stiffer and more brittle bitumen (Hunter, 2000). Asphalt binder hardening occurs due to the absorption of the lighter saturate components by the aggregate (Van Gooswilligen et al., 1989). These light saturates have a smaller molecular size and an affinity to aggregate with high absorptive capabilities. This is considered as an important characteristic during the asphalt mixing process, in order to ensure that the bitumen adheres well to the aggregate. However, in the long term assessment of asphalt, this results in changing the molecular balance of the bitumen in favour of the harder, more brittle asphaltenes fraction (Thom, 2008). All these processes above occur over a long period of time, whilst the pavement is in service, after short term ageing has already taken place. Read and Whiteoak (2003) illustrate in Figure 2.7 how ageing of bitumen occurs over time.

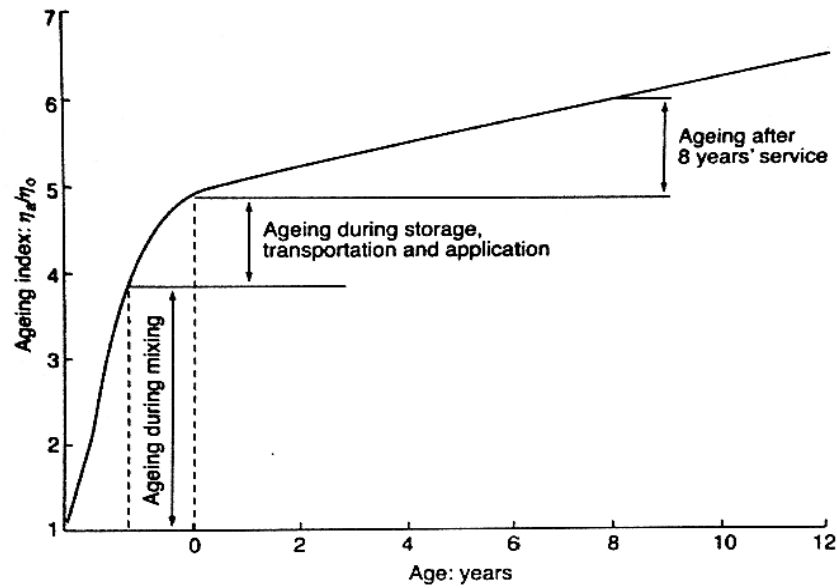


Figure 2.7: Ageing of bitumen over its life time (Read and Whiteoak, 2003).

Short term ageing starts during stages of mixing, transporting, placing and compaction of asphalt mixture and construction of the road pavement. Short-term ageing, therefore, occurs when the bitumen is at an elevated temperature and it is responsible for significant changes in asphalt properties, such as increasing the binder viscosity by up to 50% of the original (Thom, 2008). It is evident that there is no decisive test to forecast the probable long-term binder properties as the ageing of bitumen is complex and there are numerous variables that contribute to it. Many methods have been investigated in order to preserve asphalt pavement, such as rejuvenator emulsions, fog seals and other different thin overlay techniques (Boyer, 2000). The only one of these methods that can restore the original properties of the pavement is the application of rejuvenators, which work primarily on restoring the original asphaltene/maltene ratio (Garcia et al., 2010).

2.4 Failures in asphalt mixture

There are two primary failure modes in asphalt pavement; these are cracking and deformation. Considering that the likelihood of aggregate failure is low, these failures are dependent, to some extent, on the type, quality, quantity and rheological behaviour of the bitumen used in the mix and its susceptibility to ageing.

Crack failure is a complicated failure mode, which is caused by the repetition of traffic loading and the tensile stresses produced due to the bending of the asphalt layer, the susceptibility of binder to temperature changes as well as the increasing viscosity at low temperatures that leads to a higher stiffness making cracks appear (Thom, 2008). The fact that all asphalt mixtures are visco-elastic materials, because they contain bitumen; therefore most types of distress induced by traffic loading will be likely to dissipate if enough time is given. This process is known as stress relaxation. When both (or either) the tensile stresses coming from traffic loading and their related strains, and the temperature drop, exceed the maximum permissible strength of the pavement, cracking will occur. At higher temperatures, stress relaxation can stop the strain from reaching a value that may cause cracking; at lower temperatures however, the tensile stresses may continue, which is highly likely to cause cracking. As illustrated in Section 2.3.3, long term ageing of bitumen leads to an increase in viscosity and stiffness modulus of the asphalt, which means a decrease in stress relaxation capability. This further increases the possibility of pavement cracking (Read and Whiteoak, 2003). Thom (2008) suggested that the continuous traffic loads impose a strain on the mortar (fine aggregate and bitumen), which may cause inter-particle slip to happen. Figure 2.8 illustrates this slip at particle contacts.

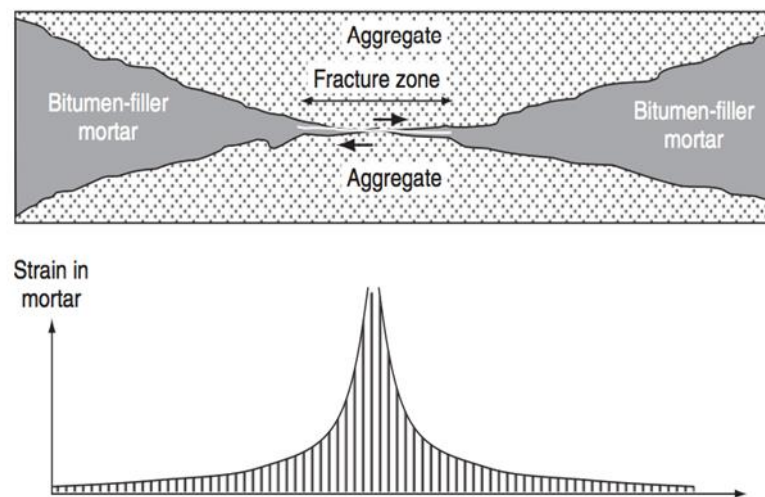


Figure 2.8: Stress distribution in the fracture zone (Thom, 2008).

When contact between aggregate particles happens, the strain in the mortar reaches a value of infinity, which is a description of a fracture (Thom, 2008). The fracture leads to a further

particle slip and a separation to occur. Fractures can spread until they reach a region where stress and strain are sufficiently low, resulting in gradual weakening of the structure.

The fracture mechanism depends on temperature and rest periods between applied stresses. The critical situation happens when the temperature is low accompanied by short rest periods. Rest periods, the load-free times between consecutive traffic load applications, are essential to allow cracked zones to heal and stress to relax due to the viscous flow of the bitumen (Osman et al., 2004). The stiffness of low temperature bitumen is higher due to the restricted inter-particle movement; the higher stiffness of the asphalt mix results in increased stresses in the binder increasing the chances of its fracture. The possibility of the phenomenon of healing occurs with high temperatures where the stresses in the binder are considerably reduced and the bitumen becomes less viscous and flows into the fractures.

According to Osman et al. (2004), the temperature and rest periods act dependently; when there is a high temperature, shorter rest periods might be required to achieve healing or vice versa. The possibility of modelling rest periods is not an easy task, particularly when considering their effect on self-healing. This results from the fact that rest periods are entirely dependent on the road and the variable traffic volume at different times (Read, 1996).

Fatigue cracks are the propagation and enlargement of those fracture zones at particle contacts, which are controlled by the strains in the mixture, as shown in Figure 2.9. These cracks are generated by the continuous application of stresses that are lower than the tensile strength of the material. Fatigue cracks usually occur after local micro-cracks have been initiated. Fatigue converts these micro-cracks into macro-cracks; this happens as a function of the elastic strain within the asphalt mixture (Thom, 2008).

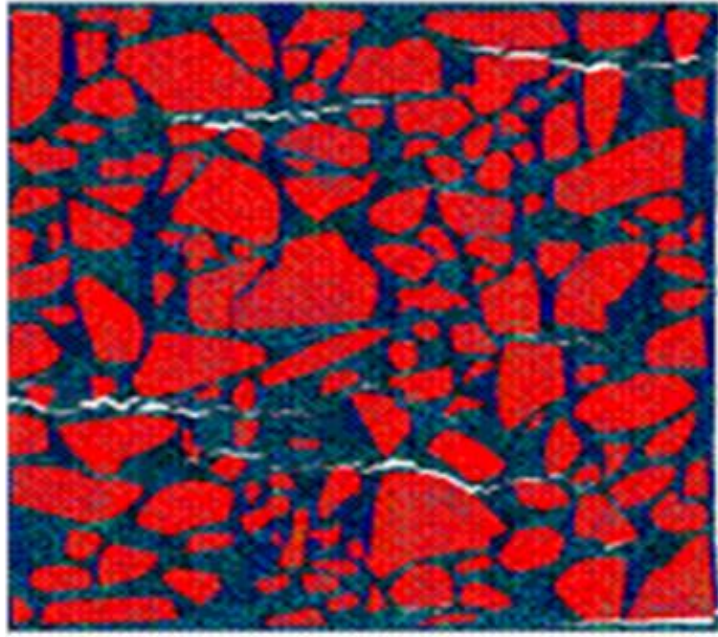


Figure 2.9: Development of cracks within the asphalt mix (Asphalt Research Correspondent, 2011).

Steyn et al. (2009) proposed an equation to determine the number of load repetitions (N_f) that cause cracks to initiate and propagate by using the number of load repetitions to generate a micro-crack (N_i) and the number of repetitions required for the macro-crack to propagate to the pavement surface (N_p), as follows:

$$N_f = N_i + N_p \quad 2-1$$

Asphalt pavement definitely deforms under loading, which can result in permanent deformation (rutting) if plastic deformation occurs. The amount of deformation is mainly related to the aggregate skeleton within the material. Plastic deformation differs in the amount and susceptibility depending on the binder; a hard binder needs a higher temperature to cause plastic deformation, whereas a soft binder is more susceptible. Resistance to permanent deformation cannot be defined by a single property; therefore, testing can only be indicative. A common test used for this purpose is the repeated load axial test (RLAT), where a sample is subjected repeatedly to compressive loads resulting in axial deformation.

Research by Nunn et al. (1997) developed the concept of long life pavement by showing that changing the long-term properties of bitumen can improve the fatigue resistance and extend pavement life. The adhesive properties of the bitumen are fundamental to bind aggregate particles together, and play an important role in pavement life and related deformation. Bitumen-aggregate adhesion can be affected by many factors; some of these factors can be controlled during production. The mineralogical composition is one of the main factors that influence asphalt adhesion. The physical and chemical properties of the aggregate, such as its chemical composition, shape/size/texture, structure and residual valence can influence bitumen adhesion as well (Read and Whiteoak, 2003).

In addition, unstable surface charges on an aggregate may consume the surface energy that can magnetise liquids of opposite polarity, creating an adhesive bond between them. Liquids adhere better when they can best satisfy the surface energy requirements of the material in contact. Read and Whiteoak (2003) and Domone and Illston (2010) state that the process of stripping and separation of bitumen happens when water can better satisfy the surface energy requirement of the aggregate. Another significant factor in bitumen-aggregate adhesion is the physico-mechanical absorption properties of bitumen. The absorption of bitumen depends on the petrographic characteristics of the aggregate.

Qiu (2012b) states that cracks can appear on bituminous materials at different levels depending on the sample section and location. For instance, at pavement level, cracks can develop due to tensile strains at the bottom of the asphalt layer, which are called bottom-up cracks, or at pavement surface due to tensile and shear stresses, where they are called top-down cracks. At asphalt specimen level, cracks can result from load repetitions. Furthermore, at the binder level, cracks can either be cohesive cracks within the bitumen or adhesive cracks within the bitumen and aggregate. Figure 2.10 shows the mains types of cracks of asphalt pavement.

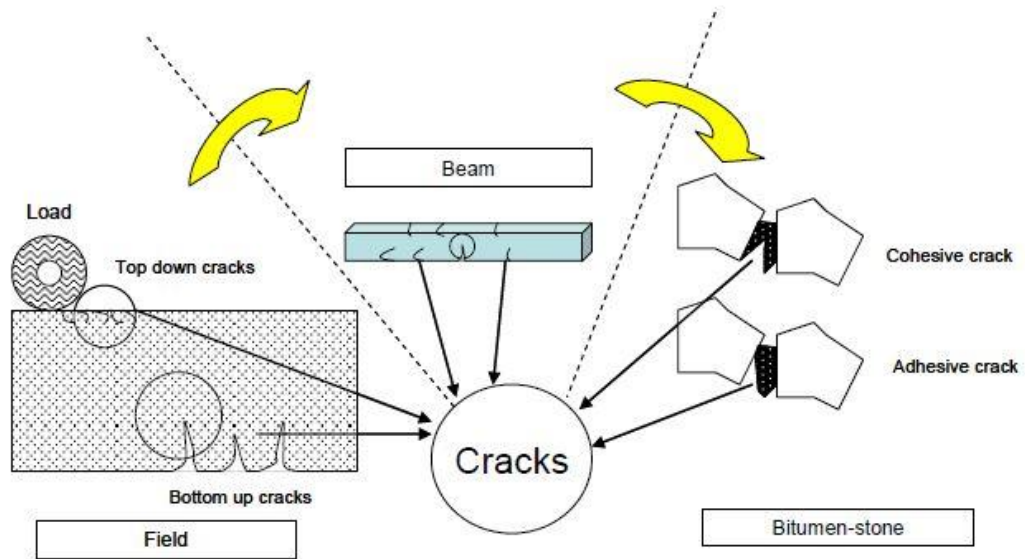


Figure 2.10: Type of cracks at multi-scales of bituminous materials (Qiu, 2012b).

Domone and Illston (2010) found that the free surface of bitumen could increase by a considerable amount due to a fine microstructure of pores, voids and micro-cracks, although a general assumption is that with rougher surfaces there is a better adhesion. In addition, the desirable adhesion requires a balance between a smooth surface (i.e. aggregate wettability), which allows the bitumen to coat the aggregate and a rough surface texture that holds the binder once wetted.

Hagos (2008) demonstrated that the majority of pavement failure modes, such as ravelling (shown in Figure 2.11), are adhesive or cohesive. Adhesive failures predominantly result from the damage caused by water effects while cohesive failures occur when the stress levels applied to the asphalt binder are excessive. Water can cause cohesive failures as well, by affecting the viscosity of the binder, reducing its structural integrity and strength. Although the effect of water on asphalt mixture can be reduced when the binder hardens with time, the chances of crack propagation are greater. Kanitpong and Bahia (2003) investigated the harmful effect of water with respect to the cohesive and adhesive properties of binders. They found that water can reduce the resistance to traffic induced stresses (cohesive failure) besides the damage that causes stripping (adhesive failure). There are several mechanisms that lead to failure in asphalt adhesion and hence debonding of bitumen and aggregate, most of which involve the presence of water.

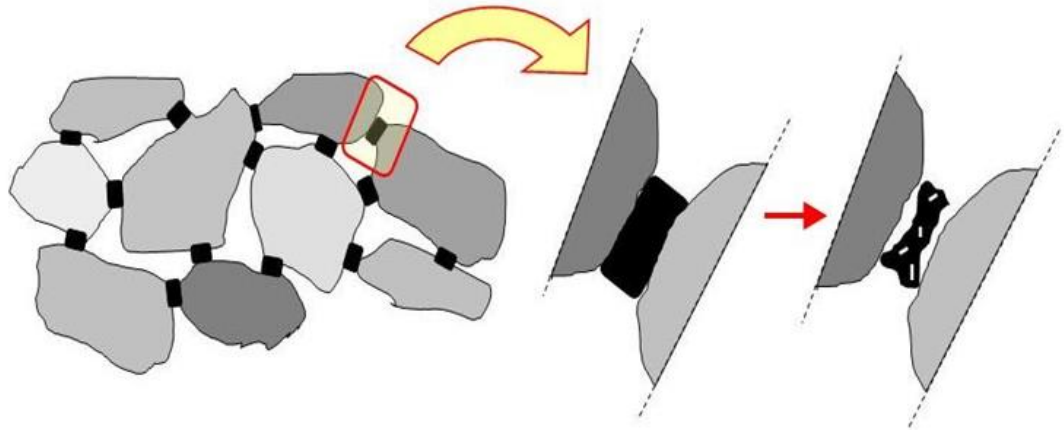


Figure 2.11: The mechanism of ravelling (Schlangen et al., 2011).

2.5 Current maintenance techniques

Designers and engineers can demonstrate their skills and abilities when deciding which pavement maintenance technique is suitable and appropriate to make pavement life longer. There is a variety of variables, which must be considered when deciding maintenance measures and techniques, each of which creates different challenges.

2.5.1 Crack sealing

Water can accelerate the stripping between asphalt particles when it infiltrates to the cracks, making the asphalt become degraded. When this water changes with climate, as it suffers freezing and thawing cycles causing the pavement to expand and heave, which eventually causes more damage. It is, therefore, very important to keep the water intrusion as low as possible by sealing the cracks (Thom, 2008).

Crack sealing is considered as a routine repair once the cracks have appeared and the pavement starts to fail. The functional use of the pavement might be disrupted for the duration of the repair, which may have an impact on road users both socially and economically. An advanced maintenance system that reduces the amount of damage in the pavement is a preferential and more economical approach that may reduce the level of disruptive maintenance required.

2.5.2 Recycling

The recycling process includes the asphalt materials that are supposed to be thrown away after removal from a road pavement to be used again to pave new areas, such as drives or car parks. This type of recycling is still practised and may continue for a long time (Nicholls, 1998).

There is very limited knowledge of how modern recycled construction materials with their impurities can perform when crushed and converted to aggregates and used to produce new concrete and asphalt (Byrne, 2005). A certain amount of re-use of old pavement surfacings has been implemented in the UK for many years. Material removed from roads before resurfacing has been used as fill material and for regulating and blinding purposes in the construction of paved areas for light traffic use. It is recognised that asphalt is the most recycled product in many countries. This possibly results from a shortage of mineral aggregate resources in these countries or there may not be enough space to landfill the material because of the population density.

The recycling of old asphalt pavements has significant economic benefits. This results from the fact that asphalt binder represents more than 30% of the cost of a new pavement and its cost is directly related to the oil price; when oil prices are rising, the cost of binder will rise as well. Byrne (2005) states that unrecycled old asphalt can be used in a lower quality pavement application as a granular base, or might go to landfill. In the UK, recycling is widely considered as a key part of the aggregate industry. Over the last 10 years, there has been heavy investment in recycling operations. The amount of recycled asphalt is expected to represent about 19% of the total aggregate market.

When the main consideration is focused on the cost of the materials themselves, then reclaimed or recycled materials can be cheaper than new. From a purely economic point of view, if the cost of processing the material is less than the cost of its disposal and producing new material, recycling that material is worthwhile. Processing and production costs of both new and recycled materials are highly likely to increase due to their environmental impact and the consequent need to provide an alternative maintenance technology. The difference in economics for or against recycling might be small, and specific to individual projects (Humphreys, 1994).

2.5.3 The application of a rejuvenator on pavement surface

A relatively new maintenance system applied to asphalt pavements is to use rejuvenators. The purpose of using rejuvenators is to reverse asphalt ageing and prevent brittle pavements. They work on softening the binder by decreasing its viscosity, restoring its original characteristics and extending the fatigue life. Boyer (2000) stated that rejuvenators have been used as recycling agents to reverse the process of asphalt ageing by restoring the rheological properties of bitumen. This is, to some extent, an economical way to extend pavement life without the necessity of major maintenance cost. To achieve this, rejuvenators should replace the maltenes fraction lost during the short-term and long-term ageing of asphalt by restoring the ratio of maltenes to asphaltenes in the bitumen. Rejuvenators are required to contain a high proportion of aromatics, which is necessary to improve both hardening and temperature susceptibility, and a low saturates content to decrease the stiffness (Tran et al., 2012). The influence of a rejuvenator should be such that it increases the peptizing powers of the maltene fraction in the asphalt binder (García et al., 2011a).

Kiggundu and Newman (1987) researched asphalt pavement rejuvenation, in a study funded by the Air Force Weapons Laboratory. Their study was based on laboratory investigations using rejuvenators on bitumen and asphalt mixtures to measure their effect on viscosity and particle loss. Based on their results, they found Reclamite and Koppers Bituminous Pavement Rejuvenator (BPR) to be the most effective rejuvenators, as they reduced the viscosity of bitumen and showed less particle loss from the asphalt samples, compared to untreated samples. A road maintenance company in Michigan in 1974 used Reclamite on an asphalt pavement to test its effect on bitumen penetration, and found that the penetration increased to about 120% and the asphalt binder became more workable (Venable et al., 1983). The above examples show that rejuvenators can enhance pavement life and improve the performance. However, the environmental effect of using rejuvenators is a concern as all these rejuvenators are applied to road pavements by spraying the chemicals onto the asphalt surface.

Safety and applicability

Boyer (2000) was biased to some extent in his article towards the benefits of rejuvenators. The article only mentions the benefits of the rejuvenators and how they have been successful in spite of concern about the disadvantages of using them. One of the issues of using

rejuvenators is that, since they are usually spread on the surface of the pavement, they may only rejuvenate the pavement on the upper surface. The upper surface of the pavement is the place where bitumen is subjected to high oxidation where ageing is more likely to happen. However, to enhance the long term asphalt performance, rejuvenators have to be mixed with bitumen throughout the entire pavement layer. In addition, the amount of applied rejuvenator is hard to control to obtain an appropriate balance of rejuvenator content that can work perfectly without adversely affecting other properties of the asphalt, such as stiffness and permanent deformation resistance. Furthermore, before applying the rejuvenator, the pavement surface must be cleaned of impurities, such as dust, grease, oil and petroleum, otherwise, the effectiveness of the rejuvenator to infiltrate the pavement is substantially decreased. The penetration of the rejuvenator, on the other hand, can be restricted if densely graded asphalt is used. Therefore, the success of using rejuvenators on a pavement surface is very limited.

The release of harmful hydrocarbons into the atmosphere and the possible runoff of the rejuvenator into nearby water sources are considered other environmental issues that are significant when applying rejuvenators onto the pavement surface. The skid resistance of pavement can also be affected, as the oily rejuvenator may stay on the pavement surface. The mentioned drawbacks of using rejuvenators indicate that further research is required to remedy some of these issues and to make rejuvenators into a viable solution to bitumen degradation. Figure 2.12 shows the effect of spreading a rejuvenator on an asphalt mixture.



Figure 2.12: Asphalt mixture before and after the application of rejuvenators (Macismo, 2012).

The rejuvenator's capability to penetrate an asphalt layer is known as diffusivity, which is calculated by a diffusion coefficient. According to Kim et al. (1990), rejuvenator diffusivity is increased through binders with a chemical structure with long chains and fewer branches. For the aged binder, the effective healing is triggered when the self-diffusion of molecules occurs across a crack interface (Bhasin et al., 2009). Furthermore, the diffusivity will increase if there is a large difference in concentration of rejuvenator molecules on the faces of the crack. Diffusion coefficients are variable depending on the type of rejuvenator, based on their different levels of aromatic content and molecular size. To obtain the optimum rejuvenator diffusion, the type of bitumen and asphalt mixture used in the pavement must be known, so that suitable type of rejuvenator can be applied.

Economics

Production and construction of self-healing materials are always expected to cost more than traditional maintenance since they require additional compounds and resources, as well as additional processing steps and precautions. However, the advantage of self-healing materials may be revealed in later stages of pavement life. This is because of their potential ability to improve the fatigue resistance of a pavement, which can eliminate the necessity for expensive and time consuming maintenance and inspections.

According to Statistics Netherlands (CBS), in 2009, more than €40 billion of the amount allocated to the construction industry was spent on maintenance and rehabilitation. This explains how self-healing materials can be beneficial to an economy since a small reduction in maintenance might save large amounts of money (van der Zwaag, 2007). It is expected that periods between road maintenance operations will extend when using self-healing asphalt, leading eventually to reducing traffic jam costs and traffic hindrance.

Rijkswaterstaat (2010), found that the average annual costs for major maintenance of 74km² of asphalt pavement in the Netherlands are expected to be 180 million euros. The study showed that by extending the life span of the asphalt pavement by 25 percent, which means increasing the average from 12 years to 15 years, the annual costs for major maintenance can be decreased by 35-50 million euros. In addition, by extending the life span from 12 years to an average of 18 years (by 50 percent), the yearly savings on major maintenance will be as much as 60-80 million euros. The additional costs for applying self-healing asphalt were not considered in these amounts. Other benefits, which can be considered non-financial, include customer satisfaction, with no or little defect appearance and no interruption due to maintenance, there is a decrease in environmental effects as well (van der Zwaag, 2007).

According to Rijkswaterstaat (2010), the traffic jam costs, expressed as capitalised hours of time loss of people waiting or taking alternative routes, were estimated in 2008 in the Netherlands to be 2.8 billion euros, only four percent of which or about 110 million euros were due to road maintenance. The study concluded that the number of traffic jams would decrease proportionally with the length of the maintenance period. Therefore, a life span extension for self-healing asphalt of 25 percent from 12 years on average to 15 years would render 22 million euros less traffic jam costs. At a life span extension of 50 percent, i.e. from 12 years on average to 18 years, the social traffic jam costs would be reduced by 37 million euros. Again, the additional costs for applying self-healing asphalt were not considered. Table 2.1 presents the annual savings of maintenance expenditure that can be achieved using asphalt with extended life span, according to Rijkswaterstaat (2010).

Table 2.1: Benefit of extending the life span of asphalt pavement.

Savings	% Annual savings (M€/year)		
	Original pavement life	25% life extension	50% life extension
Social savings	-	20	40
Maintenance savings	-	45	70
Net savings	-	50	90

To find the net savings, the additional costs for self-healing asphalt have to be subtracted. A 100 percent (or 200 percent) higher bitumen price results in 8 (or 16) million euros as additional annual costs. So even if the price of self-healing bitumen was double the price of normal bitumen, the Netherlands would save approximately 90 million euros annually by investing in self-healing asphalt with a 50 percent extension of life span. Self-evidently, the principles of the example from the Netherlands could be applied all over the world.

2.6 Asphalt self-healing

Asphalt can be considered as a self-healing material due to bitumen's composite nature and its material properties. Qiu (2012b) found that the self-healing ability of the asphalt binder is a viscosity based process, which works on stopping the growth of cracks and restoring the asphalt properties. Bhasin et al. (2009) call the location of the crack surface tip as the fracture/healing zone, where cracks gradually develop during loading and heal when the load is removed. Figure 2.13 shows the crack propagation process in bitumen and the fracture/healing process zone. The asphalt self-healing process is complex due to its dependence on various conditions and demands certain climatic and physical circumstances including temperature, time, bitumen viscosity and confinement (Qiu et al., 2012b).

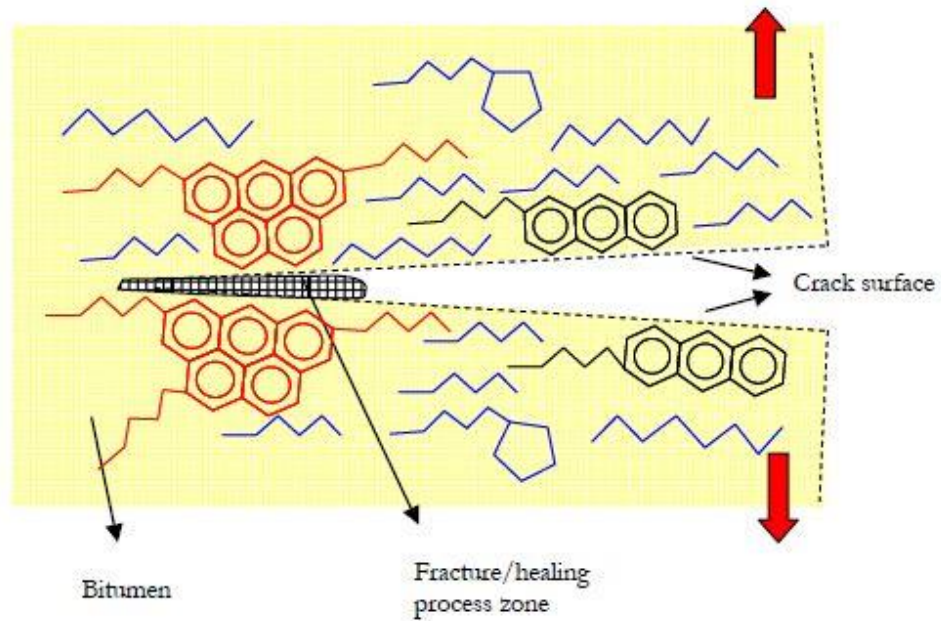


Figure 2.13: Crack propagation process and the fracture/healing process of bitumen (Bhasin et al., 2009).

Bitumen critical fracture always happens at low temperature, while binder workability can be restored when subject to a higher temperature. The bitumen can easily flow and its molecules can remix because of its viscous characteristic (Thom, 2008). At temperatures ranging from 30°C to 70°C, bitumen starts to behave like a Newtonian fluid. At higher temperatures, the viscosity begins to decrease leading to crack propagation in the asphalt, in a sort of capillary flow. Figure 2.14 shows how the healing levels in the bitumen are affected by temperature in a function of time. The self-healing of cracks in asphalt is highly dependent on the capillary flow of the rejuvenator and bitumen through the crack. When bitumen behaves like a Newtonian fluid, its viscosity can be predicted empirically by using the Arrhenius equation. This equation is used to model variation of diffusion coefficients with temperature depending on the activation energy for flow and viscosity of the material at a reference temperature, as follows:

$$k = A e^{-E_a/(k_B T)} \quad 2-2$$

where: k is the rate constant of diffusion, T is the absolute temperature (Kelvins), A is the pre-exponential factor (the prefactor), E_a is the activation energy, and K_B is the Boltzmann constant.

This behaviour of asphalt binder could happen naturally, in hot climates or in summer for instance. Also, it can be initiated artificially by induction heating, which is illustrated in section 2.7.1. As a result, García et al. (2012a) demonstrated that asphalt can be classified as a thermally induced self-healing material. This property of self-healing can be proved during fatigue tests, where enhanced fatigue patterns of asphalt can be found at higher temperatures (Thom, 2008).

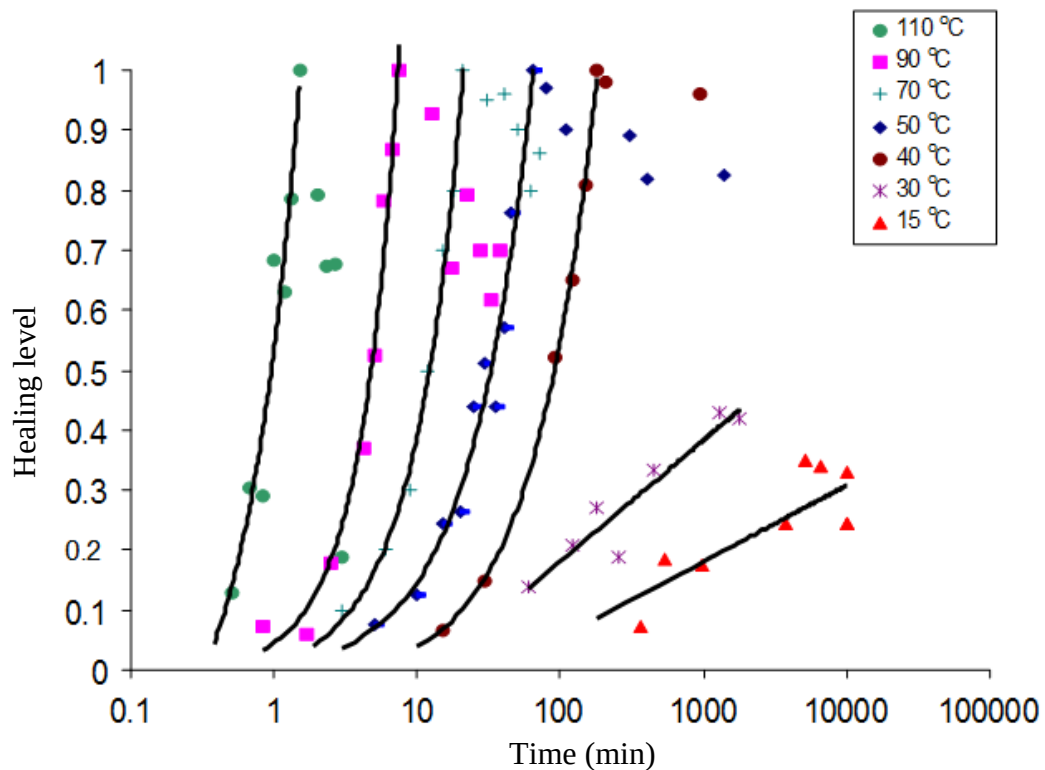


Figure 2.14: Healing levels of asphalt bitumen at different temperatures (García et al., 2012a).

Research by García (2012) proved how self-healing is also dependent on the loading rest experienced; with enough time given, the level of flow of the bitumen will increase. The rest time given is important for molecule remixing, the higher the period the greater the self-healing result. This was investigated by Little et al. (2001), who implemented a conventional flexural bending experiment on bitumen beams, with rest periods of 24 hours. The results indicated that there is an increase in the fatigue life by over than 100%, depending on the bitumen used. In reality, it is unlikely for a road pavement to have enough rest period. Therefore, it is essential to develop a fast self-healing process, which allows cracks to heal

and disappear with considerably reduced rest period. Figure 2.15 shows the process of healing at different loading rest periods.

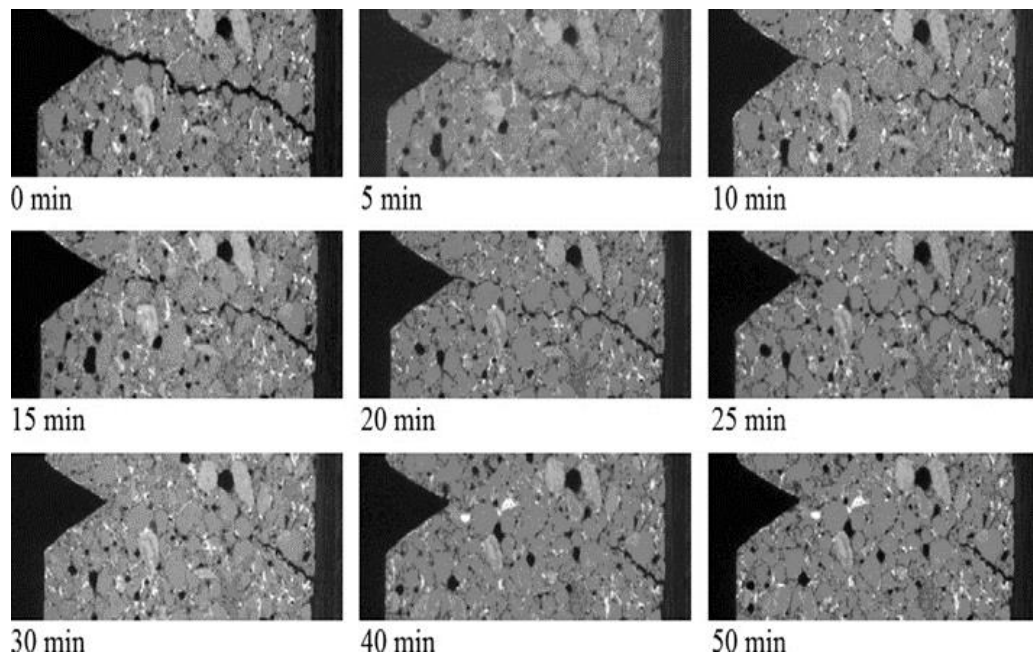


Figure 2.15: CT-Scan images of a beam studied by (García et al., 2012a).

Wool and O’connor (1981) proposed a model of the healing mechanism of asphalt, which suggests that there are three critical stages in the self-healing process. The first one is called wetting. This term refers to the contact points between two cracked surfaces. The wetting rate is affected by the mechanical properties of the material, such as residual confining stress, visco-elastic properties and brittleness of bitumen, as well as the bitumen’s surface free energy (Bhasin et al., 2009). Asphalt binder with higher free surface energy can have strong intermolecular forces of interaction between the crack faces, and will, therefore, wet at a quicker rate (Bommavaram, 2008). As long as a region is completely wet, there will be an instantaneous limited strength recovery in the crack. This might result from the cohesive effect of the crack faces, which is also dependent on the surface free energy. Asphalt binder with higher surface free energy and, therefore, a rising level of cohesion will enable higher instantaneous strength recovery (Bommavaram, 2008). Qiu (2012b) presents in a schematic diagram (Figure 2.16) the healing mechanism of bitumen.

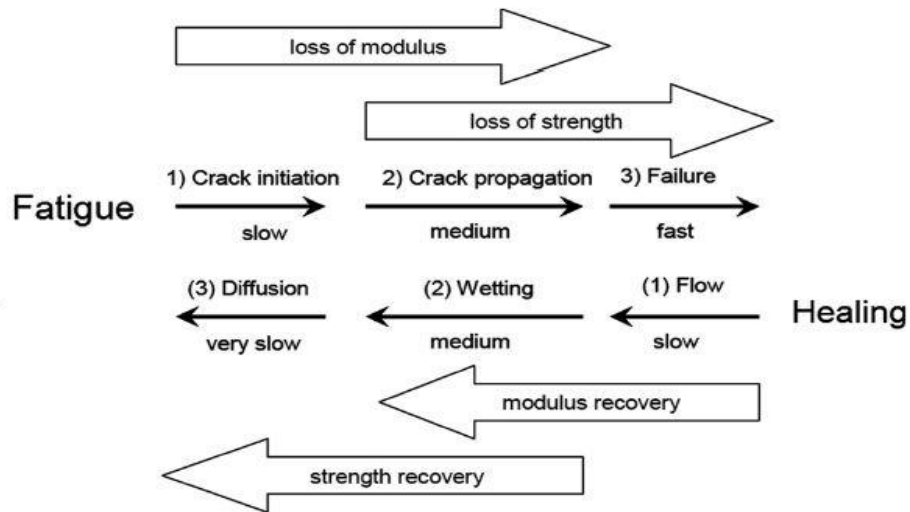


Figure 2.16: A schematic diagram of the healing mechanism in bitumen (Qiu, 2012b).

Based on the fact that asphalt self-healing is triggered by the diffusion mechanism of asphalt molecules, Shen et al. (2016) investigated the effect of crack width on asphalt self-healing from both microscopic and macroscopic perspectives. They developed a model of the asphalt system under various temperatures and different crack sizes to describe the healing behaviour of asphalt with time. Results show that crack width is an important factor that can affect the healing capability of asphalt as it affects the speed and amount of molecule diffusivity of asphalt binder. They found that for the same crack length, asphalt heals faster when the width of the crack is narrower. In this research, as the focus is on the effect of capsules on asphalt self-healing, crack width will not be considered as the main objective and only hairline cracks (narrow) will be studied.

Tang et al. (2016) investigated the optimal self-healing temperature of asphalt binders in a study performed on fatigue-healing-fatigue tests for both fresh and aged bitumen. The fatigue-damaged binders were heated to different temperatures. The study found that the ideal healing temperatures for base asphalt binders are their softening points, which are transition temperatures of Newtonian behaviour as well. In addition, they find out that ageing of the binder increased its optimal self-healing temperature, as its softening point temperature increased with ageing. Furthermore, their results showed that the healing level of the binders started to decrease slightly when the temperature exceeded their softening

point. Based on this, overheating could affect a real asphalt mixture and could result in decreasing the healing level due to drainage of bitumen.

The long term strength recovery of the original crack surface rises with time. Theoretically, damaged bitumen is able to regain its original strength if it has sufficient time. This is known as intrinsic healing, which is normally controlled by the diffusivity and random movement of molecules from one face of the crack to the other (Little and Bhasin, 2007). Qiu (2012a) defines self-healing of asphalt as the ability to recover the mechanical properties. Generally, the healing process consists of two main stages, namely the crack closure and the strength gain. Figure 2.17 explains these stages of self-healing.

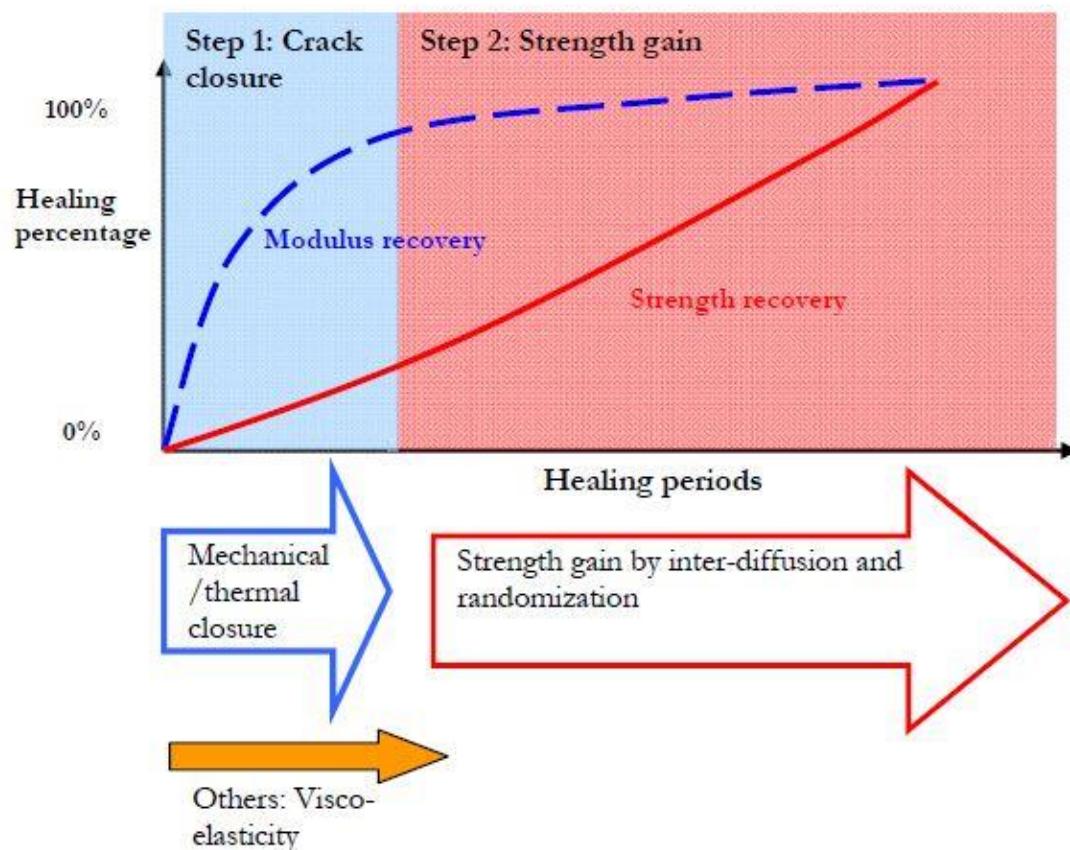


Figure 2.17: A schematic diagram of the conceptual self-healing mechanism (Qiu, 2012a).

In this way, a material with higher thermally induced diffusion coefficient and wetting could increase the mechanical recovery and promote self-healing. According to Tang et al. (2016),

the minimum healing time needed for full healing of asphalt binder depends on the binder type (penetration grade) and the healing temperature. They found that the healing time decreased with higher healing temperatures and increased with higher penetration grade bitumen.

Sun et al. (2017) studied the effect of chemical composition and structure on the ability of asphalt binder to self-heal fatigue cracks by using four different penetration grades of asphalt binders characterised by Fourier Transform Infrared spectrometry (FTIR). They investigated the self-healing abilities of asphalt binders by fatigue-rest-fatigue in the Dynamic Shear Rheometer (DSR) test. It was found that the chemical composition of bitumen and its molecular structure play a significant role in determining its self-healing ability. In this way, binders with higher ratio of small molecule content to large molecule content have a greater self-healing ability. The self-healing ability could increase greatly if the chemical structure of asphalt binder is combined with a higher aromatics content.

2.6.1 Rejuvenator diffusion

In order to restore its rheological properties, rejuvenators, which are recycling agents, are mixed with aged bitumen. Roberts et al. (1996) state that rejuvenator helps restore the physical and chemical properties of the bitumen because of its high proportion of maltene constituents (naphthenic or polar aromatic fractions), which help re-balance the chemical composition of the aged bitumen that lost its maltenes during construction and service (Terrel et al., 1989). Since rejuvenators are required to contain a high proportion of aromatics, which are necessary to keep the asphaltenes dispersed, they should, as well, have a low saturates content (Bullin et al., 1997).

The effectiveness of a rejuvenator is dependent on the uniform dispersion of the rejuvenator within the aged bitumen mixture and the diffusion of the rejuvenator into the aged bitumen binding the aggregate. Lee et al. (1983) investigated the dispersion of rejuvenators within aged mixtures at several asphalt plants. They detected, visually, the dyes that had been mixed with the rejuvenators, and they drew the conclusion that uniform distribution of rejuvenators could be achieved by mechanical mixing at the asphalt plants.

According to Carpenter and Wolosick (1980), the diffusion of a rejuvenator into aged bitumen includes the following four steps:

- 1- The rejuvenator causes a very low viscosity of the bitumen layer surrounding the aggregate particle.
- 2- The rejuvenator starts to penetrate into the aged bitumen layer; this process decreases the amount of the rejuvenator surrounding the aggregate and leads to softening of the aged bitumen.
- 3- The penetration of the rejuvenator continues within the bitumen layers until the viscosity of the inner layer decreases and this will gradually increase the viscosity of the outer layer as the rejuvenator leaves it.
- 4- After a certain time, a balance will be reached in almost all the healed bitumen film.

Carpenter and Wolosick (1980) verified this concept of diffusion through a multistage extraction technique in which the inner and outer layers of the rejuvenated bitumen film were extracted separately at specified time intervals. The researchers found that the rejuvenator starts to diffuse into the aged bitumen during mixing and continues after construction through a period of time during pavement service life. This conclusion was later confirmed by Noureldin and Wood (1987) and Huang et al. (2005). Karlsson and Isacsson (2003) suggested that the diffusion rate can be controlled by the viscosity of the maltene phase instead of the viscosity of the aged bitumen as a whole. In an earlier study, Oliver (1975) assumed that there is a possibility to accelerate the diffusion by adding diluent oil fractions and/or increasing the mixing and compaction temperatures. Figure 2.18 shows the penetration values at 25°C for the inner and outer layers as a function of time after mixing. The two layers seem to approach the same consistency, which is the same or close to that of a mixture of the same rejuvenator and bitumen binder contents.

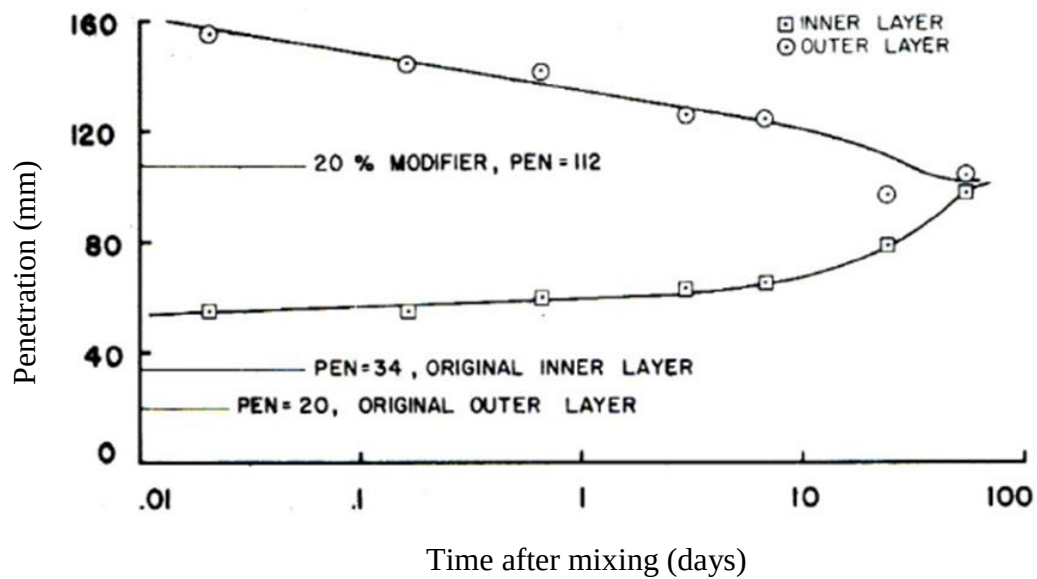


Figure 2.18: Penetration of the outer and inner layers during diffusion (Carpenter and Wolosick, 1980).

Bommavaram (2008) stated the three essential properties of asphalt binder that control the rate and magnitude of self-healing to be the surface free energy, self-diffusion and randomisation of the molecules. Wetting and initial strength gain are highly dependent on the surface free energy, whilst the properties of the bitumen diffusivity determine their long term healing ability (Bhasin et al., 2009). The total strength recovery of asphalt cracking is, therefore, dependent on rate of wetting, binder cohesion and the internal diffusion. Wu et al. (2008) suggested a model to state five stages of crack healing with respect to surface rearrangement, surface approach, wetting, molecule diffusion and randomisation, as shown in Figure 2.19.

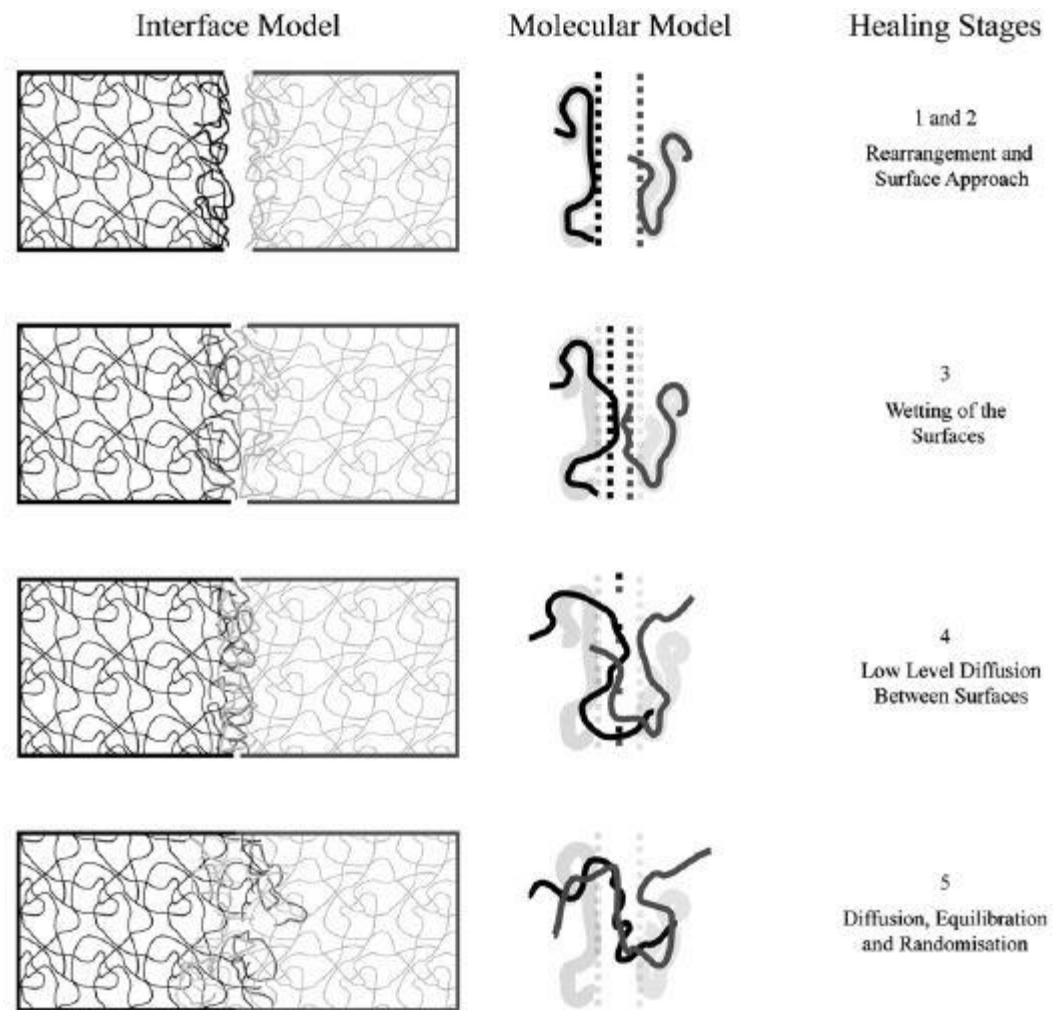


Figure 2.19: Schematic diagram illustrating the steps of crack healing (Wu et al., 2008).

A full crack closure does not necessarily indicate that the original strength has been fully recovered. This is because of the possibility that some micro cracks and air bubbles are still within the bitumen. In order to fully regain the strength of the material, longer healing time might be necessary. The viscosity of the asphalt binder governs the healing process at this stage (Qiu et al., 2012a). Understanding the rejuvenator diffusion within asphalt mixtures is vital to optimise the type and amount of rejuvenators that are used in asphalt mixtures to improve the performance in an economic and safe way.

The Fourier Transform Infrared Spectrum (FTIR) test is used to indicate the diffusion of a rejuvenator by tracking the chemical changes in the bitumen specimen containing a rejuvenator. The amount of the rejuvenator and the time given to diffuse will definitely affect

the results of the test. The FTIR spectrum measurements can be variable depending on the average number of scans, the wavenumber range and the resolution of the wavenumber.

There are two methods used for index calculation of the FTIR (Marsac et al., 2014):

- RILEM method: this method was first used for area calculation of the carbonyl band by the round robin test (RRT) organised by RILEM. It is called, as well, the area method, fixes area limits then a baseline drawn between the values at these limits as shown in Figure 2.20. In this method, only the positive areas above the base line are taken into account.

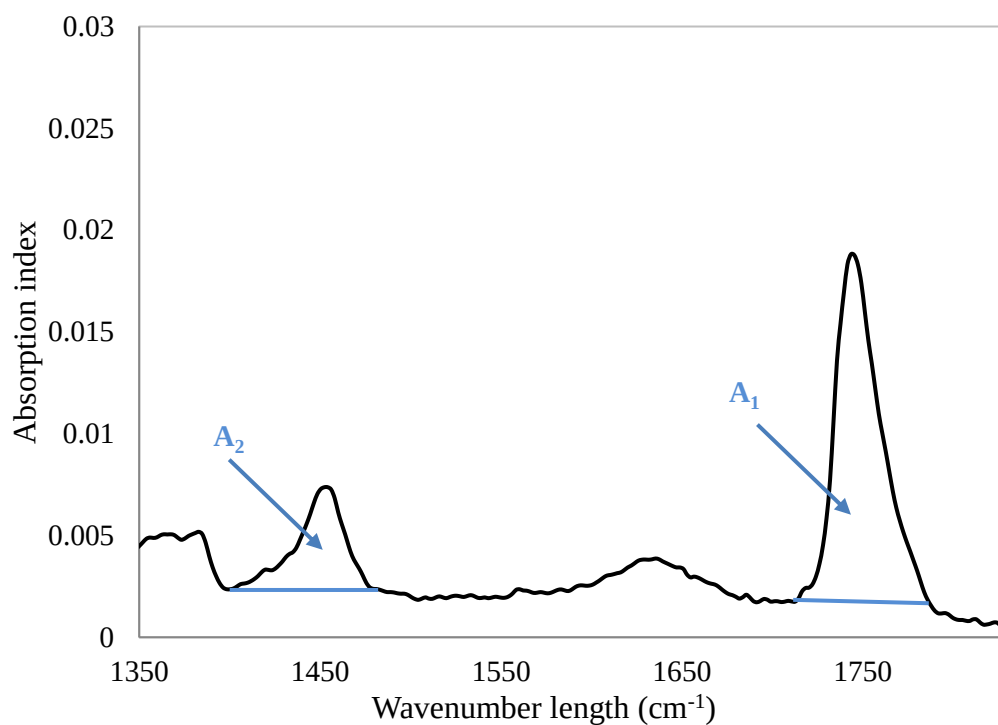


Figure 2.20: Determination of the areas for the FTIR index calculation.

- BRCC method (A1700 and H1700): this method is focused on determining the bitumen oxidation from the carbonyl oxidation at the peak 1700cm⁻¹, which is usually to measure bitumen ageing. In this research, the peaks of interest are between 1700-1800cm⁻¹, which is the aromatic range. Therefore, the area method will be appropriate here.

2.6.2 Capillary flow

A sufficiently high temperature makes bitumen act as a Newtonian fluid, which means a differential pressure will develop at the contact points of a crack. This differential pressure causes capillary flow, which is the process that leads to crack healing. The healing process will, therefore, happen faster in deep cracks, as there will be higher pressure due to gravity. As the increased temperature makes the viscosity of the bitumen reduces, the rate of capillary flow increases. This is due to its direct relation to the viscosity of the bitumen. Figure 2.21 shows an experiment performed by García et al. (2012b), which was used to obtain the activation energy for capillary flow.

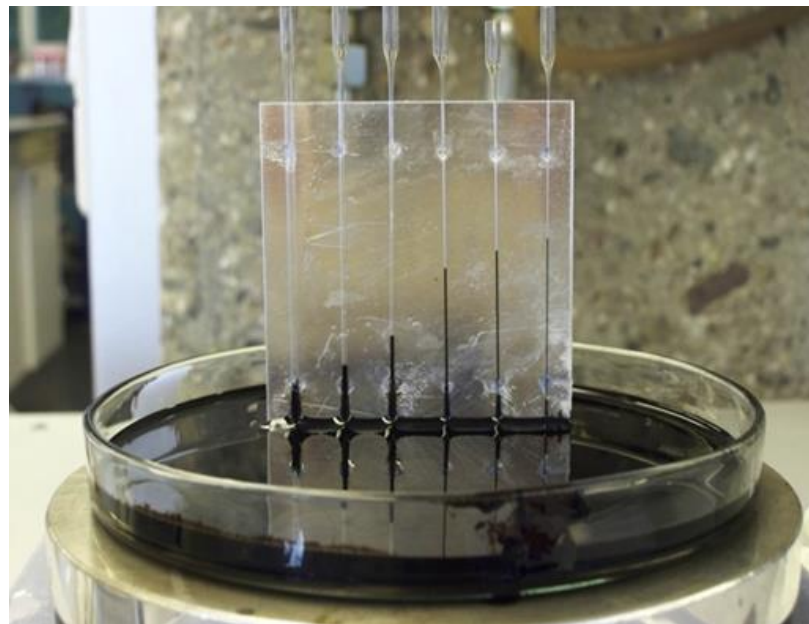


Figure 2.21: Capillary flow experiment.

2.6.3 Activation energy

The Arrhenius equation (mentioned in Section 2.6) is used to estimate the healing time required to obtain particular healing level of asphalt samples at different healing temperatures. In this way, the self-healing ability of the bitumen can be defined by its activation energy, which may change depending on the age and type of the bitumen used. The main parameters that considerably influence asphalt self-healing are the activation energy for bitumen to flow and the capillary flow. García et al. (2012b) indicate that the activation energy for bitumen flow is higher than the activation energy for asphalt self-

healing. This implies that the flow of bitumen alone does not have a high influence on asphalt self-healing.

According to Salomon and Zhai (2002), the range of activation energy for bitumen flow is between 44kJ/mol and 90kJ/mol, as it depends on the asphalt type, service life and additives. Salomon and Zhai (2002) stated that this range is highly fluctuated in other, similar research, which means more research is required to obtain accurate range of activation energy. In addition, they found that when the capillary diameter increases, the activation energy of bitumen flow decreases. The capillary flow, on the other hand, is possibly the main factor influencing asphalt self-healing as results show that the activation energy for capillary flow is similar to the activation energy for asphalt self-healing. However, it is difficult to compare accurately and directly between these activation energies. This may result from the fact that the contact angle between the bitumen and the capillary tube is not similar to that between bitumen and asphalt (García et al., 2012b).

2.6.4 Cooking oil as a rejuvenating agent

Cooking oil is not the only kitchen material that has been used in civil engineering, and possibly not the last. Yang et al. (2010) presented a systematic study using a mortar of sticky rice with lime to restore ancient buildings. They prepared lime mortar with varying sticky rice contents and tested their physical properties and mechanical strength, and they found that the compatibility of lime mortar is significantly improved by the introduction of sticky rice. Therefore, they suggested that sticky rice-lime mortar is suitable for repairing mortar in ancient masonry. Old writings reveal that sticky-rice mortar was used in China as far back for 1500 years ago, and probably longer.

The need for a cheap and sustainable alternative to rejuvenate bitumen raised the possibility of using waste cooking oil (WCO), which is a waste material from the food industry that pollutes landfills and rivers, as an alternative natural rejuvenating agent for aged bitumen to make it resemble the condition of the original bitumen (Zargar et al., 2012).

The possibility of using a higher percentage of RAP (up to 80%) in the pavement can be given by using a rejuvenator (Shen et al., 2007). Because of the high demand for rejuvenators recently, the application of waste products as rejuvenating agents, such as recycled motor oil

(RO), have also been investigated. Some researchers applied RO and other rejuvenators in recycled HMA mixture. The results indicate that by applying RO as a rejuvenating agent the permanent deformation is delayed compared to a sample of the original bitumen. Additionally, Romera et al. (2006) reported that a mixture of 80% aged bitumen with 20% rejuvenator (recycled RO) totally obtained from waste materials, can compete with new 60/70 bitumen with respect to quality.

Zargar et al. (2012) assessed the susceptibility of virgin bitumen and aged bitumen by means of their ageing index, which is defined as the ratio of a chemical or physical parameter of the binder before and after the ageing process. They observed from the results of softening point, penetration and viscosity that rejuvenated bitumen had fewer tendencies to ageing than the original bitumen. Additionally, they measured the chemical changes of rejuvenated and virgin bitumen with respect to the asphaltenes and asphalt volatility ratio. The results indicated that the changes in the asphaltenes are higher in virgin bitumen compared to the rejuvenated bitumen, after short-term ageing. The same behaviour was obtained with respect to asphalt volatility, where the virgin bitumen had a tendency to evaporate. This can be related to the lower volatility susceptibility of bio oil (Le Guern et al., 2010), which is possibly related to its high percentage of saturated hydrocarbons.

According to García et al. (2010a), rejuvenators are classified into two types: rejuvenating agents (highly aromatic) and softening agents (lower viscosity), and can restore the original proportions of asphaltenes to maltenes in oxidised (aged) bitumen. Therefore, they can soften the aged binder and create a broad-spectrum rejuvenation that replenishes the volatiles again and disperses oils while improving adhesion (Hollaran et al., 2006). Asli et al. (2012) and Zargar et al. (2012) found that cooking oil is a highly aromatic material that can rejuvenate aged asphalt binder efficiently. The self-healing ability of asphalt binders is more sensitive to the content of aromatics in the rejuvenators. In this way, a higher content of aromatics in the rejuvenator will result in better asphalt self-healing (Sun et al., 2016, Sun et al., 2017).

Ji et al. (2016) studied the optimum amount of vegetable cooking oil that can be used as asphalt rejuvenator to recover aged bitumen without affecting its desired physical and mechanical properties. The test was performed with five different cooking oil contents to recover aged asphalt binder. The physical property tests showed that the use of cooking oil

as a rejuvenator can successfully recover aged asphalt binder, and can more effectively reduce the binder hardness and improve its plasticity. They found that the optimum cooking oil content that can be used as a rejuvenator should not exceed the range 6-8% by weight of the binder. Based on this, vegetable cooking oil is used in this research as an asphalt self-healing agent with contents within the allowable range.

2.7 Engineered self-healing techniques

The concept of self-healing materials was used over 2000 years ago by the Romans, they used lime to dissolve in rainwater in order to seep into cracks and fill them when the water evaporated leading to healing taking place. Self-healing materials are expected to remain reliable and durable throughout the pavement service life. The multiple use of a material will degrade its performance due to fatigue, which leads to the initiation of micro cracking. As fatigue worsens, the cracks will propagate resulting in failure of the material. Self-healing materials have built in the ability to repair themselves with time (Hager et al., 2010).

Nature has inspired the concept of modern self-healing materials. For example, the ability of trees to repair cracks on their branches or the ability of human bones and skin to heal and repair themselves when subjected to an injury. The difference is that organs are able to sense the damaged then repair themselves while other materials cannot sense damage, such as cracks in buildings and highways. White et al. (2001) state that the first modern self-healing was seen in the USA in 2000, where microcapsules containing a healing agent were manufactured and embedded in a polymeric material. The results of that experiment showed that the cracked surfaces had melted and the material had maintained about 75% of its strength. Since then, self-healing materials have been developed and new technologies have been employed, such as self-healing polymers, metals, concretes and asphalts.

According to van der Zwaag (2007), the self-healing process must be a combination of damage detection and damage repair, where the material itself has to identify damage in order to repair it. In this type of autonomous self-healing material, some of their molecules are able to move and fill the cracks. The need for reliable and durable materials has driven the construction industry to search for appropriate self-healing materials to be used in structures and places that are difficult to access for normal maintenance.

In asphalt pavement, the concept of natural self-healing has been known about since Bazin and Saunier (1967) studied the self-healing process of asphalt mixtures after fatigue damage and their ability to recover after a rest period. This study was one of the pioneers investigating the phenomenon, although tests were carried out in a laboratory in different circumstances from those on roads. The concept of healing after a rest period, with respect to the recovery of material properties, has been further investigated by many other researchers. Raithby and Sterling (1970) developed multiple attempts to characterise the self-healing mechanism from a molecular level to the whole pavement level and to model the behaviour of asphalt self-healing based on experimental work. However, these mechanisms are still scarcely understood. Figure 2.22 shows how the natural self-healing phenomenon takes place in an asphalt sample.

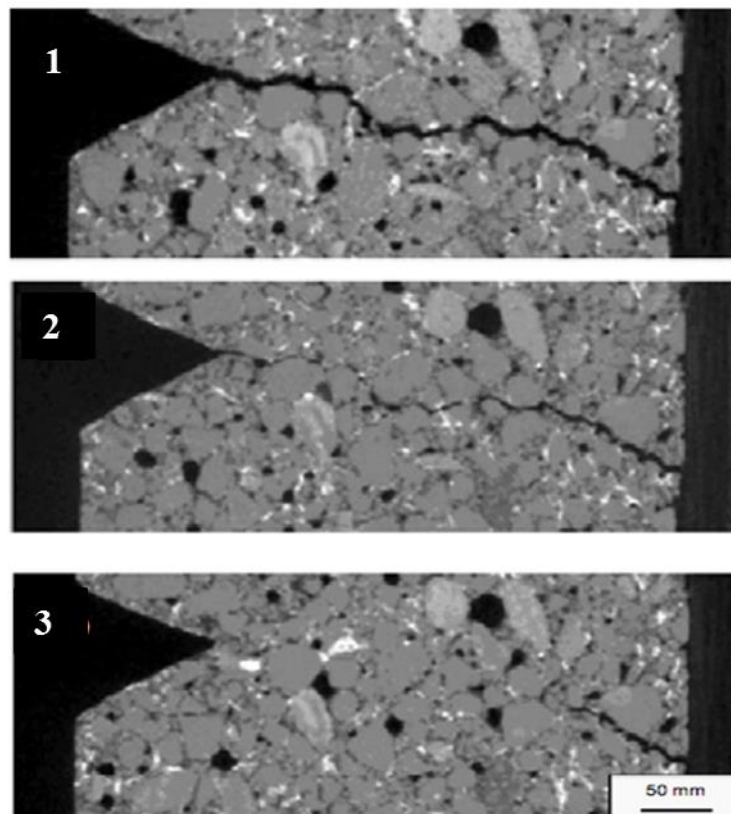


Figure 2.22: Natural self-healing in asphalt pavements accelerated by temperature rises (García et al., 2013).

Boyer (2000) investigated the use of rejuvenators as a new pavement maintenance technique to remedy fatigue cracks. As mentioned earlier, these rejuvenators are applied on the

pavement surface, and they are expected to extend the life of a pavement for few years after their application. However, they are only effective a few centimetres down from the pavement surface, and may not have an influence on deeply rooted cracks in the pavement layer. Chiu and Lee (2006) conducted an experiment to confirm this by using three different percentages of rejuvenators on a 12 year old pavement section to assess their effectiveness. It was found that none of the three rejuvenators had penetrated into the pavement more than two centimetres despite the high air void content of the pavement, which was almost 10%.

Recently, two novel techniques have been developed to improve the healing rate of asphalt pavements without the side effects that have been discussed above of using rejuvenators or sealants. The two techniques are: a passive self-healing mechanism as rejuvenators are encapsulated and embedded within the asphalt mix; and an active self-healing mechanism where heat induction is used to stimulate the healing process.

2.7.1 Self-healing by induction heating

As previously mentioned, temperature and viscosity have a considerable influence on the healing process of asphalt and based on this principle, induction heating to extend pavement life has been developed. The asphalt must provide electrical conduction by using fibres or fillers, which must be added to the asphalt mixture during the production stage. García et al. (2011c) have researched the effectiveness of fibres and fillers; they stated that fibres are likely to be more effective than fillers in heat generation. They found that the amount of fibres used should be optimised with respect to the proportion of sand/bitumen in the mixture. Therefore, the conductivity of the material could be optimised. The optimum level of heat generation was determined for each mixture by increasing the volume of added fibres until the percolation threshold was reached. This level was then considered as the optimum. In this way, the induction energy can be applied very fast to the damaged asphalt. This energy is usually supplied by an induction heating device. This process is supposed to increase the level of self-healing, and melt the cracks. Figure 2.23 shows how the cracks close due to the effect of fibres and induction heating.

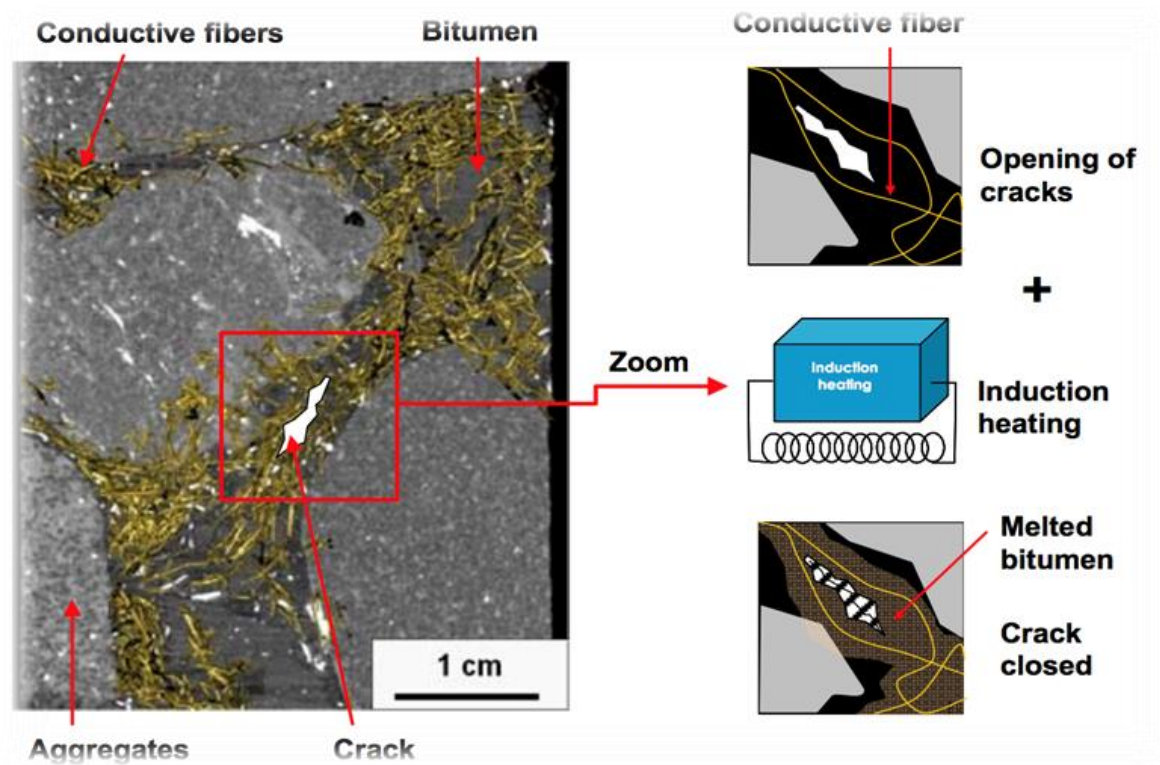


Figure 2.23: The mechanism of induction heating(García et al., 2011c).

Although this method of performing self-healing seems straightforward and effective, there are still practical issues requiring further research before induction heating can become a worldwide industrial process. Since the test samples in the laboratory are relatively small, the induction heating devices can be small too, which will not be the case in the field, where much larger devices must be used. This may not be economic and can cause road disruption when applied, eliminating one of the main advantages of the self-healing technique. It is necessary as well, to determine the time for heating and cooling the asphalt pavement, in order to set the speed at which the induction heating device is moved (García et al., 2012a). Images of the induction heating devices that are used in the laboratory and in the field are shown in Figure 2.24.

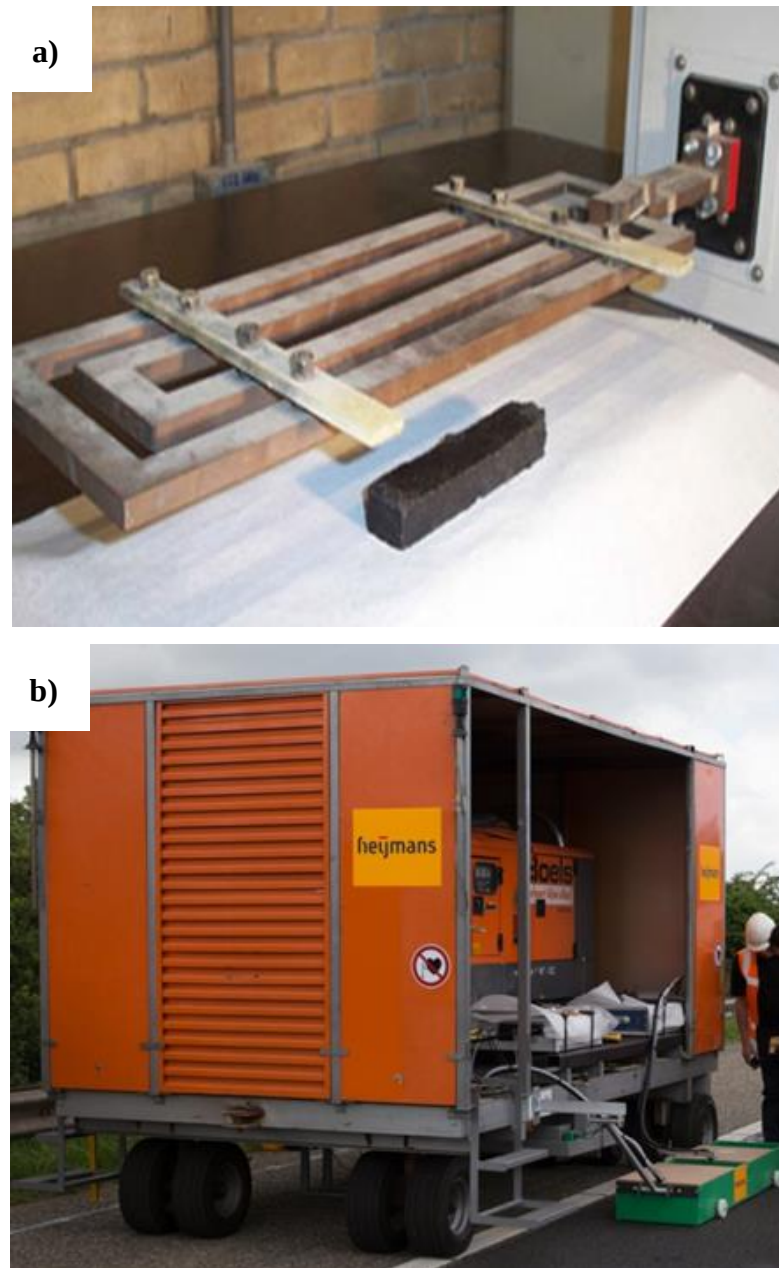


Figure 2.24: Induction heating device (García et al., 2011b), (a) laboratory induction heating device and (b) induction heating generator installed in a test truck.

Induction heating should be applied carefully so that the asphalt will not be heated too much since the bitumen might melt and lose its material properties. The electrical frequency of heating and cooling times must be considered as well. Heating time reduces considerably when using a higher frequency, which can be useful when applying heat to an in-service road. However, the high frequency applies heat to shallow depths only, which, as for

rejuvenators, indicates that self-healing by induction heating could be limited to the uppermost part of the asphalt pavement.

Liu et al. (2017) compared the induction heating behaviours of warm mix asphalt with hot mix asphalt through the damage-healing-damage tests. They used steel fibres to make the asphalt mixture conductive, then studied the induction heating characteristics and self-healing ratios of both warm and hot mix asphalt mixtures. The results showed that the type of mix, whether it is warm or hot, does not affect the induction heating speed. In addition, they found that induction heating of asphalt mixtures showed strong heating gradient characteristics, as the top parts of the samples could be heated much faster than their lower parts, which can result in a higher healing ratio in the top parts of the sample.

2.7.2 Self-healing by encapsulated rejuvenators

To overcome the shortcomings of spraying rejuvenators on an asphalt surface, they can be encapsulated and added to the asphalt mixture during the production process. The work includes encapsulating the rejuvenators and mixing them with the asphalt materials as part of the coarse or fine aggregate or as part of the bitumen.

The idea is that, when the cracks occur, some of the capsules in contact will produce oil, which can diffuse out within the asphalt, restoring the properties of the bitumen, which means enhancing the natural healing ability, as illustrated in Figure 2.25. This process is supposed to repair or considerably reduce the cracks and prevent new ones from propagating, in a completely autonomous process. The basic assumption is that when fatigue and/or thermal cracks apply a stress on the capsules that is higher than their capacity, the capsules will break. This will permit the rejuvenator to diffuse out through the asphalt binder, decreasing its stiffness and restoring its original chemical balance (García et al., 2010b, García et al., 2011a). According to García et al. (2010b), capsules with average mechanical strength of 14N have survived the mixing process. This means that capsules within this range of mechanical strength are the preferred ones to survive mixing and still break under loading.

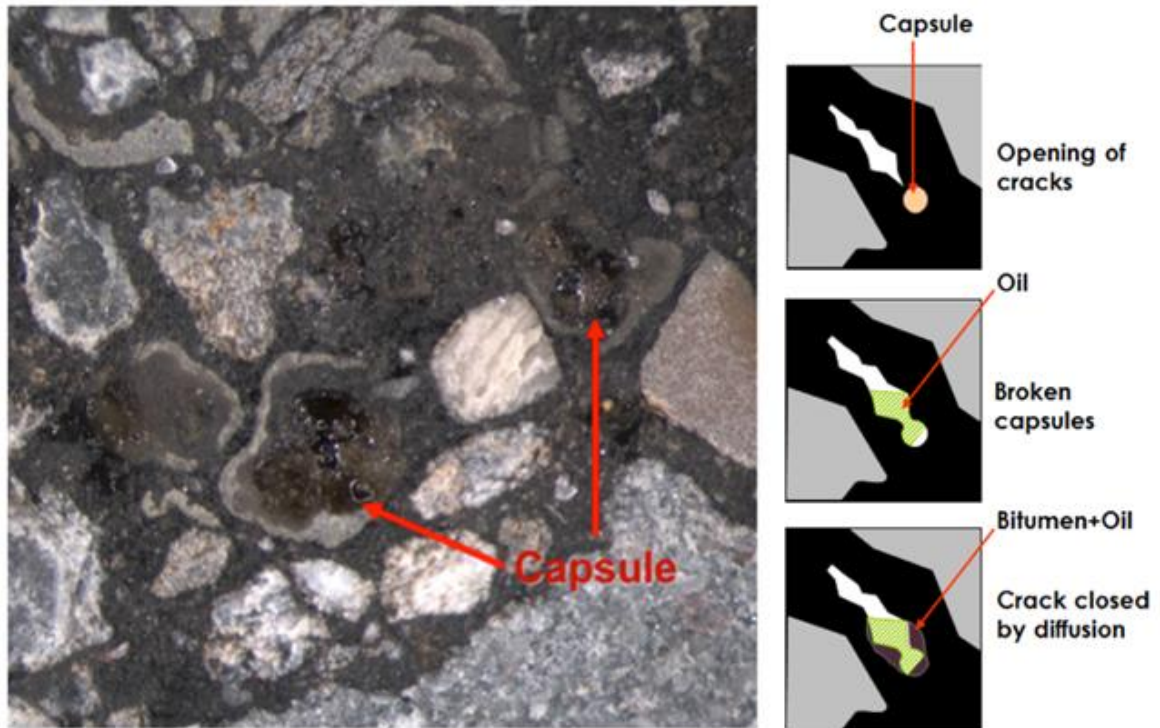


Figure 2.25: Encapsulated rejuvenator healing mechanism (García et al., 2010b).

As previously mentioned, White et al. (2001) were the first to investigate the use of microcapsules containing healing agents for the self-healing process of structural polymers. They produced microcapsules encapsulating a healing agent, which could be released into the polymer when the cracks occur, see Figure 2.26. The healing agent polymerised after its release when it came into contact with the embedded catalysts resulting in bonding of crack damaged surfaces. Results obtained from using the microcapsules in self-healing indicated that they had successfully restored the polymer to as much as 75% of its strength, increasing the lifespan of the structure.

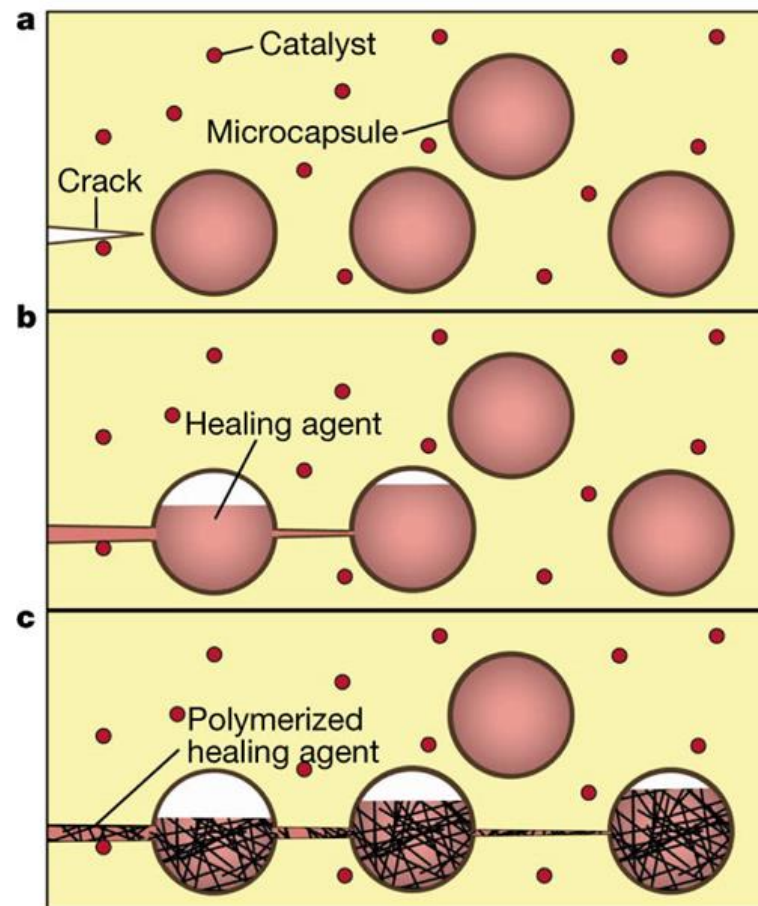


Figure 2.26: Microcapsules healing mechanism (White et al., 2001).

The results obtained by White et al. (2001) opened the possibility for further investigation to use microcapsules for self-healing in other materials, such as asphalt pavements. In this way, two types of encapsulated rejuvenators have been manufactured for use in asphalt self-healing: capsules consisting of an epoxy-cement shell with sizes ranging from 1.5-5 mm in diameter (García et al., 2010b) as in Figure 2.27; also, microcapsules consisting of a shell of methanol-melamine-formaldehyde (MMF) prepolymer with sizes of about 23.5 μ m in diameter (Su et al., 2013b), see Figure 2.28.

The size of the capsules supposedly indicates the amount of healing agent that is contained within them; hence capsules made of epoxy-cement shells have a greater amount of healing agent. The capsules with an epoxy-cement shell are easily produced by combining the materials manually, while the MMF prepolymer microcapsules are manufactured by using a complex polymerisation technique as a sequence of preparing the chemical structure of the

polymer, two steps of cross-linking the polymer to contain the rejuvenator inside, then making the microstructure of the microcapsules (Su and Schlangen, 2012).

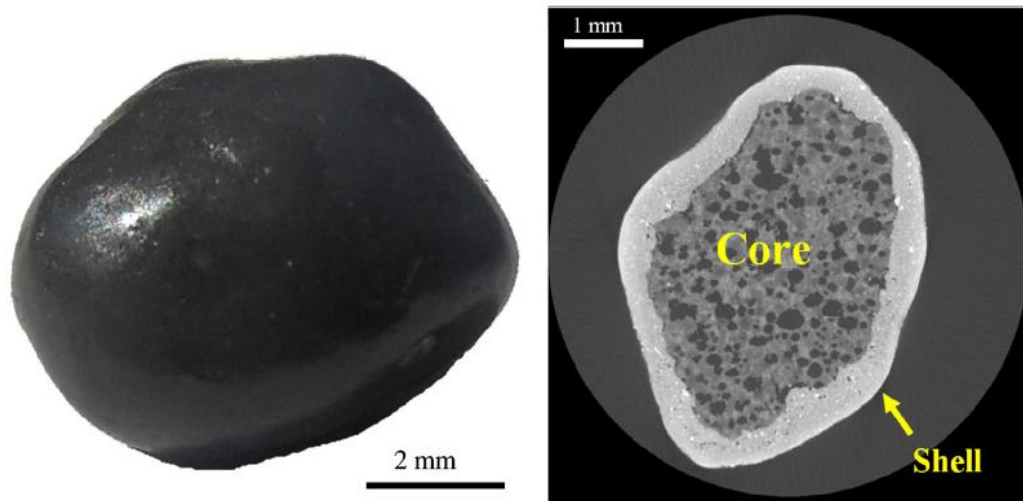


Figure 2.27: External shape of epoxy-cement capsule and its internal configuration (Garcia et al., 2015).

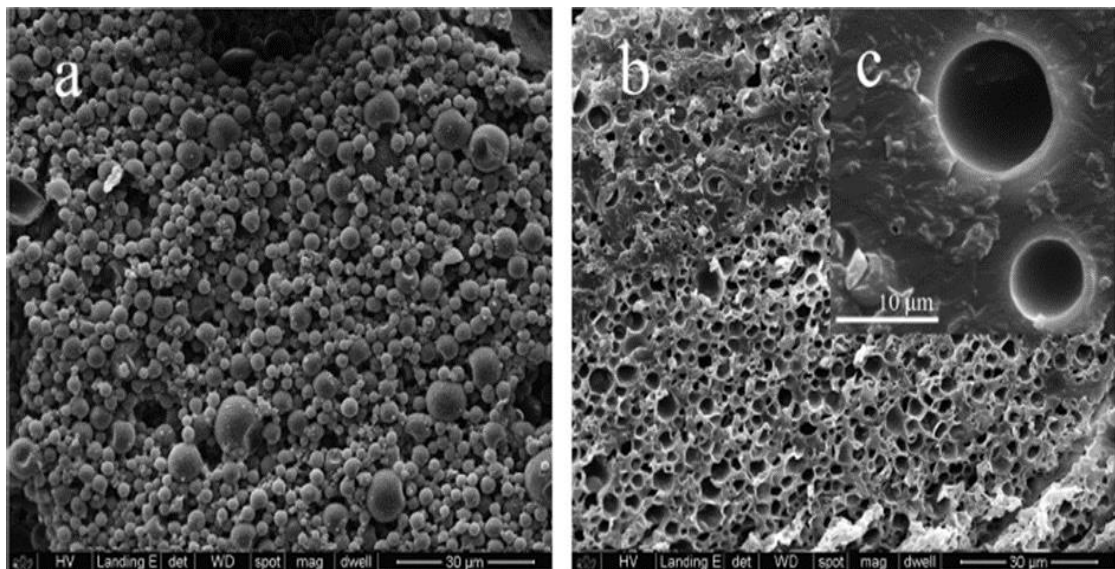


Figure 2.28: SEM morphologies of microcapsules; a) dried microcapsules, b) the cross-section of the microcapsule composite and c) the shell thickness can be measured (Su et al., 2013b).

Su et al. (2013c) state that, to induce a stress to cause the microcapsule shell to break, it is necessary that a crack tip to penetrate the shell or passes close to allow the rejuvenator to diffuse out. However, it is not necessarily the case that a fatigue crack or damage is guaranteed to occur near the microcapsule, which means that the self-healing process may never have the opportunity to work (Su et al., 2014). In addition, Su et al. (2013a) found that some microcapsules do not break because of their high plastic deformation. They suggest that this plastic deformation might result from the combination of heat and applied load. Figure 2.29 shows SEM images of microcapsules in bitumen with their plastic deformation.

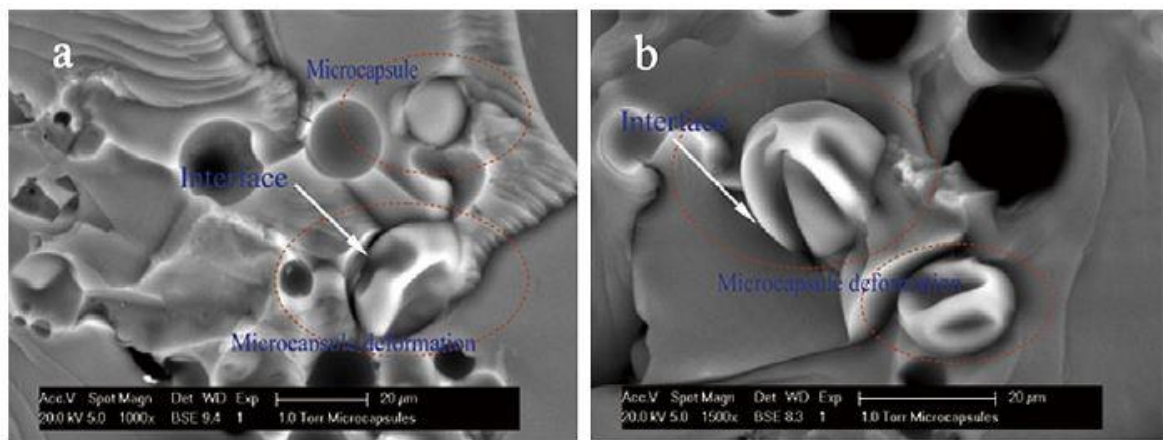


Figure 2.29: Interface morphology of bitumen/microcapsule sample (Su et al., 2013a).

The two methods of encapsulating rejuvenators described above have several advantages over the traditional rejuvenation system. These advantages can be summarised as: total volumetric penetration of the rejuvenator inside the asphalt mix; no negative side effects on pavement surface friction; and a better environmental performance. In addition, it can be considered as one of the pioneer steps towards producing clever roads.

2.8 General encapsulation technique

There are numerous applications that use encapsulated materials. They can be utilized in agriculture, pharmaceuticals, foods, textiles, paper, paints, coatings and adhesives, printing applications and many other industries. Historically, pesticides are encapsulated materials that are released over time, permitting farmers to apply a small quantity of the pesticides instead of requiring higher concentrations and possibly toxic initial applications followed by

repeated applications to reduce the loss of efficacy due to leaching, evaporation, and degradation. Preventing the pesticides from full exposure to the elements reduces the risk to the environment and provides a more efficient strategy for pest control (Sliwka, 1975).

Recently, Mallepally (2009) stated that carbonless copy papers were the first marketable product to employ capsules. A coating of microencapsulated colourless ink is applied to the top sheet of the paper and a developer is applied to the following sheet. The capsules break when pressure is applied by writing, leading the ink to react with the developer to produce the dark colour for the copy.

Mallepally (2009) also prepared a system of enzyme trigger controlled release based on hyperbranched polyesters. His attempts to encapsulate drugs with the synthetic polymers often required the use of organic solvents, which can be an obstacle for pharmaceutical applications. The work was based on the emulsification of the polymer melt and was firstly applied to hyperbranched polymers. The researcher found that it is possible to produce tailor made formulations based on hyperbranched polymers by using the melt dispersion method. The polymer properties controlled the enzymatic reaction, whereas the release of the drugs comes from the combination of nonspecific and enzymatic hydrolysis.

Centis et al. (2011) showed that encapsulating human haemoglobin by liposomes is possible and can transfer oxygen to be delivered to cells dispersed in fibrin gel. Experimental results of the oxygen transfer from these liposomes containing haemoglobin to the dispersing aqueous medium were consistent with the observed positive effects over cells. They recommend future studies to determine if the vesicles could be used in a perfusion bioreactor and reloaded in order to continuously supply oxygen over longer cell and tissue culture periods.

Poncelet et al. (2011) state that encapsulation can be an essential technology for functional food applications. They suggested that encapsulation is going to be of high importance for food engineers. By encapsulation, food powders can be protected during storage or processing, released at the right time and place and can be supplied by their inherent aromas, vitamins and other properties. They showed that encapsulated additives will provide all their potential to the food.

Kanellopoulos et al. (2015) presented a study to heal cement-based composites using the mineral compounds as healing materials. They use three liquids and one powdered minerals for this purpose: sodium silicate, colloidal silica and tetraethyl orthosilicate, and magnesium oxide powder, respectively. These materials were encapsulated in thinly covered soda glass capsules. The load recovery was evaluated for samples tested at three different healing conditions: ambient conditions, high humidity exposure and immersed in water. Figure 2.30 shows the healing process of this method.

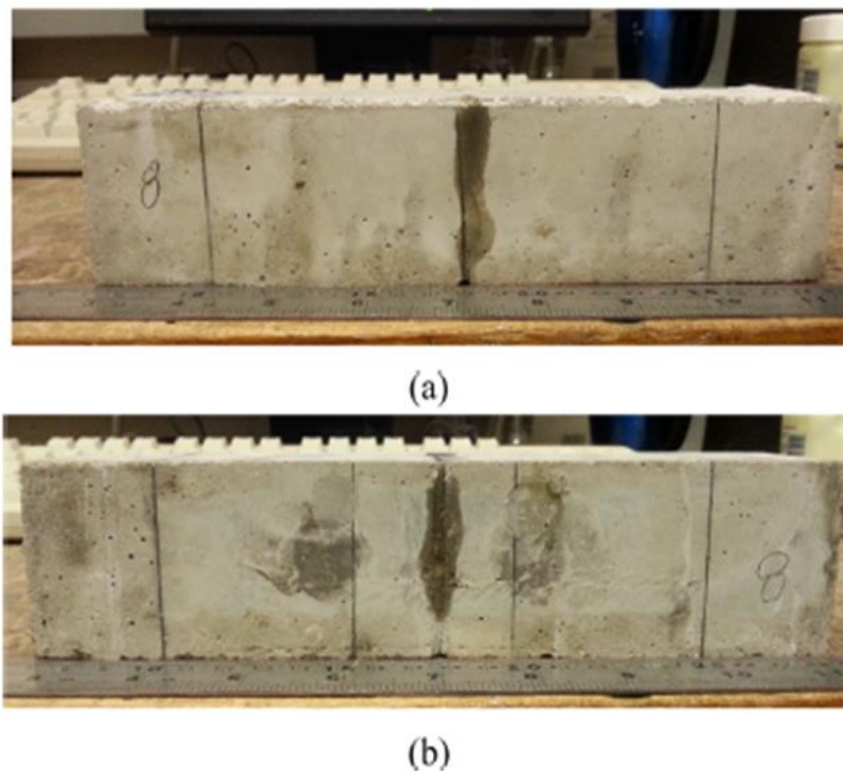


Figure 2.30: Representative image of specimen where the liquid was observed immediately after crack: (a) side face and (b) bottom face (Kanellopoulos et al., 2015).

All samples treated by mineral capsules showed an 85% to 100% crack recovery when subjected to water immersion. The intrinsic gas permeability reduced by 18% to 69% depending on the mineral type and measuring the parameter. In terms of load recovery and durability enhancement, sodium silicate and colloidal silica showed a more consistent response in all applied parameters. Based on these results, Kanellopoulos et al. (2015)

demonstrate the possibility of how self-healing can be achieved by utilising cost effective mineral compounds which are also compatible with the host cementitious matrix.

2.8.1 Capsule materials and constitution

García et al. (2010a) explained that epoxy-cement capsules consist of four parts: cooking oil as a rejuvenator (CO), porous sand, cement and epoxy. The porous sand used comprises calcium silicate granules for their microporous structure; they are selected specifically to absorb the liquid and keep it inside their pores. Their size (porous sand particle sizes of 1-1.7mm) was chosen so that it could be a replacement of an aggregate fraction when using the capsules in an asphalt mixture. The significance of the epoxy-cement shell is that it allows the capsules to survive the asphalt mixing process and throughout the pavement life until the crack occurs due to ageing and fatigue. Figure 2.31 shows an experiment conducted by García et al. (2010b) to produce capsules by immersing the porous sand in the rejuvenator (the cooking oil). Consequently, a hard shell of the epoxy-cement mixture is prepared before adding the immersed porous sand. It was proved that this type of capsule resisted the mixing process.

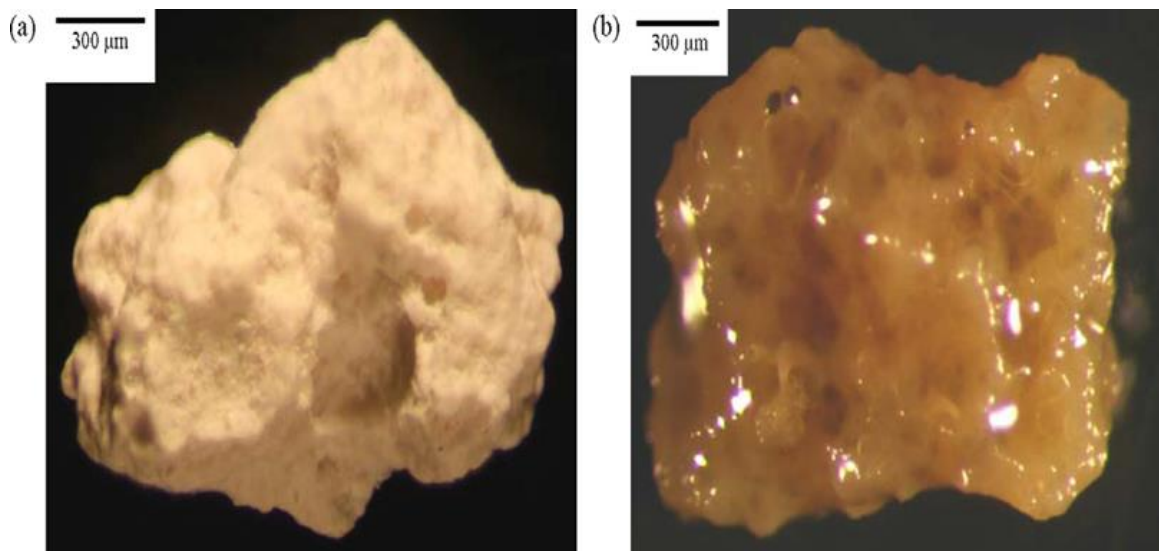


Figure 2.31: Optical micrograph of the core materials of the capsules, (a) porous stone core, (b) porous stone core with rejuvenator (García et al., 2010b).

Su et al. (2013b) stated several shortcomings of using the epoxy-cement shell material encapsulation process, such as the high cost of the epoxy, the relatively high viscosity of the

rejuvenator which makes it difficult for the rejuvenator to flow out from the capsule when the crack happens, the rejuvenator release is limited by the capillary action of the porous microstructure and finally, the capsules might be too large to fit between aggregate particles. Some previous researchers investigated the technique of using urea-formaldehyde and melamine-formaldehyde to manufacture microcapsules. These microcapsules did not show sufficient strength to survive the asphalt mixing process, and the rejuvenating agent prematurely released the into the asphalt mixture (García et al., 2010a).

A new technique for encapsulation was developed by Su et al. (2013b) and Su et al. (2016), by in-situ polymerisation using methanol-melamine-formaldehyde (MMF) prepolymer shells and styrene maleic anhydride (SMA) as a surfactant. This technique enhances the compaction resistance and thermal stability of the microcapsules. By adding more MMF prepolymer during the fabrication process the shell thickness can easily be increased if necessary. However, an important note to be considered is that the whole process of this microencapsulation technique is complicated and requires special equipment and chemicals. Still with microcapsules, Yang et al. (2017) designed self-healing microcapsules containing bituminous rejuvenator with the nano- CaCO_3 /organic composite shell. They studied their thermal stability and mechanical properties, besides their ability to improve self-healing of aged bitumen. The results show that these nano- CaCO_3 particles have greatly enhanced the thermal stability and mechanical properties of the microcapsules, which allowed the microcapsules to survive in melting bitumen without destruction. However, none of these trials of microcapsules have been applied to a real asphalt mixture to measure their ability to survive the mixing and compaction, nor their ability to heal.

García et al. (2011a) investigated the use of four types of rejuvenators and their effect on the properties of capsules. The results showed that the characteristics of the capsules are affected by the rejuvenator type. The capsules used in the research were of the epoxy-cement shell. The rejuvenator types were as follows: rejuvenator A was obtained from Kuwait Petroleum (0.98Pa.s), rejuvenator B was from Petroplus Refining Antwerp (4.33Pa.s), rejuvenator C was from Repsol (43.22Pa.s) and rejuvenator D was from Tricolor Refining (1.38Pa.s). They stated that the viscosity of the rejuvenator has a significant effect on its diffusivity as lower viscosity rejuvenators produce thicker capsules, which indicates a displacement of the rejuvenator to the shell. Higher shell volumes and low rejuvenator content can be found in capsules that contain low viscosity rejuvenators (rejuvenator A). The CT-scan analysis

showed clearly that the bond between the porous sand and the shell was not strong, as shown in Figure 2.32.

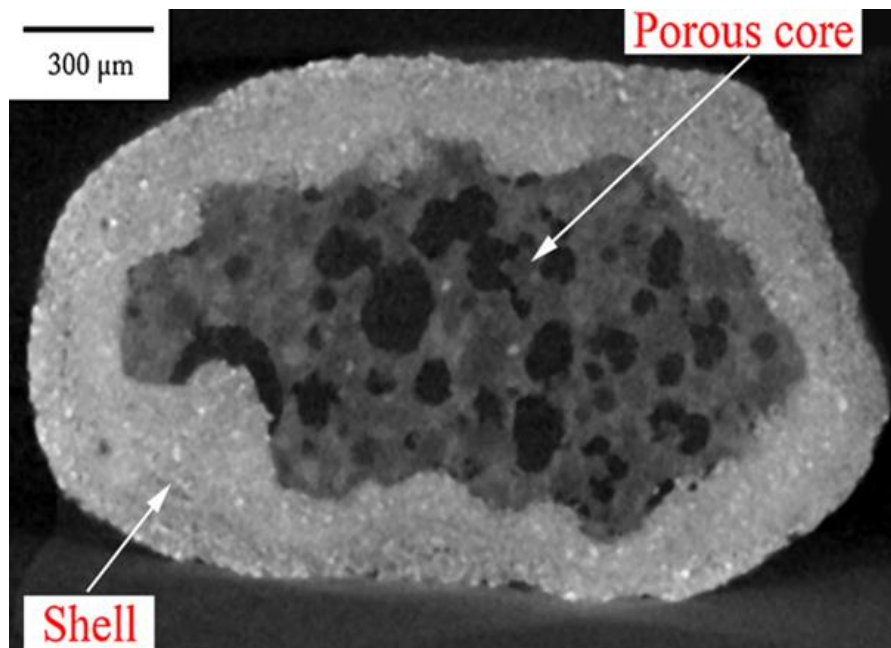


Figure 2.32: CT scan image through a capsule (García et al., 2011a).

Capsules that contained rejuvenators with high viscosity (rejuvenator C) showed higher rejuvenator content but low shell volume. This type of capsule was found to be the strongest with an acceptable bond between the porous sand and the epoxy-cement shell. The shell of this type of capsule is relatively thin and this was found to be proportional to the viscosity of the rejuvenator used. The effect of the rejuvenator viscosity was extended to affect the volume of oil within the capsule, as it increases when the viscosity increases. Therefore, in order to maximise the volume of the capsules, higher viscosity rejuvenators must be selected. Furthermore, the above research showed that lower viscosity rejuvenators are capable of better resisting compressive forces because of their increased shell size. The different shell layers and varying densities can be found in SEM images shown in Figure 2.33.

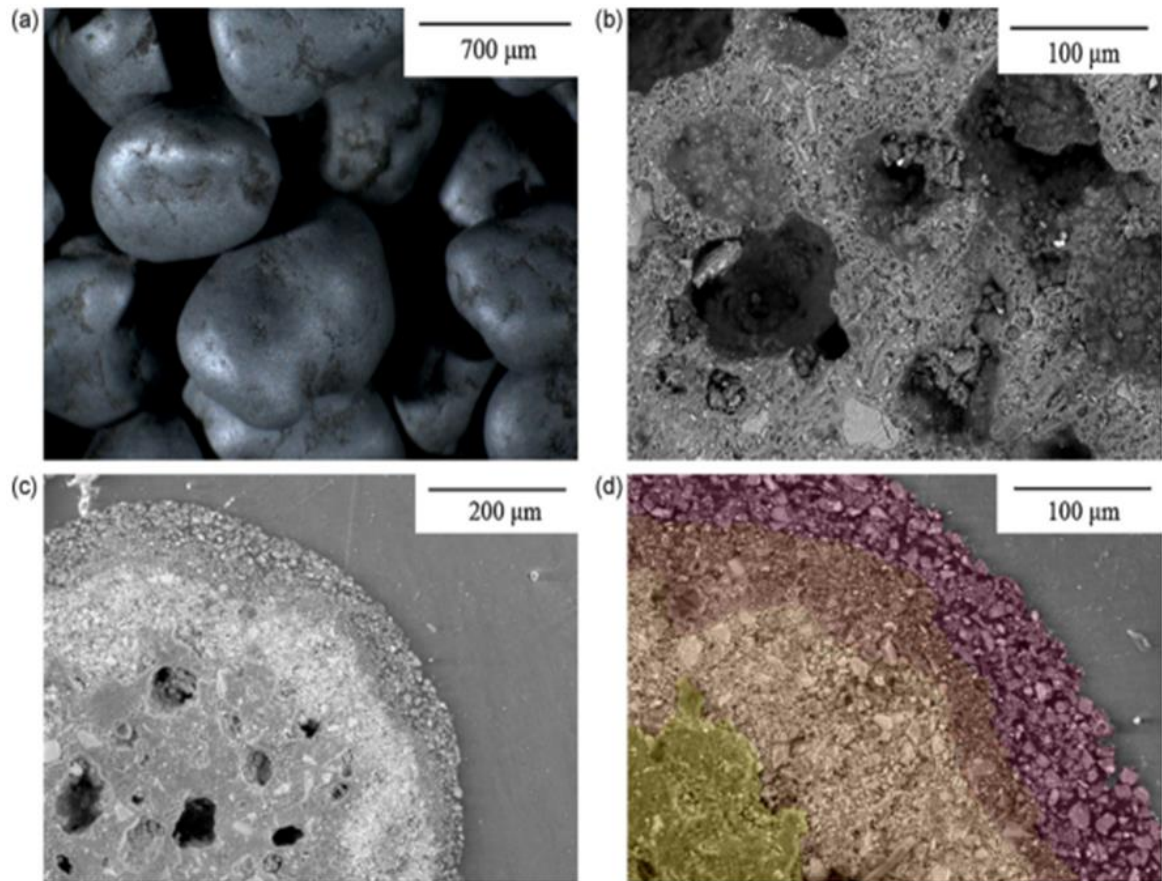


Figure 2.33: Images of the capsules, a) optical micrograph of the core materials of the capsules, b) SEM image of the porous sand used, c) SEM image of capsules showing its different layers with varying densities, and d) A detail of shell materials showing the interior and exterior walls (García et al., 2010b).

The same shell material used by García et al. (2010b), which is an epoxy-cement based resin, is used in this research. The rejuvenator is cooking oil (CO) with different amounts covered by the variable amount of alginate as a polymer. Different coatings of epoxy-cement shells are made; other types are made without an epoxy-cement shell. All types are characterised by the mechanical strength, chemical effect and thermal susceptibility. The effect of adding a hardener material such as chitosan is investigated and tested as well.

2.8.2 Capsule properties

The idea of using capsules containing rejuvenators as a self-healing material in asphalt pavements is new and incompletely researched, and hence capsule characterisation is currently basic. Previous studies have aimed to analyse the size of the capsule, internal structure, thermal susceptibility and the mechanical strength. For the epoxy-cement shell,

porous sand capsules, the characterisation was implemented by García et al. (2010a). The following tests shown in Table 2.2 were conducted for the characterisation.

Table 2.2: Characterisation methods for cement and epoxy resin capsules.

Capsule Characteristics	Characterisation method
Size and size distribution	- Optical microscope photos analysis using ImageJ analysis software to measure the capsules.
Morphology	- Scanning Electron Microscopy (SEM) - CT-Scan analysis
Thermal Capability	- Thermogravimetric Analysis (TGA) to analyse mass loss - Differential Scanning Calorimetry (DSC) to analyse energy changes and phase transitions
Mechanical Strength	- Tension tests - Compression tests - Universal Testing Machine to carry out indirect tensile tests

The characteristics of size and size distribution are important to identify the possibility of improving other characteristics, and since the capsules have been made by hand, measuring size and size distribution can be considered as a method of monitoring quality as well. The capsules created by García et al. (2010a) had an average size of 1.60mm; the idea of using porous sand inside the capsules was to substitute part of the aggregate fines in the asphalt by the capsules. Some of these characteristics are interdependent to some extent, for example, to increase the mechanical strength of the capsule, which increases the threshold value needed for capsule breakage, the thickness of the capsule shell (cement-epoxy) needs to be increased.

To understand the capsule structure, analysis of morphology should be applied. By using SEM imaging, García et al. (2010b) found that the shell of the capsule was very dense from the inner side that is in contact with the rejuvenator, which helps prevent outward seepage and was rough from the outer side that is in contact with the asphalt binder, improving

adhesion. Thermal susceptibility analysis showed that the capsules are able to resist temperatures of 180°C, which is the temperature at which asphalt pavement materials are mixed. The thermal test lasted for two hours, the mass loss was about 3%; this loss was a result of evaporation of the porous stone, not the rejuvenator (García et al., 2010b). Analysis of mechanical properties showed that the capsules can resist higher tension than compression. The capsules can resist mixing with asphalt materials, although they may fracture when subjected to indirect tensile load, which means that they are not too strong to break in the pavement.

Su et al. (2013a) performed characterisation of MMF prepolymer shell microcapsules. The following tests in Table 2.3 were implemented for their characterisation.

Table 2.3: Characterisation methods for MMF Prepolymer microcapsules.

Capsule Characteristics	Characterisation
Size and size distribution	- Optical microscope - Scanning Electron Microscopy (SEM) imagery
Morphology	- Optical microscope imagery analysis - Environmental Scan Electron Microscopy - Fluorescence Microscope to analyse materials interface
Chemical Structure	- Fourier Transform Infrared Spectroscopy FTIR
Thermal Analysis	- Thermogravimetric Analysis
Mechanical Strength	- Nanoindenter in tandem with TestWorks interface

The findings of these tests were: the average size of the microcapsules was within the range 23.5-5.0µm depending on the stirring rate, where increasing the stirring rate reduces the microcapsule size. Obviously, the microcapsule sizes are considerably smaller than those of cement-epoxy shell capsules. The size and shell thickness were found to be the main characteristics that affect the mechanical properties of the microcapsules (Su and Schlangen, 2012). The thickness and density of the shell can be increased by adding more MMF

prepolymer during the production process of the microcapsules. According to the morphology test, they found that the shells of the microcapsules can be smooth with a low dropping speed, which can give poor adhesion and higher compaction ability. In addition, the lower dropping speed led to the better homogeneity of the material and therefore, improved stability.

The microcapsules were tested for their temperature susceptibility and found to be able to survive the mixing temperature of the bitumen, which is 180°C. The nanoindentation test showed that the microcapsule shell manufactured of MMF prepolymer showed an elastic-plastic deformation with the ability to resist temperature changes and the mixing process (Su and Schlangen, 2012). When rupture of the microcapsules occurs, contents will diffuse out to the bitumen to perform the healing process. The yield point at which the microcapsules fractured was dependent on the thickness and density of the shell. (Su et al., 2013a) found that chemical analysis of the microstructure showed that chemical bonds can be responsible for improving the interaction between the shells and bitumen (not the case with the cement-epoxy shell and bitumen interface). Further analysis can be performed for more understanding of the use of MMF prepolymer shell capsules, for instance investigating the rejuvenator leakage rate once the capsules fracture.

2.8.3 Capsule healing mechanism

When the capsules are mixed with the asphalt pavement and applied to the field, they are supposed to resist all the loads and stresses a pavement would be subjected to due to traffic and temperature drop. This means that the maximum resistance of the capsules is required to be higher than the maximum stresses caused by traffic loading. Compressive loads cause the capsules to initially display an elastic reaction, although they cannot sustain any damage (Garcia et al., 2015). If this load is sustained, the capsules will undergo permanent deformation and rupture, allowing the rejuvenator to diffuse out of the capsules. Figure 2.34 shows external bleeding from asphalt samples containing capsules after being subjected to repeated compressive loads.



Figure 2.34: Asphalt sample after cyclic loading with broken capsules (Garcia et al., 2015).

Results showed that the compressive loads make the porous sand become compacted, leading to reduced porosity and forcing the rejuvenating oil to diffuse out. Additionally, with time the bitumen will start to lose its ability to relax due to the effect of ageing, which can be considered another stress that can cause the capsules to break and release their content. Cycles of repeated loading can also increase the possibility of capsule fatigue damage. Once damage happens, the oil will diffuse out through the binder, soften it, and eventually increase the self-healing ability of the asphalt mixture by restoring the material properties (Garcia et al., 2010). Figure 2.35 shows a scheme of the capsule failure process.

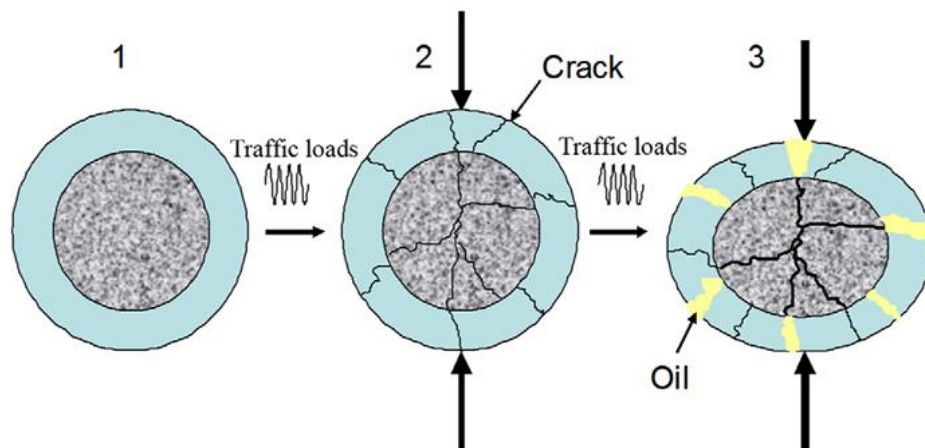


Figure 2.35: Schematic of capsule failure mechanism (García et al., 2011a).

García et al. (2011a) noted that almost 4% of the porous sand capsules added to an asphalt mix, had released their rejuvenator during the mixing process, which means they could not all survive mixing process. In addition, results from an indirect tensile fatigue test identified that all the capsules in the damaged surface were broken. Additionally, their results showed that capsules may have a detrimental influence on asphalt stiffness, which would result in degrading the mechanical properties of the asphalt pavement. This may have happened for two reasons: the first is that some capsules may break during the mixing stage; secondly, the level of adhesion between the capsules and bitumen might simply be low compared to that between aggregate and bitumen leading to a weakness in the total mix. García et al. (2010b) thought that the problem of weak bonding could be solved by creating capsules with rough surfaces, which would improve the force transfer between the capsules and bitumen to minimise the issues that come from unstable capsule-bitumen adhesion.

García et al. (2010b) stated that capsules have the potential to increase the permanent deformation (rutting) of an asphalt pavement since they are relatively weak points in the pavement and can be less resistant than the binder. To minimise this issue, García et al. (2010b) suggest using capsules combined with a reinforcing technique, such as the addition of fibres. However, some of their conducted tests show that the number of cycles the asphalt can resist with the presence of capsules is approximately the same as that for asphalt with no capsules added. Results also show that the compressive strength of the capsules might be reduced when applying a single force, which could not break the capsules. Instead, multiple forces produced by traffic are necessary (García et al., 2011a). The tests showed that the capsules which first exhibited elastic behaviour during loading would demonstrate a higher resistance to tensile stresses than compressive. The process of breaking a capsule is shown in Figure 2.36.

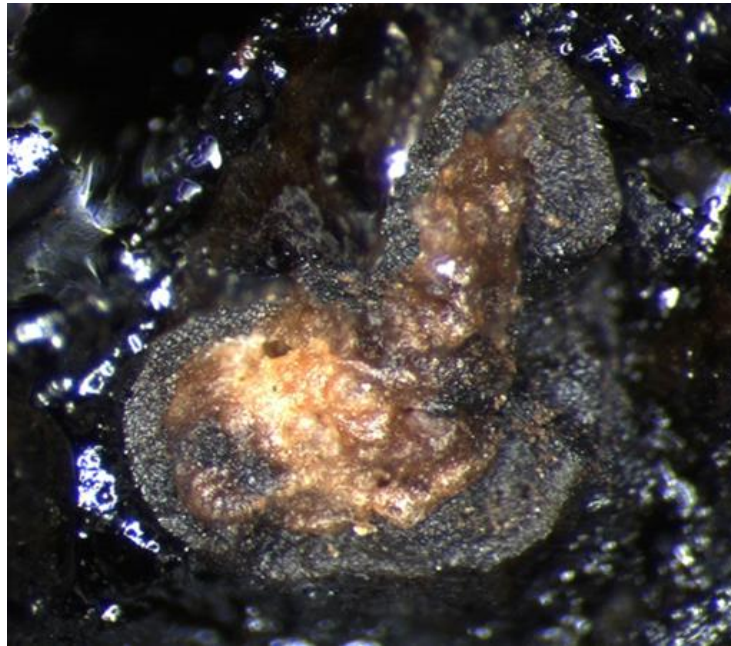


Figure 2.36: A broken capsule after the indirect tensile test (García et al., 2011a).

2.9 Summary

Based on the extensive literature review, the following points can be summarised:

- **Asphalt composition, fatigue and fracture**
 - The type of bitumen affect the mechanical properties of the asphalt mixture. The constitution and structure of the bitumen define its physical and mechanical properties. Bitumen mainly consists of two fractions: asphaltenes and maltenes, the ratio of one of these to another affects the rheological properties of the bitumen.
 - Properties of bitumen are influenced by oxidation, which occurs in the presence of oxygen and temperature, leading to bitumen ageing. The effect of ageing of bitumen on asphalt pavement causes many drawbacks, such as reducing its flexibility, reducing the maximum bearing ability to stresses that lead to failure and their stress relaxation behaviour, increasing vulnerability to fretting and cracking.
 - The strain in the mortar continues to increase to an infinity, which causes particles to slip and separate as damage happens when the aggregate particles contact each other. Fracture mechanism depends on temperature and rest periods between loadings. The literature review showed that it is not simple to model rest

periods or cyclic loading since they are completely different from one road to another.

- Using rejuvenators as healing agents helps improve the adhesion of bitumen and aggregate through enhancing material properties.

➤ **Asphalt self-healing**

- Self-healing nature of asphalt has been known about for some time, although the mechanism of how to accelerate it and apply it properly is still under research. The literature shows that self-healing can be a result of two processes, visco-elastic healing process and viscous healing process. Visco-elastic healing is caused by the relaxation of stresses; the viscous healing, however, caused by the rising temperature. The level of healing increases in the presence of temperature and this mechanism can be modelled by Arrhenius equation.
- Asphalt self-healing can also be vital for the environment, materials can be sustainable and continue to function for longer. Also, fewer unnecessary raw materials need to be extracted, and little processing will be needed to remove and replace failed materials. Furthermore, reduced energy required for maintenance during their lifetime will considerably reduce CO₂ emission.
- Two novel methods of asphalt self-healing are presented in the literature, which are: encapsulated rejuvenators and induction heating, both aims to trigger and accelerate the natural self-healing of asphalt pavements.
- Induction heating proved to be an effective self-healing technique by using conductive materials within the asphalt binder to generate heat, which reduces the viscosity of the binder near cracks.
- The application of induction-heating on a real asphalt pavement section showed promising results in terms of extending fatigue life of the asphalt pavement. However, this technique is still in its early stages and there is a lack, as well, of research into the sustainable and economic benefits of this technique. Currently, the significant issue in this method is that it is only applicable to repair the top surface of the pavement and not able to penetrate the full depth of the asphalt layer. In addition, the induction-heating device used on roads is large and slow moving, which causes disruption during the maintenance works.
- Another self-healing mechanism is using encapsulated rejuvenators embedded in the asphalt mixture is also presented in this chapter. This method has the potential

to restore the asphaltene and maltene ratio within the asphalt pavement. Traffic load stresses have a certain threshold that can break the capsules releasing their rejuvenator to heal the cracked asphalt. Initial studies about this method have been successful.

➤ ***Epoxy-cement resin shell capsules***

The literature review shows different ways of producing encapsulated rejuvenators. One of these is using porous sand to absorb the rejuvenator covered by a hard shell of epoxy-cement resin. This type of capsule can be summarised as:

- The size of the porous sand should be designed in a way that substitutes the fraction of aggregates displaced due to using the capsules.
- Mechanical resistance of the capsules is important to protect the capsules during mixing and compaction of asphalt, and during the service life of asphalt pavement. This resistance is usually provided by the shell of the capsule. Thickness of the capsule shell should be proportional to the viscosity of the rejuvenator, the higher the viscosity, the less the shell thickness.
- Rejuvenators with high viscosity should be selected to maximise the volume of rejuvenator absorbed by the core. Low viscosity rejuvenators better resist compressive forces because of their increased shell thickness. In addition, high viscosity rejuvenators have difficulty to flow out of the porous sand due to pore pressure.
- The epoxy-cement shell must be dense enough from inside to avoid rejuvenator leakage, and rough from outside to improve the adhesion between capsules and the asphalt binder.
- Capsules resisted temperatures up to 180°C, which means they are able to resist the mixing temperature of the asphalt pavement.
- Capsules were shown to be able to release the rejuvenator once they are sufficiently stressed, as they broke after being subjected to certain indirect tensile stresses.
- This type of capsules have no detrimental effect on asphalt surface friction. In addition, they show no effect on environment and they do not require human intervention during maintenance.

➤ **MMF prepolymer shell microcapsules**

This type of rejuvenator encapsulation can be summarised as:

- The MMF prepolymer shells were produced chemically by in situ polymerisation.
- Mechanical properties of the microcapsules were mainly influenced by the size and shell thickness. Adding more MMF prepolymer can easily increase the shell thickness. The shell thickness does not influence the rejuvenator content or release as with cement-epoxy shell capsules. The stirring rate controls the size of the microcapsules, where increasing stirring rate reduces their size.
- The lower prepolymer dropping speed the better homogeneity in the sample and the more improved stability. Chemical bonds are necessary for improving interface stability between shells and bitumen.
- The microcapsules were proved to be able to survive temperatures up to 180 °C, which means they are able to survive when added to asphalt during mixing process.
- This type of microcapsule is newly presented and requires more understanding. Although they were easily spread throughout the mix, future research of this type of encapsulation method could focus on the interaction between the microcapsules and bitumen, the rate of rejuvenator release and whether there is enough rejuvenator stored inside them to ensure acceptable healing. In addition, they can not break easily as they require a crack to pass through them to create a stress on their surface to release their content. This process is not assured yet; as a result, this method of encapsulation may not be applicable to asphalt self-healing.

Chapter 3: Materials and Methods

3.1 Introduction

This chapter presents the materials generally used in this research. These include the capsule materials, asphalt mastic materials and asphalt materials. The manufacturing procedure of the capsules is also presented in this chapter. The asphalt mixtures are generally classified as mixtures with capsules and mixtures without capsules. Standard mixture design that comprises a dense-grade asphalt skeleton with 4.5% air voids is used for both asphalt slabs and asphalt cylinders (gyros). Another hand-mixed asphalt mastic is presented as well.

In addition, this chapter presents the methods and tests used to investigate the capsule's effect on asphalt properties as well as on asphalt self-healing.

3.2 Capsule materials and encapsulation procedure

Different materials are used to manufacture the capsules, they range from cheap and safe such as sunflower cooking oil to expensive and needing special safety awareness such as fine cement and epoxy. This section presents these materials and the capsules manufacturing process.

3.2.1 Capsule materials

The capsules mainly consist of the rejuvenator and calcium-alginate polymer that encapsulates the rejuvenator, which is trapped in the core of the capsule. An external

protective shell made of epoxy-cement was added to some capsules to investigate whether this can optimise the oil content and increase the capsule strength. The rejuvenator material used in the capsules was sunflower cooking oil (CO), which is a commercial sunflower oil supplied by East End (UK). The smoke point of the oil is 227°C, while the flash point is 315°C. This rejuvenator was selected due to its low cost and since it does not require extra health and safety procedures for handling. Similar oil has been used before as a rejuvenator (García et al., 2011a, Zargar et al., 2012). Nevertheless, other rejuvenating agents can be encapsulated using the same method.

The polymeric material in the inner core of the capsules was composed of (1) sodium alginate ($C_6H_7O_6Na$), provided by Sigma-Aldrich, which is an anionic polysaccharide widely distributed in the cell walls of brown algae. The name alginate is given to a family of linear polysaccharides consisting of guluronic (G) and manuronic (M) units (Thu et al., 1996). It is sold in filamentous, granular or powdered forms, and mixing it with water creates a viscous white to yellowish-brown gum; (2) a calcium source, provided by Sigma-Aldrich as anhydrous, granular pellets of calcium chloride ($CaCl_2$), of 7mm diameter, and 93% purity.

The extra epoxy-cement shell used in some capsules was composed of a liquid epoxy resin (Gurit SP106 Multi-purpose Epoxy System Resin and Gurit SP106 Multi-purpose Epoxy System Fast Hardener) and micro-cement type I52.5R with average particle size ranging from 5 to 10µm. The epoxy resin worked as a binder for the cement particles. Any other crushed filler could be used instead; cement was selected in this research simply because of its availability in the laboratory. Care should be taken to prevent the cement from hydration; the water makes the cement hard, and too difficult to break afterwards.

3.2.2 Capsules production

To prepare the polymeric capsules, different amounts of sunflower oil were introduced as an oil-to-water ratio to make a 600ml of oil-water liquid in a 1 litre glass water container. To produce a stable emulsion, different amounts of alginate were added and stirred at 400 rpm, in a laboratory gear drive mixer for approximately 10 minutes. The amounts of alginate tested were 7.5g, 15g and 22.5g. Then, oil was added to produce an oil-to-water (o/w)

emulsion with the mixture being stirred at 400 rpm for 1 extra minute. Five different oil/water ratios (1.0, 0.5, 0.2, 0.1 and 0.05) were used and an oil-in-water emulsion produced.

At the same time, a calcium chloride solution was prepared by mixing 600 ml of deionized water with 12g of calcium chloride in a 1 litre glass water container. Capsules were formed by letting the oil-in-water emulsion drop into the calcium chloride emulsion from a 1000ml pressure-equalizing dropping funnel with 3mm socket size. During the capsule formation process, the calcium solution was gently agitated using a magnetic stirrer. Capsules were allowed to stay in the solution until the end of the encapsulation process, which lasts approximately 2-4 hours, depending on the amount of oil used. The alginate molecular weight and the concentration of the calcium chloride (CaCl₂) can affect the mixture and possibly the properties of the capsules (Thu et al., 1996). The process can be defined as producing capsules by ionotropic gelation of alginate in the presence of calcium, as shown in scheme (1) by Peniche et al. (2004). The schematic diagram of preparation of polymeric capsules is displayed in Figure 3.1. Calcium-alginate capsules were fabricated at 20°C.

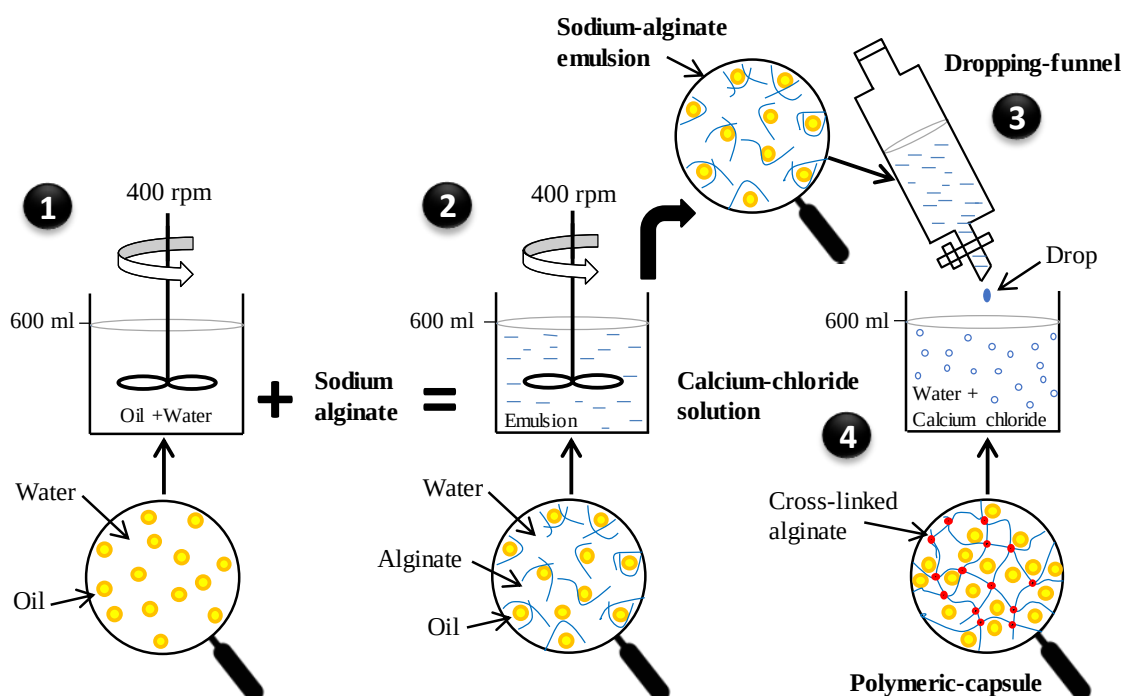


Figure 3.1: Schematic diagram of preparation of polymeric capsules.

Finally, the capsules were decanted and washed with deionized water. They were dried during 12 hours under a constant movement of air produced by a fan. To increase their strength, dry capsules were covered with an outer shell made of epoxy-cement. The process of making the shell started by spreading the epoxy on the polymer capsules, with a mass ratio of 14% (14g of epoxy for each 100g of capsules) and mixing the mixture by hand until the capsules became totally covered by the epoxy. Then, 7 steel balls of 2cm diameter were placed in a plastic container, together with approximately 1kg of micro-cement. To this, approximately 250g of capsules and epoxy were added. Then, the container was closed, and vigorously shaken by hand in a circular movement for 15s. After this, the capsules, cement, and steel balls were separated using a 2mm sieve, and the capsules were left to rest for 12 hours. The external coating process was repeated several times. In this research, capsules were prepared with one to four coatings. The flowchart in Figure 3.2 presents the fabrication process in more detail, the left hand side shows the procedure to fabricate the polymeric capsules, and the right hand side flowchart shows the procedure to fabricate the hard shell capsules (epoxy-cement shell). All tasks were performed at room temperature. Figure 3.3 shows sample of capsule at the three stages: directly after production, dry and ready to use capsules, and capsules with the epoxy-cement shell.

For comparison purposes, other types of capsules have been made in this research as follows: (1) capsules without protective shell (epoxy-cement); (2) treatment of the polymer capsules with a chitosan solution before making the shell. Because these capsules (with external shell) proved to be too strong, capsules without shell were also produced to assess the necessity of an external shell for the capsules to survive asphalt mixing and compaction. Indeed, the capsules without external shell are cheaper and consume less time to produce.

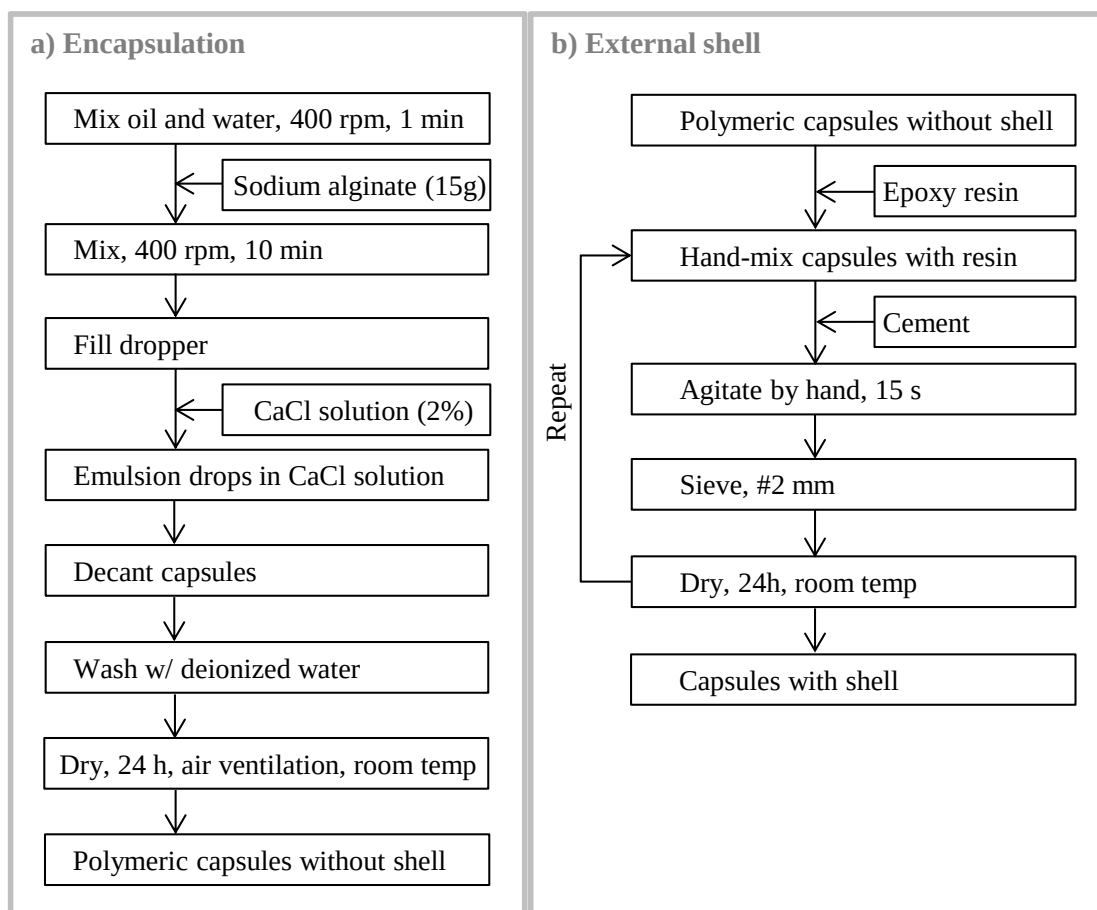
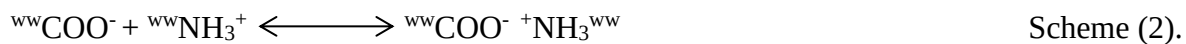


Figure 3.2: Flowchart of the capsule fabrication process: (a) polymeric (calcium-alginate) capsules; (b) hard shell.

Some types of the capsule were placed in a chitosan solution as a polycation solution in order to investigate if this could improve their mechanical properties and reduce the permeability of the polymer layer. The chitosan used in this research is a commercial product provided by Sigma-Aldrich Co. (UK). Gåserød et al. (1999) state that chitosan is a polysaccharide composed essentially of β (1-4) linked glucosamine units along with some proportion of N-acetylglucosamine units. It can be obtained by extensive deacetylation of chitin and is widely spread in nature (Dutta et al., 2004). The reaction of the alginate capsules with the chitosan solution creates a thin chitosan layer around the capsule as shown in scheme (2). The thickness of this shell is highly dependent on the pH value and the concentration of the chitosan. In previous studies (Peniche et al., 2004), it was found that oil leakage of calcium-alginate capsules can be prevented with the chitosan/alginate polyelectrolyte complex. It is used in this research to check if it can enhance the mechanical strength of the capsules as an attempt to produce cheaper capsules without an external epoxy-cement shell. The

concentration of chitosan used in this research was 1% in a solution with a pH value of 5.2 resulting from the addition of 20% of acetic acid as a solvent. Table 3.1 presents all capsules types and their contents.



3.3 Preparing the bituminous materials

Different asphalt mixtures were used in this research. Hand mixing is used in manufacturing asphalt mastic beams. Other asphalt mixtures ranged from cylindrical samples to asphalt slabs depending on the purpose they were produced to achieve. The bitumen used in all the tests of the research was virgin bitumen 40/60 pen, with softening point 49.8°C and density of 1.03g/cm³. The aggregate was a crushed limestone aggregate from Tunstead quarry, UK, with an approximate density of 2.700g/cm³.

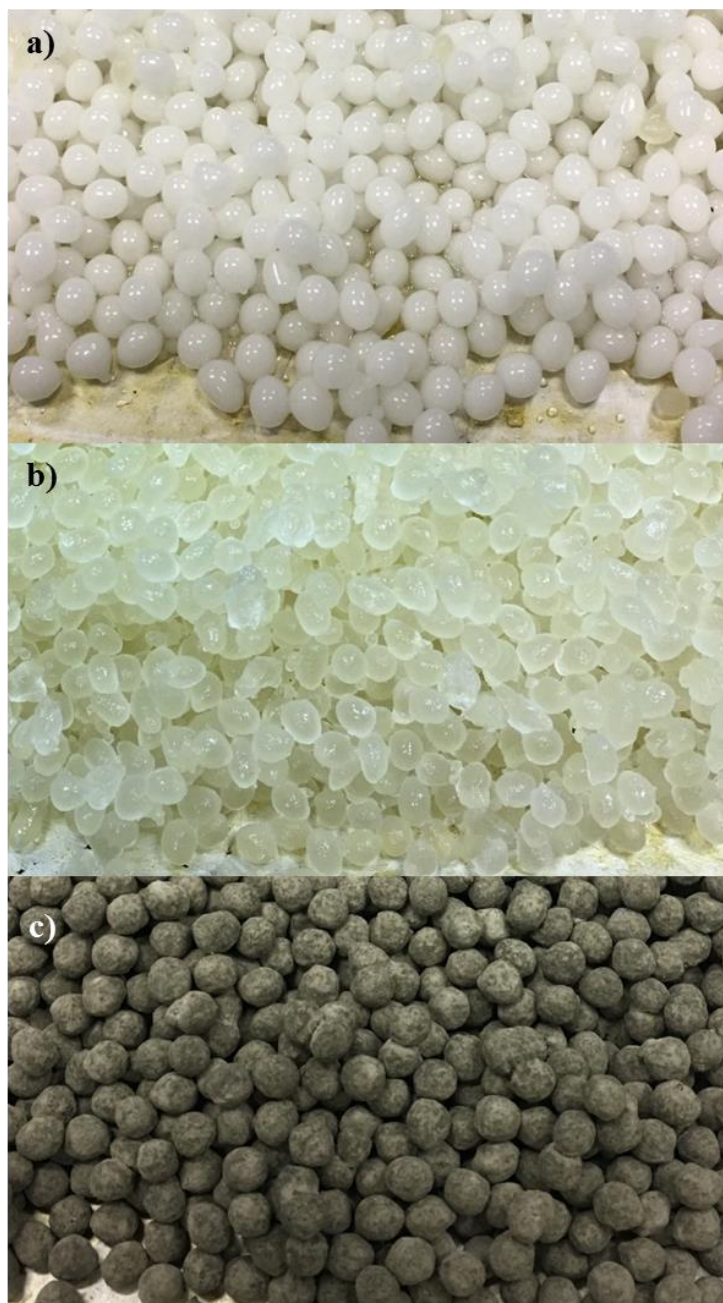


Figure 3.3: Samples of capsule produced in this research, a) wet capsules, b) dry capsules, and c) capsules with a hard shell.

Table 3.1: Composition of the capsules.

Capsule type	Alginate (g)	Oil (ml)	Water (ml)	Chitosan (g)	Number of cement-epoxy coatings
C1	15	25	575	-	-
C2	15	50	550	-	-
C3	15	100	500	-	-
C4	15	200	400	-	-
C5	15	300	300	-	-
C6	15	25	575	-	3
C7	15	50	550	-	3
C8	15	100	500	-	3
C9	15	200	400	-	3
C10	15	300	300	-	3
C11	15	25	575	6	-
C12	15	25	575	6	3
C13	15	100	500	6	3
C14	15	300	300	6	3
C15	15	300	300	6	-
C16	7.5	200	400	-	3
C17	22.5	200	400	-	3
C18	15	200	400	-	1
C19	15	300	300	-	1
C20	15	200	400	-	2
C21	15	300	300	-	2
C22	15	200	400	-	4
C23	15	300	300	-	4

3.3.1 Asphalt mastic preparation

Asphalt mastic is used in this research to mechanically evaluate the effect of self-healing as a first step towards investigating the self-healing of cracks in the presence of capsules. Two

different bituminous mastics were prepared, bituminous mastics with capsules, and others without capsules. The capsule content in the asphalt mastic is dependent on the oil content of each type of capsule. Ji et al. (2016) determined the optimum content of sunflower oil that can rejuvenate the asphalt binder without compromising other binder properties to be (6-8%) by weight of the bitumen in the asphalt mixture. According to this rule and from the oil percentages of the capsules presented in Table 3.3, the approximate mass percentage of capsules to bitumen used in the mastic beams is 26.6% of C1, 22.5% of C2, 19.5% of C3, 12.1% of C4, and 9.0% of C5. In this way, the estimated oil to bitumen ratio in mastic beams was 7.2%. Table 3.2 presents the properties of the asphalt mastic used in the study.

Table 3.2: Asphalt mastic design properties

Mixture type	AC 20 base 40/60
Aggregate gradation(% remaining)	
0.500/2.000 mm	47.8
0.125/0.500 mm	18.7
0.063/0.125 mm	6.4
0/0.063 mm	27.0
Binder content (% _M)	12.5

Apparently, the asphalt material that is most likely to heal under the effect of capsules is the asphalt mastic. Therefore, the design properties of asphalt mastic presented in Table 3.2 above were made to represent the part of asphalt material that has the higher bitumen content and only fine aggregate.

Prior to mixing, the different aggregate fractions and the bitumen were pre-heated in an oven at 140°C, for 10 hours, and 170°C, for 2 hours, respectively. The graded sand and bitumen were mixed by hand until the mixture became homogeneous, then the capsules at 20°C were added and mixed for 20 seconds. Later, the mixture was poured into prismatic shaped TeflonTM moulds (30*30*100mm) as shown in Figure 3.4, and compacted by hand. The bottom inside surface of the mould was fabricated with a triangular cross section protrusion at the mid-point of the length to create a notch in the specimens for the purpose of obtaining

a straight crack at the middle of the mastic beam. In total, 260 asphalt mastic beams were manufactured in this study, with and without capsules.

Table 3.3: Capsules composition

Capsule type	%Polymer	%Rejuvenator
	Calcium-alginate	(Oil)
C1	73.0	27.0
C2	52.0	48.0
C3	42.0	58.0
C4	29.0	71.0
C5	20.0	80.0

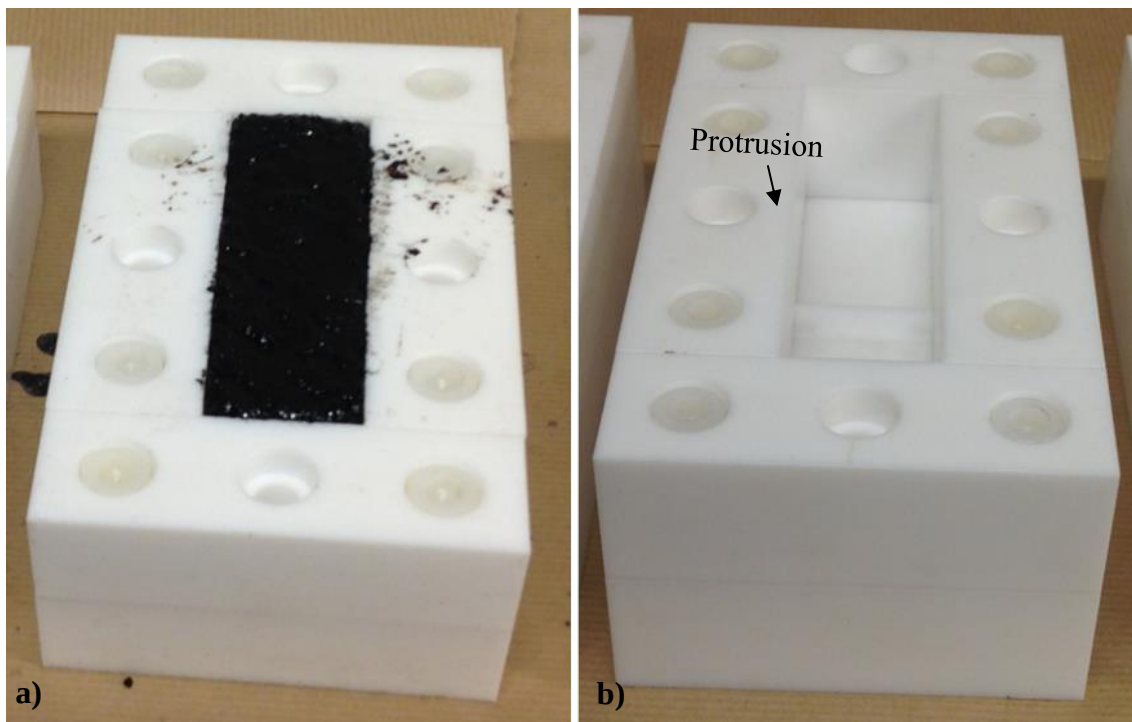


Figure 3.4: The Teflon mould, a) with a mastic beam, and b) empty.

3.3.2 Asphalt mixture

A dense asphalt concrete mixture, AC 20 base (EN 13108-1), was selected for this research and Table 3.4 presents the aggregate gradation and volumetric properties of the asphalt mixture. The aggregates and binder were pre-heated at 160°C for 12h and 4h, respectively, while the capsules were left to defrost for two hours at 20°C before mixing. The materials were mixed for 2min at 125revs/min at 160°C, for adequate dispersion. The capsules were added to the asphalt mixture just 20sec before the end of the mixing process.

Table 3.4: Asphalt mixture design properties

Mixture type	AC 20 base 40/60
Aggregate gradation (% passing)	
20 mm	100.0
10 mm	80.2
6.3 mm	60.3
4 mm	45.3
2 mm	29.7
0.5 mm	15.5
0.125 mm	9.9
0.063 mm	8.0
Binder content (% _M)	4.5
Bulk density (kg/m ³)	2384
Air voids (%)	4.5
Voids in mineral aggregate (%)	14.9
Voids filled with bitumen (%)	69.8

Figure 3.5a shows the process of adding the capsules type C2 to the asphalt mixture. This type of capsule was chosen because these capsules have no hard shell (epoxy-cement) that can protect them from higher temperature during mixing. Figure 3.5(b & c) show randomly extracted capsules after the end of mixing process in order to evaluate their damage before compaction process. It can be seen that capsules have changed their colour to a darker one due to the partial peroxidation of the encapsulated oil (Siriwardhana and Jeon, 2004). This

chemical phenomenon occurs when the sunflower oil is exposed to high temperatures (160-200°C), causing the hydrogen atoms to separate from the oxygen and carbon bonds. As a result, peroxides are formed in the bonds that oxidise the oil thus making it darker with more viscous texture. The variation of the capsules' diameter after mixing with asphalt was not significant. To evaluate this, an average diameter of 20 individual capsules randomly taken before, and after mixing process (as in Fig. 3.5c) was measured by using an ImageJ software. As a result, the average values of the capsule diameter before, and after the mixing process were 2.572mm and 2.895mm, respectively. This shows that capsules after mixing were surrounded by a bitumen layer with an average thickness of 0.271mm ($<53\mu\text{m}$), which is not significant and capsules can be considered as thermally stable at the mixing temperatures (140-160°C).

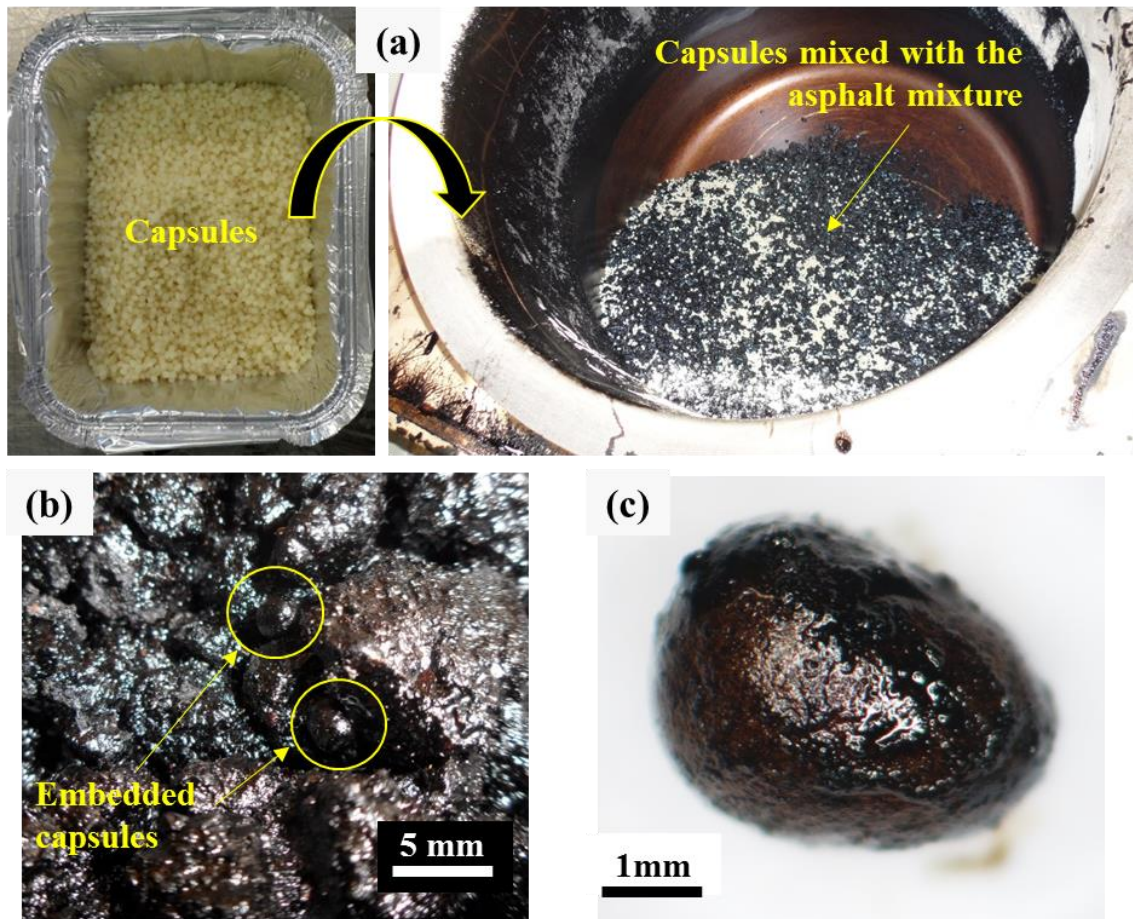


Figure 3.5: Images of mixing process of asphalt materials and capsules, a) adding capsules to mixture during mixing, b) embedded capsules in the mixture before compaction, and c) an individual capsules extracted after mixing process.

Asphalt mixtures were produced in the laboratory in approximate 14kg batches using a laboratory mixer equipped with a helical horizontal mixing shaft (shown in Figure 3.6a). Then, the mixture was transferred into the moulds for subsequent compaction. Cylindrical and prismatic test specimens were used for the research. The cylindrical test specimens (100mm diameter and approximately 50mm height) were compacted using a gyratory compactor (Figure 3.6b), with an inclination angle of 2.0° and 650kPa of static pressure. Not more than 250 gyrations were applied during compaction. These specimens were used for testing the effect of the capsules on the mechanical properties of asphalt mixture, such as stiffness, rutting, particle loss and water sensitivity.

The prismatic specimens (approximate $150 \times 100 \times 60 \text{ mm}^3$) were cut from ($306 \times 306 \times 60 \text{ mm}$) asphalt slabs compacted using a laboratory roller compactor (Figure 3.6c) to reach an air voids content of 4.5%. To facilitate the creation of a single crack in the asphalt beam during testing, a transverse notch of 5mm depth was sawn at the mid-point, on the bottom surface of the test specimens. These specimens were used to evaluate the crack healing level under the action of capsules. A total of 360 asphalt beams with and without capsules were manufactured in this study. Figure 3.7 shows the asphalt slab and the prismatic asphalt beam with dimensions.

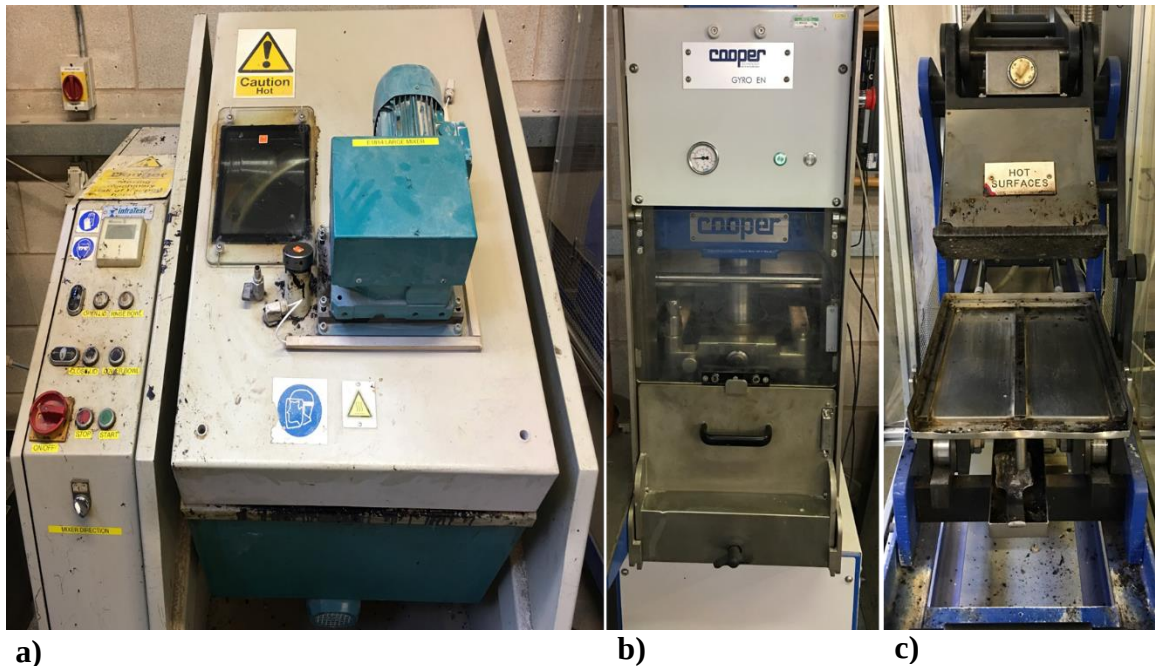


Figure 3.6: Asphalt mixture preparation and compaction. a) asphalt mixer, b) the gyratory compactor, and c) slab roller compactor.

Furthermore, some of the asphalt mixtures were pre-fabricated and aged in the laboratory before adding the capsules in order to simulate the natural ageing process of roads. According to BS EN 12697-26, (2004), the ageing procedure consisted of storing the mixture for 12 days in an air-ventilated oven at 85°C. Before remixing and compacting, the aged asphalt mixture was heated to 160°C. The capsules were added to the aged mixture and stirred for a short time (15sec) at the end of the re-mixing process. For comparison reasons, asphalt specimens without capsules were manufactured with aged and non-aged asphalt.

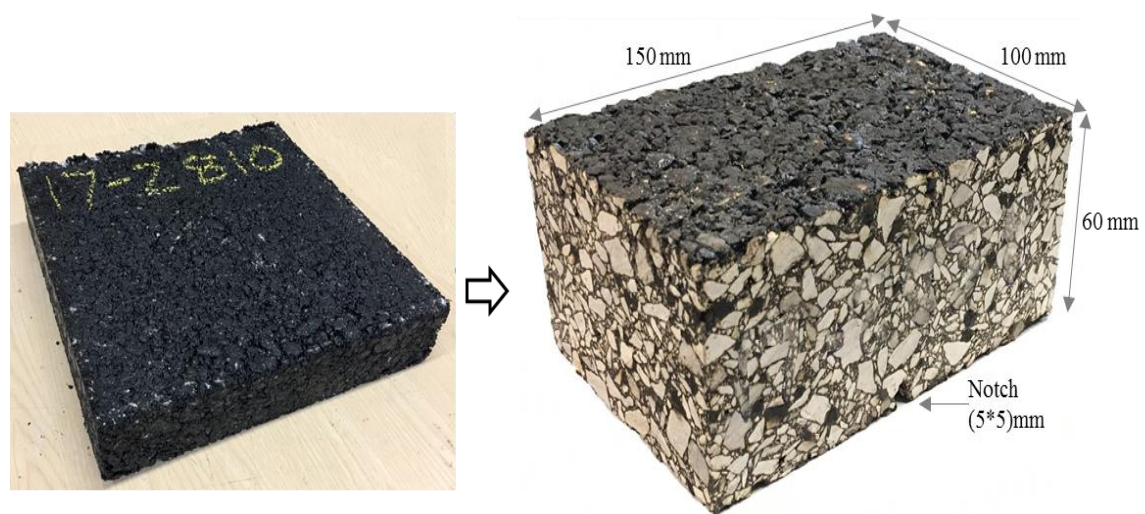


Figure 3.7: Asphalt mixture slab and the produced beam for the healing test.

3.4 Incorporation of capsules into the asphalt mixture

To prove whether the manufactured capsules can survive inside the asphalt pavement after mixing and compaction processes, Figure 3.8 shows different asphalt cores with capsule types C2 and C9, as the capsules are clearly visible on the surface of these cores as in Figure 3.8a. Capsules type C9 were not fully coated with bitumen. The possible reason for this is that cement and bitumen can not mix easily given the short time of adding the capsules to the mixture (20sec to the end of mixing process). Due to this and the thermal shock, the epoxy-cement shell of all the capsules was either broken or damaged to some extent, see Figure 3.8b. To see if the polymer capsule core inside the epoxy-cement shell was still intact and containing oil after the mixing and compaction processes, the shells of selected capsules was carefully removed (Figure 3.8c). Next, cores of various capsules were punctured and the flow of oil was observed, which confirmed that capsules survived the mixing and compaction processes, as shown in Figure 3.8d.

In addition, capsules without an epoxy-cement shell (type C2) also resisted the compaction process as can be seen in Figure 3.8e. In addition, due to the ductile nature of capsules without epoxy-cement shell, these capsules adapted their shape to the shape of the surrounding aggregates, which created a more intimate bond between the capsules and the mixture. Finally, some of these capsules were also punctured, and they were also full of oil. From these results, and for economic and safety reasons, it can be inferred that the cement-epoxy shell was not necessary to create high-quality capsules that survive the mixing and compaction processes.

Moreover, the condition of the capsules inside the asphalt test specimens was evaluated using computed tomography scanning (CT Scans), using an XRadia Versa XRM-500 scanner operated at 160kV and 63 μ A. The samples were assembled on a rotational table at a distance of 80.6mm from the X-ray source and 40.0mm from the X-ray detector. To do this, small specimens of 40 $\times$ 40 $\times$ 50mm³ were cut from the cylindrical specimens. These were adequate to obtain a pixel resolution of 45 μ m.

Cross-sections of two specimens are shown in Figure 3.9(a & b). It can be observed that (1) all capsules were deformed, (2) voids appeared between the cracked epoxy-cement shells and the capsules (see Figure 3.9a), and (3) capsules without the hard shell, had adapted their shape to the aggregates around them. As noted previously, at high temperatures the polymer structure is soft and allows large deformations with little oil release. Moreover, it was concluded that a compressive strength of 6N at high temperature is sufficient for these capsules to survive mixing and compaction.

ImageJ software was used to quantify the percentage of capsules in the mixture as represented in Figure 3.10. In this figure, it can be observed that capsules were mostly accumulated at the bottom of the test specimen. This happened due to the short mixing time and, possibly, due to some oil release on the capsule surface that makes them slippery in the asphalt mixture, causing them to sink down while the asphalt sample still hot.



Figure 3.8: Images of asphalt specimens with capsules, (a) overall image of a test specimen with capsules with hard shell; (b) zoom-in of a capsule on top surface; (c) capsule with epoxy-cement shell removed; (d) the oil flowing from the capsule; (e) overall specimen with capsules without a hard shell.

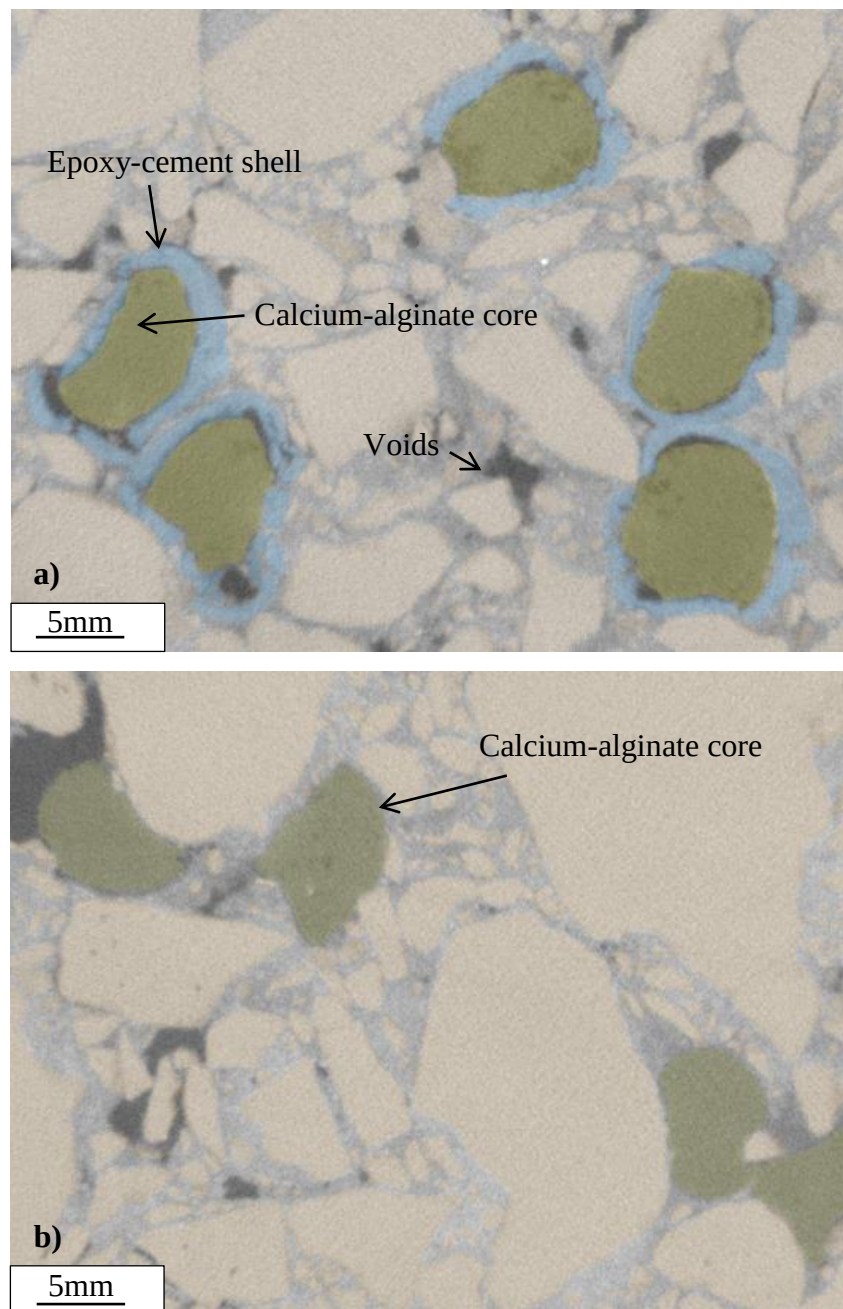


Figure 3.9: CT scan images of asphalt mixtures with capsules, (a) with epoxy-cement shell, and (b) without an epoxy-cement shell.

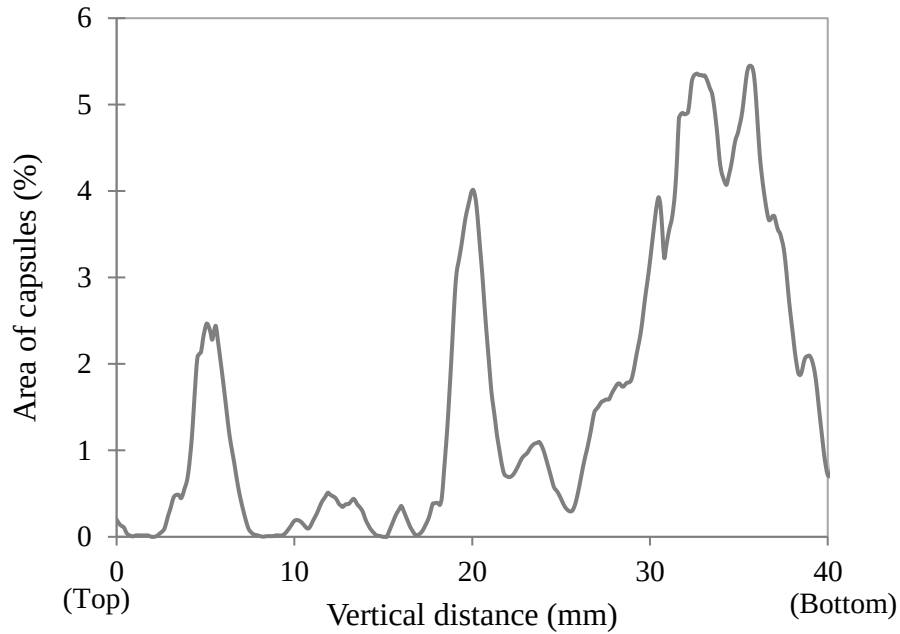


Figure 3.10: Percentage of capsules in the mixture.

Only two types of capsules were used in all asphalt mixture tests for healing and durability evaluations. The selection of those two types was based on their mechanical strength enabling them to survive mixing and compaction processes but to break as soon as a crack appears in their proximity allowing the oil to flow through the mixture. Moreover, it was concluded that these capsules release oil to the mixture during mixing and compaction. It is assumed that the oil released during mixing and compaction is uniformly dispersed within the asphalt mixture. Therefore, an equivalent amount of sunflower oil, calculated by FTIR test (as detailed in Section 3.5.4), was added to the asphalt mixture without capsules to differentiate the self-healing caused by the capsules from that caused by the oil released during the fabrication process. This procedure was also applied when dealing with asphalt mastic beams.

On the other hand, all capsule types without epoxy-cement shell (C1 to C5) were used in asphalt mastic tests. These capsules were used with different percentages of capsules-to-bitumen to control the same oil percentage in all mastic beams, which is within the optimum oil-to-bitumen content in the mixture.

Capsules effect on compaction and stiffness of aged asphalt was evaluated with cylindrical asphalt samples and the results were compared to unaged samples tests. The height evolution

of these specimens during compaction is presented in Figure 3.11. Three types of capsules were used in this study, with variable epoxy-cement shells and oil content: C20, C10, and C4 (see table 3.1). These capsules were selected based on their different morphology, size and strength characteristics. In Figure 3.11a, it can be observed that the final height was similar for the three types of materials tested, but that mixtures with capsules type C10 and type C4 were easier to compact. The reason for this is that some of the weaker capsules may have broken during compaction. In addition, Figure 3.11b shows the air void content of the compacted specimens. The air voids content of specimens with capsules type C20 is approximately 3% higher than that of specimens with capsules types C4 and C10.

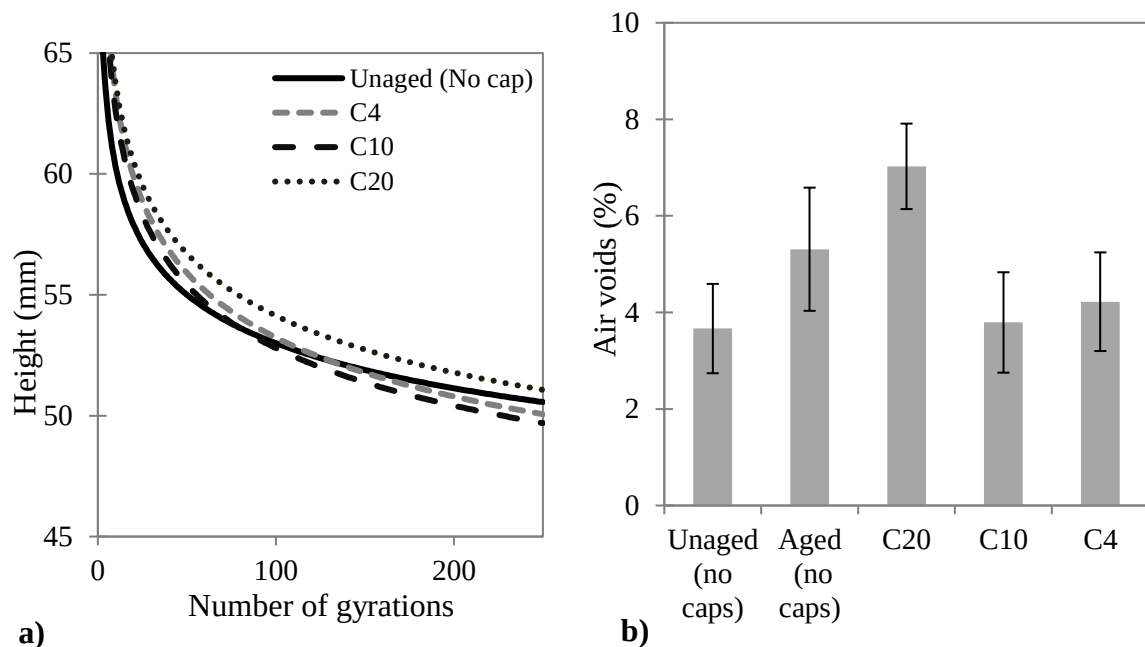


Figure 3.11: Specimen behaviour during compaction, a) compaction evolution with the number of gyrations, and b) air voids.

In addition, Figure 3.12 compares the variation of air voids with height, obtained from CT Scans, for a test sample of aged asphalt mixture without capsules and another sample containing capsules type C4. It can be observed that despite the similar compaction level and voids content in the two specimens, the specimen with capsules showed very low air voids content at the bottom. This could result from the higher capsules concentration at the bottom of the specimen (see Figure 3.10), which might soften the mastic allowing it to flow into the empty spaces and fill them.

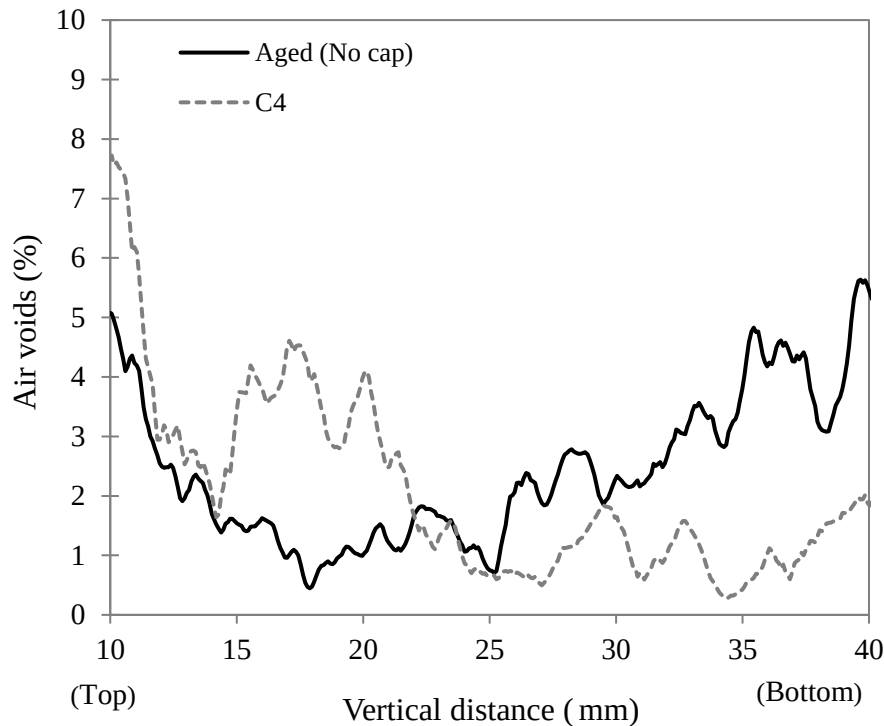


Figure 3.12: Variation of air voids with height.

Furthermore, capsules type C2 with three different contents, in terms of mass proportion in the total asphalt mixture: 0.10%; 0.25% and 0.50% were used to correspond approximate oil-to-bitumen contents in bitumen of 1.1%, 2.8% and 5.5%, respectively. These capsule contents were used to evaluate the effect of the capsules on asphalt durability and resistance to permanent deformation and fatigue as well as to evaluate asphalt self-healing. Capsule incorporation in these mixtures was after mixing the asphalt materials. The FTIR tests show that there was some oil leakage from the capsules during mixing and compaction. Therefore, an equivalent amount of leaked oil is added to the mixtures without capsules to eliminate the leakage effect on healing. The amount of oil added is explained later in asphalt self-healing chapter.

Cylindrical test specimens (100mm diameter) were compacted using a gyratory compactor with two inclination angles of 1.25° and 2.0°, and two static pressures of 600kPa and 650kPa. These variations were used for comparison reasons to get the desired void content and specimen height. Unaged asphalt mixtures were used in all samples with and without capsules.

Figure 3.13 shows the compaction results of all samples with all capsule contents. Figure 3.13a shows the height variations with number of gyrations compacted at an inclination angle of 1.25° . The curves show that the average heights of the samples obtained after 250 gyrations were 52.5mm and 53.5mm for samples with and without capsules, respectively. In comparison, the average height of the samples after the same number of gyrations compacted with an inclination angle of 2.0° was 50.0mm and 51mm for samples with and without capsules, respectively, as shown in Figure 3.13b. Figure 3.13c shows the variation of the air voids to the samples compacted with inclination angles of 1.25° and 2.0° .

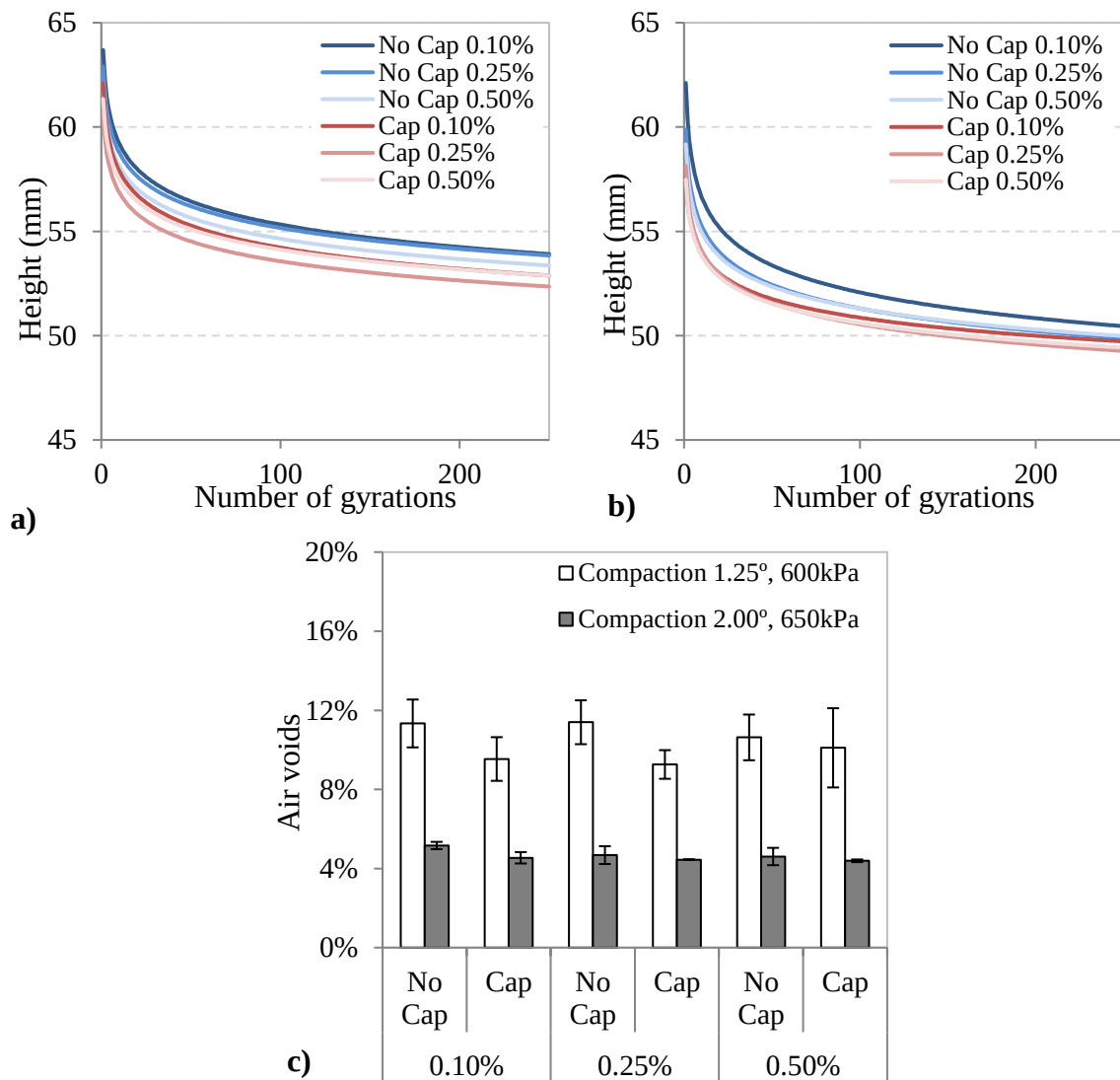


Figure 3.13: Specimens behaviour during compaction at two different inclination angles and stresses. a) compaction evolution with 1.25° inclination angle and static stress of 600 kPa, b) compaction evolution with 2.0° inclination angle and static stress of 650 kPa, and c) the air voids variation with the inclination angle and static stress.

3.5 Testing methods

Different test methods were applied on aged and unaged asphalt mixtures and asphalt mastic to evaluate the influence of the capsules on asphalt self-healing. Durability and fatigue life were also investigated on asphalt mixtures with and without capsules.

3.5.1 Capsules effect on aged asphalt

Asphalt specimens were tested under cyclic uniaxial compression without lateral confinement, in a load-control mode using a universal testing machine (MAND 100kN). The vertical deformation of the specimens was determined from the cylinder cross-head displacement. Testing was performed at 20°C. The testing procedure consisted of three stages: initial loading, resting and re-loading. During initial loading, a significant level of crack damage was induced in the test specimens, and the effect of the resting period was evaluated from the stiffness of the test specimens during the re-loading period. The resting period was introduced to give time for the oil to diffuse and change the properties of the bitumen in the asphalt mixture. To assess the time for the oil to diffuse, different resting periods were used: 3h, 6h, 12h, 24h and 48h. This procedure was performed with all asphalt specimens, with and without capsules. Three types of the capsule were used in this test, namely C20, C10 and C4.

The maximum loading level during cyclic loading for asphalt containing capsules type C20 and C10 was 20kN. This value was found to be equal to 28% of the peak load obtained from uniaxial compression of specimens without capsules, measured at a constant deformation rate of 5 mm/min. In the case of test specimens containing capsules type C4, 20kN resulted in test specimens breaking during initial loading. For this reason, the loading level was reduced to 14kN. Moreover, the loading frequency was 1Hz with 0.5s of rest between loading cycles.

The variation of the load and strain during one loading cycle is illustrated in Figure 3.14a. The vertical stiffness K (Pa) was determined in every cycle from the loading path as:

$$K = \frac{P_i}{\pi \cdot r^2 \cdot \varepsilon_i^v} \quad 3-1$$

where P_i is the load applied in cycle $I(N)$, r is the average radius of the specimen cross-section (m), and ε_i^v is the vertical strain in cycle i (m/m). In every loading cycle there is a small fraction of the deformation that is not recovered. The evolution of permanent deformation (d) with loading cycles (n) is illustrated in Figure 3.14(b). The slope of the accumulated permanent deformation (DS) is determined from fitting a linear model to the region with nearly constant increase rate.

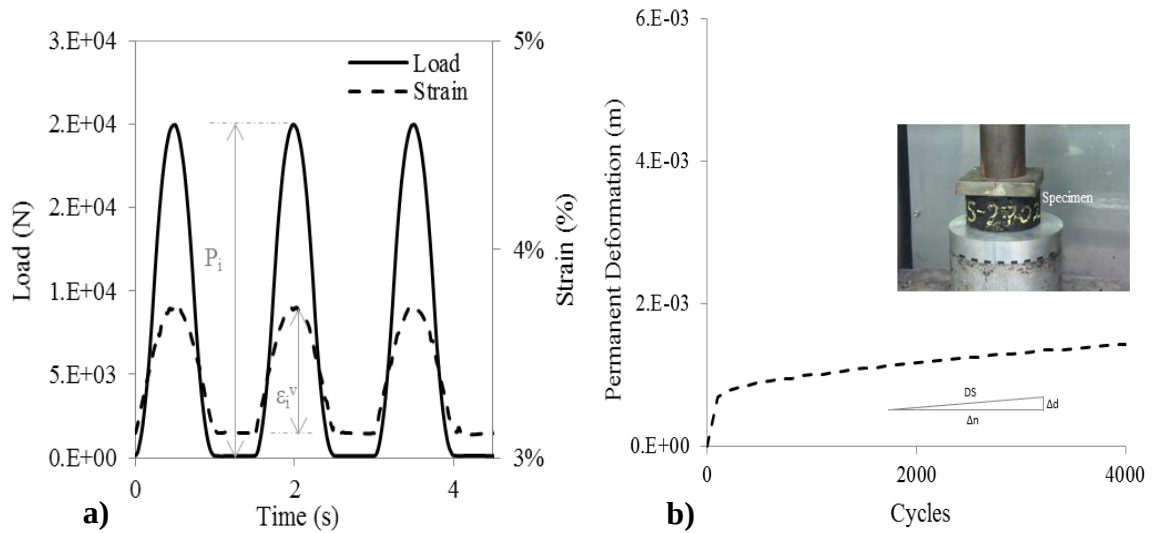


Figure 3.14: Mechanical test results: a) load and strain variation, and b) vertical deformation accumulation.

3.5.2 Durability and permanent deformation of asphalt mixture with capsules

To provide a global vision of the effect of capsules on the mechanical properties of the asphalt mixture, an extensive experimental programme has been performed in asphalt mixtures containing capsules. Standard testing procedures were used to evaluate the most important properties, such as water sensitivity, particle loss, stiffness, resistance to rutting and fatigue. Cylindrical test specimens of unaged asphalt were used for this purpose. Three different capsule contents were used, with oil-to-bitumen mass ratios of 1.1%, 2.8% and 5.5%.

Stiffness modulus and fatigue resistance

Stiffness modulus and number of cycles until fatigue fracture was determined by means of Indirect Tensile Tests on cylindrical test specimens. The same specimens were first used to test the stiffness modulus and then fatigue failure. Stiffness modulus was measured

following the protocol defined in EN 12697-26. Testing was done at 20°C. Five loading cycles were applied along the vertical diameter, with the amplitude adjusted to achieve a target peak transient horizontal deformation of 0.005% of the specimen diameter. The horizontal deformation was measured with two linear variable differential transformers (LVDT) mounted opposite one another in a rigid frame. The stiffness modulus (S_m) was calculated for each loading cycle as:

$$S_m = \frac{F \cdot (\nu + 0.27)}{z \cdot h} \quad 3-2$$

where F is the peak value of the applied vertical load (N); z is the amplitude of the horizontal deformation (mm); h is the mean thickness of the specimen (mm); ν is the Poisson's ratio (considered 0.35). The stiffness modulus was adjusted to a load area factor of 0.6 as defined in EN 12697-26:

$$S'_m = S_m \cdot (1 - 0.322 \cdot (\log(S_m) - 1.82) \cdot (0.60 - k)) \quad 3-3$$

where S'_m is the adjusted stiffness modulus (MPa); k is the measured load area factor. The stiffness modulus of each test specimen at a certain temperature was taken as the average of the values measured over two perpendicular diameters. The test specimens were then loaded until failure (fatigue) using the same loading scheme. Testing was performed at 20°C. The specimens were loaded in load controlled mode. The load level was defined for each specimen to cause maximum initial tensile horizontal stress ($\sigma_x^{\max}$) 600kPa.

Water sensitivity analysis

Rehydration of calcium-alginate capsules may compromise the preservation of oil inside. Also, swelling of capsules may affect the capsule/mastic bonding. The method as defined in EN 12697-12 was adopted to assess the effect of saturation and accelerated water conditioning in asphalt specimens with capsules. For this purpose, two subsets of specimens were conditioned as follows:

- a) The dry group, with cylindrical specimens conditioned in a temperature controlled room at 20°C during 72h.

- b) The wet group, with cylindrical specimens conditioned in water at 40°C during 72h. Before placing the specimens in the water bath the specimens were saturated in a vacuum container for 30min, using a residual pressure of 6.7kPa.

The Indirect Tensile Strength (ITS) of the cylindrical specimens was measured following the EN 12697-23 at a test temperature of 25°C. In the test, the specimen is loaded diametrically with a loading rate of 50mm/min, and the indirect tensile strength (ITS) is determined as:

$$ITS = \frac{2P}{\pi \cdot D \cdot h} \quad 3-4$$

where, P is the peak load (kN); D and h are the diameter (mm) and the height (mm) of the specimen, respectively. Three specimens were used per subset of material.

Particle loss tests

The particle loss, as defined in EN12697-17, was used to assess particle loss durability of asphalt mixture containing capsules. The test method involves placing one specimen inside the drum of a Los Angeles machine, without steel balls, and rotating it 300 times at 30rpm. The particle loss (PL) of a single test specimen was determined as:

$$PL = 100 \cdot \frac{W_1 - W_2}{W_1} \quad 3-5$$

where W_1 is the initial specimen mass (g); W_2 is the mass of the specimen after the test. The particle loss for one material type was determined as the average value of five test specimens. This test was done in three different types of test sample:

- Cylindrical test specimens conditioned in a temperature controlled room at 20°C during 24h.
- Cylindrical test specimens conditioned in water, at 40°C during 72h, and, before testing, at 20°C during 2h.
- Prismatic test specimens after the crack healing test (described in section 3.5.3), conditioned in a temperature controlled room at 20°C during 24h.

The test configuration b) was used to complement the water sensitivity analysis from the ITS test, and configuration c) was used to evaluate the effect of the softened bitumen in asphalt, after healing, on particle loss strength.

Permanent deformation

Asphalt specimens were loaded under uniaxial cyclic compression without lateral confinement to assess the resistance to permanent deformation, following the method defined in DD226:1996. Cylindrical specimens were loaded on their flat faces for 1800 cycles, with a 1s rest period between loading cycles. In each cycle, a load stress (σ) of 100kPa was applied for 1s. Before cyclic loading, the specimen was subjected to a constant stress of 10kPa for 600s. A top plate with the same diameter of the specimens was used to distribute the load. Testing was performed at a temperature of 30°C, with the specimens preconditioned at the test temperature for at least 4h.

The resistance to permanent deformation was evaluated from the accumulation of deformation with loading. The axial strain (ε_d) of the test specimen after n cycles is:

$$\varepsilon_d(n) = \frac{\Delta h}{h_0} \quad 3-6$$

where Δh is the accumulated axial deformation of the specimen (mm); h_0 is the initial height of the specimen (mm).

The dynamic load stiffness modulus (S) of the test specimen after n cycles is:

$$S(n) = \frac{\sigma}{\varepsilon_d(n)} \quad 3-7$$

According to previous results, three different stages can be identified for the evolution of axial strain. The slope of deformation accumulation (S_d) (EN, 2004) during the second stage (steady increase) of the test is:

$$S_d = \frac{\Delta h_{nf} - \Delta h_{ni}}{nf - ni} \quad 3-8$$

where, Δh_{nf} and Δh_{ni} are the axial deformations of the specimen (mm) after nf and ni cycles, respectively.

3.5.3 Crack healing

In order to evaluate asphalt self-healing with capsules under real conditions, an experimental simplified crack-healing methodology was developed. This methodology was used for both mastic and asphalt beams and it was applied to mastic beams first to check its feasibility. Self-healing of test samples was quantified as the healing level reached in terms of flexural strength recovery of cracked beams tested under a three-point bending (3PB) test after a rest healing time. The crack-healing test was implemented according to the following steps, which were applied for both mastic and asphalt beams with slight changes:

- Step A. All test beams, with and without capsules, were conditioned at -20°C for a minimum of 4h, then the 3PB test was carried out on the beams at a loading rate of 3mm/min until the beams were broken in two pieces.
- Step B. For mastic beams, to break the capsules inside the beam, broken test beams were placed inside the TeflonTM moulds and conditioned at 20°C for 2h to defreeze. Then, 350 cycles of cyclic uniaxial compressive loading, at 1Hz, with a maximum applied pressure of 600kPa, which simulates the tyre pressure of a heavy traffic loading on the pavement (Thom, 2008). This loading was uniformly applied on top of the broken mastic beams by using a steel plate with 5mm thickness placed on top of the test samples. For asphalt beams, a thin plastic membrane, able to adapt its shape to the faces of the crack, was placed between the two broken pieces of the asphalt beam. Then, the two pieces of the broken beam were put back together and introduced into a steel mould. To break the capsules, the beam inside the steel mould was placed in a temperature controlled chamber at 20°C for 2h and a compressive load was applied to the top surface, at a loading rate of 2mm/min, until the vertical deformation reached 5mm, which exceeds the maximum allowable deformation (5% of layer thickness). Later, the broken beam was taken out of the mould and the plastic sheet removed so that the two pieces of the beam could be put together into the steel mould.
- Step C. All test beams were placed in a temperature-controlled chamber at 20°C for a defined period of time called the healing time, ranging from 6 to 216h (0.3-9 days).

Once the healing time was reached, the beams were removed from the chamber and demoulded, then Step A was repeated, thus completing the crack-healing cycle. Figure 3.15 illustrates the steps of testing the crack healing for an asphalt beam and Figure 3.16 shows the sequence of this process.

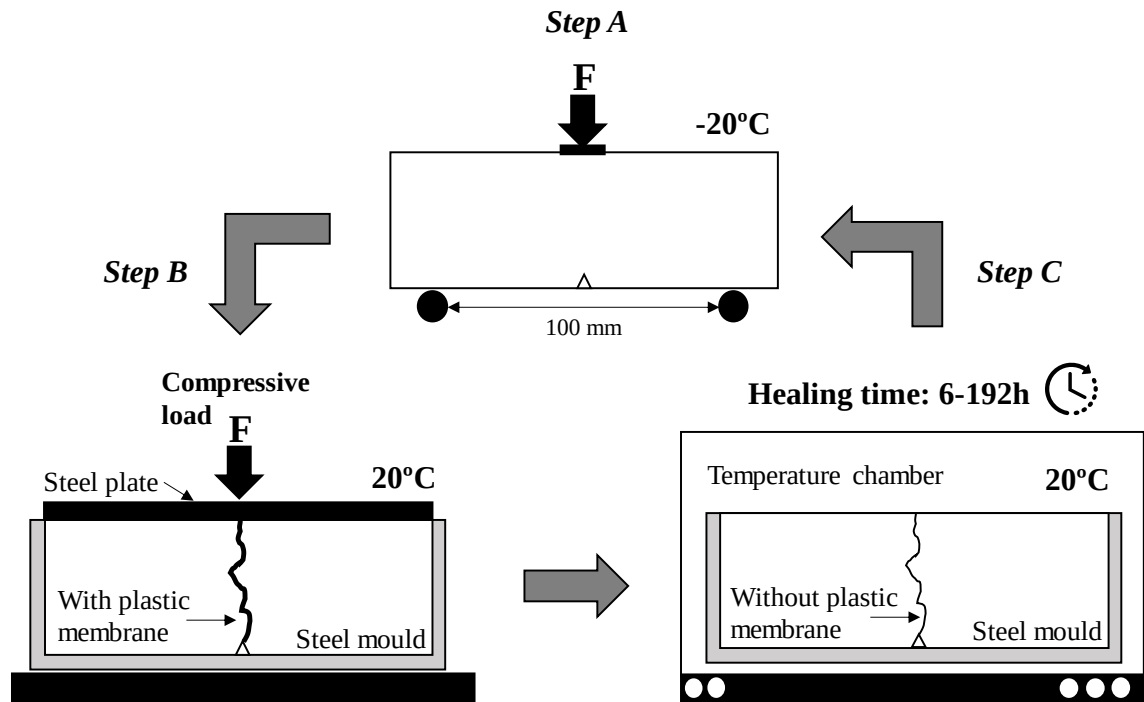


Figure 3.15: Crack healing test sequence.

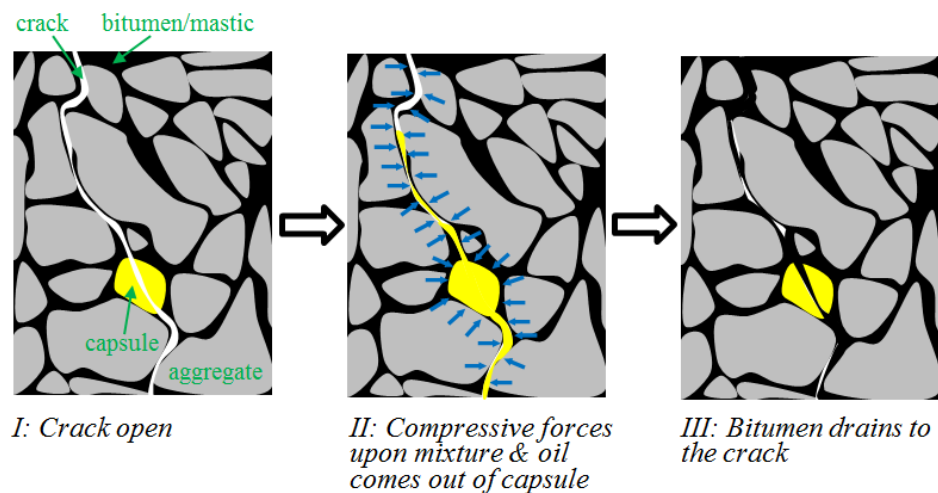


Figure 3.16: Schematic representation of crack healing in asphalt mixture with capsules.

The healing level, H_L , reached for each cracked beam after a specific healing time was defined as the relationship between the maximum load of the beam initially tested, F_i , and the maximum load measured in the same beam after the healing process, F_t (see Figure 3.17):

$$H_L = \frac{F_t}{F_i} \quad 3-9$$

Finally, with the aim of evaluating the temperature influence on the efficiency of the self-healing process of the asphalt mastic, with and without capsules, crack-healing measurements were also carried out on the asphalt mastic beams (with capsules type C4) at four different healing temperatures (5, 10, 15, and 20°C). Crack healing for asphalt beams was carried out with 0.10%, 0.25% and 0.5% of capsules by weight of the total mixture and tested at eight different temperatures (-5, 5, 10, 15, 20, 30, 40, and 50°C).

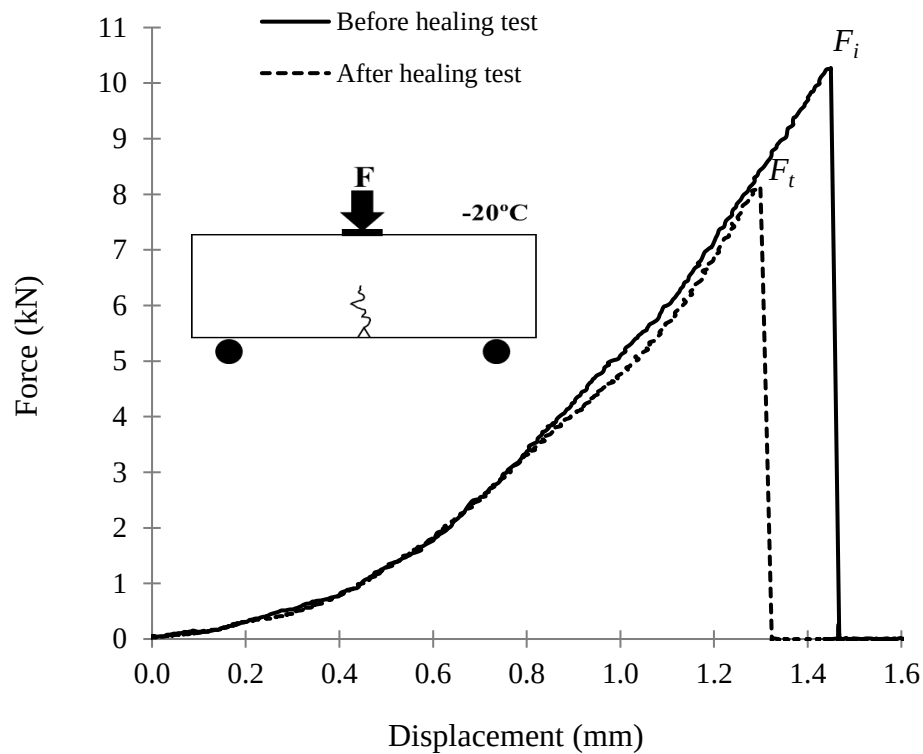


Figure 3.17: Force-displacement curve before and after healing for an asphalt beam with capsules.

3.5.4 Quantification of oil released from the capsules

The amount of oil release from the capsules during mixing and compaction, and after breaking the capsules, was analysed chemically by using Fourier Transform Infrared Spectroscopy (FTIR) on the mastic/asphalt samples for all the types of capsules used with their percentages.

The FTIR tests were carried out using a Bruker Tensor 27 spectrometer equipment. All the tests were set in the absorption mode in the range of 400 to 4000cm^{-1} and with a resolution of 4cm^{-1} . FTIR samples were taken from the mastic/asphalt samples with capsules after 72 hours of resting time. Sampling was made by using spatula to stir and scratch a loose asphalt/mastic beams, then collecting the accumulated bitumen/mastic around the spatula as a test sample. The required samples for the test were 2mm diameter and 1-2mm height, only to cover the lens of the test device. Temperatures were set according to the healing temperatures used in the crack-healing tests, as 5, 10, 15, and 20°C for mastic samples and -5, 5, 10, 15, 20, 30, 40, and 50°C for asphalt samples.

Moreover, samples of asphalt mastic with an oil content of 7.2% of the bitumen were prepared to conform the supposed amount of oil after full breakage of the capsules, and another sample without capsules was tested for comparison. For asphalt samples, three different oil contents were used to measure healing and the oil contents were added as a percentage of the total amount of bitumen with respect to the capsule percentage used in each asphalt mixture. These amounts were 1.1%, 2.8% and 5.5% for asphalt mixtures with capsule contents of 0.1%, 0.25% and 0.5%, respectively. Asphalt samples without capsules were also tested to compare the results. This test is used to measure the amount of oil release from capsules, which can be interpreted as potential amount of broken capsules. This is evaluated as a ratio of the oil released from capsules in the mixture to the total amount of oil released after full breakage of capsules.

The effect of sunflower oil in bitumen was evaluated from changes in the absorption peak between the wavenumbers 1700cm^{-1} to 1800cm^{-1} . This range was adopted to determine the amount of oil in the asphalt mixture. Vegetable oils have a distinct peak at $\sim 1745\text{cm}^{-1}$ (C-O stretch) while the bitumen has a zero index in this range (Marsac et al., 2014). The curves were normalised in the selected wavelength range and the area under the curve was measured

using the trapezoidal rule of numerical integration (Liang et al., 2012). Figure 3.18 shows an example of the FTIR curves for asphalt samples with, and without, oil, and explains the area under the curve.

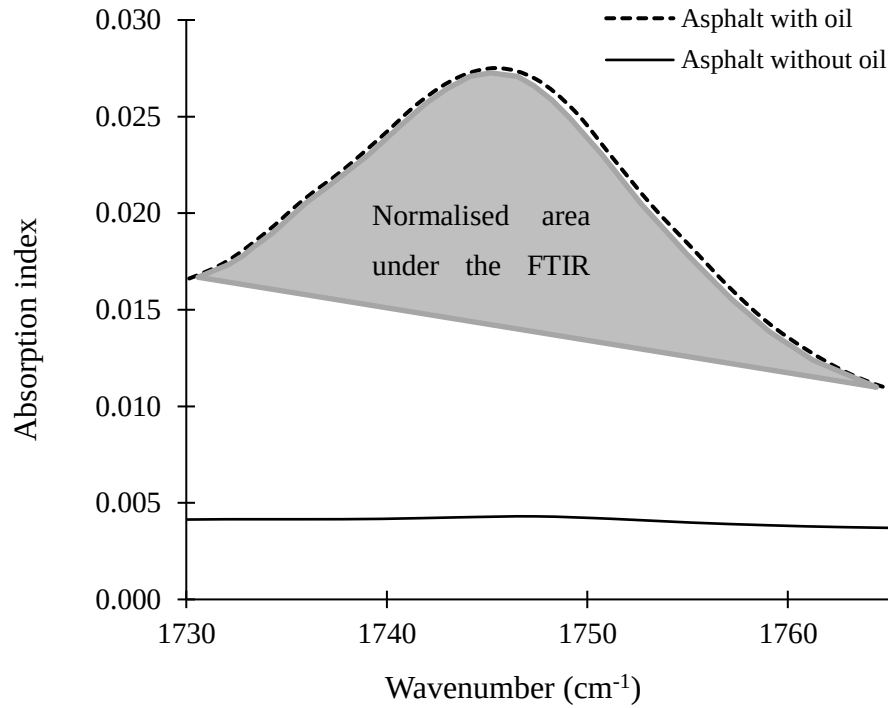


Figure 3.18: FTIR curves for asphalt mixture samples with and without oil.

3.5.5 Thermal expansion of asphalt samples

Thermal expansion measurements of asphalt samples at different temperatures, ranging from 5°C to 50°C, were developed by means of a Thermomechanical Analyser (TMA) model Q400. The thermal expansion test was applied to asphalt samples to measure the change of dimensions of the asphalt when heated, while the sample is simultaneously subjected to mechanical loading. The tests were conducted at a heating rate of 5°C/min for asphalt samples with, and without oil. The percentage of oil added to the asphalt samples was as that released from capsules inside the asphalt mixture after full breakage, and the highest content of capsules (0.50% by total weight of the mixture) was considered. Samples with dimensions 5*5*10mm were placed in a conditioning chamber and the temperature was changed in steps. Finally, all sensors and LVDTs were previously calibrated and connected to a computer to provide a continuous record of the length with every temperature change.

3.5.6 Viscosity of bitumen

The viscosity test was performed by means of a Dynamic Shear Rheometer (DSR) supplied by Malvern Instruments Ltd. The bitumen samples were tested with, and without, oil at eight different temperatures -5°C, 5°C, 10°C, 15°C, 20°C, 30°C, 40°C and 50°C with oscillatory sweep frequencies of 0.1-10Hz. The same oil percentage considered in the thermal expansion tests was used in the viscosity test for samples with oil. A two parallel-plate geometry was used: 8mm diameter for test temperatures of -5°C to 40°C, and 25mm diameter for temperatures of 40°C to 50°C. A gap of 2mm between the spindle and the sample was used to allow performing the viscoelastic measurements.

3.5.7 Skid resistance test

The skid resistance test was carried out on asphalt slabs in wet conditions following EN 13036-4 (BS, 2011). The test includes applying water to the test area and rewetting it every time before swinging the pendulum. The test was conducted at 20°C and the pendulum test value (ptv) was calculated as the average of five repetitions. Asphalt samples used were with and without capsules for comparison.

The average skid resistance values (ptv_s) were 76.2 for asphalt with capsules and 76.4 for asphalt without capsules. The results show that capsules have no significant effect on skid resistance of asphalt in wet conditions. This is reasonable because capsules are embedded in the asphalt mixture and not exposed to the surface.

Chapter 4: Properties of the Capsules

4.1 Introduction

Calcium alginate capsules containing sunflower oil were prepared by ionotropic gelation of alginate. Three main types of capsules with different coating systems have been manufactured in the laboratory. Some were coated with chitosan, others with a composite of cement and epoxy and some without coating. These capsules have different sizes, compositions, mechanical strength, besides their variable oil contents. This chapter investigates experimentally the diameter of the capsules, their morphology and structure, their mechanical strength and temperature susceptibility followed by an evaluation of the volumetric proportions of the materials that form the capsules.

4.2 Imaging techniques and size distribution

4.2.1 Structure of the capsules

To observe the internal structure of the capsules, they were first casted in an epoxy resin matrix and then abraded until the inner structure was exposed. The oil was cleaned from the section of the capsule by washing with water and using absorbing paper. Finally, the capsule morphology was investigated using scanning electron microscopy (SEM) type Philips XL30FEG SEM.

Figure 4.1 presents the SEM images of two types of the capsule, one with external epoxy-cement shell and one without. Figure 4.1a shows the internal structure of a capsule type C7 (Table 3.1). In this figure, the calcium-alginate core and the epoxy-cement shell are shown.

In addition, it can be seen in Figure 4.1b that there is a gap between the epoxy-cement coating and the inner core of the capsules. This may happen due to the permeability of the polymer membrane that allows oil out of the capsule, leading to a separation between the core and the epoxy-cement shell. This interface is also seen in capsules made with other o/w ratios and different alginate contents. Figure 4.1c shows the core of a capsule, which consists of an alveolar structure where the oil is entrapped. The pores in the core are not connected, as it was possible to cut capsules in half without these releasing their full content of oil. An image of the epoxy-cement shell is presented in Figure 4.1d, which is an array of densely packed cement particles, bonded by epoxy. Furthermore, a capsule from experiment C2 is shown in Figure 4.1e. It can be seen that a gap also exists between the capsule and resin, which could also result from the capsule permeability to oil. Finally, Figure 4.1f shows a capsule (type C2) core at a wider scale showing the alveolar structure of the polymer that entraps oil inside.

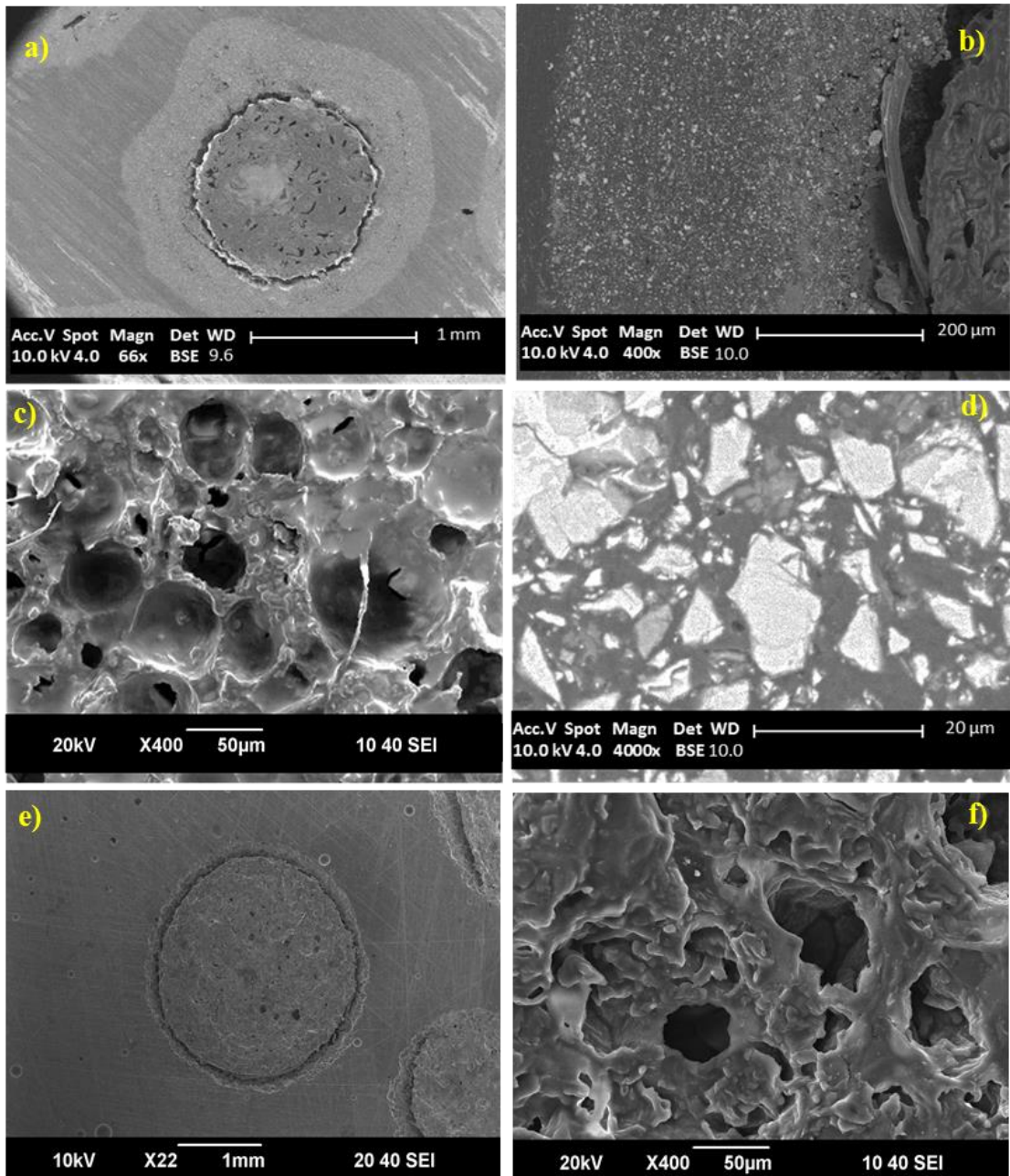


Figure 4.1: SEM images of the capsules. a) a general overview of a capsule with hard shell, b) a zoom-in of a core-shell interface, c) a zoom-in of a core of a capsule with hard shell, d) a zoom-in of epoxy-cement shell, e) a general view of a capsule without hard shell, and f) a zoom-in of a core of a capsule without hard shell.

Finally, the approximate volumetric proportion of the calcium-alginate core and the epoxy-cement shell in the capsules was determined from analysis of SEM images of several capsules. The core proportions are 19%, 28%, 38%, 41% and 58% for the capsules of types C6, C7, C8, C9 and C10, respectively. These results show a significant reduction in the

polymeric core proportion with the *o/w* ratio (see Table 3.1), which may restrict the effective healing potential of the capsules.

4.2.2 Capsules diameter

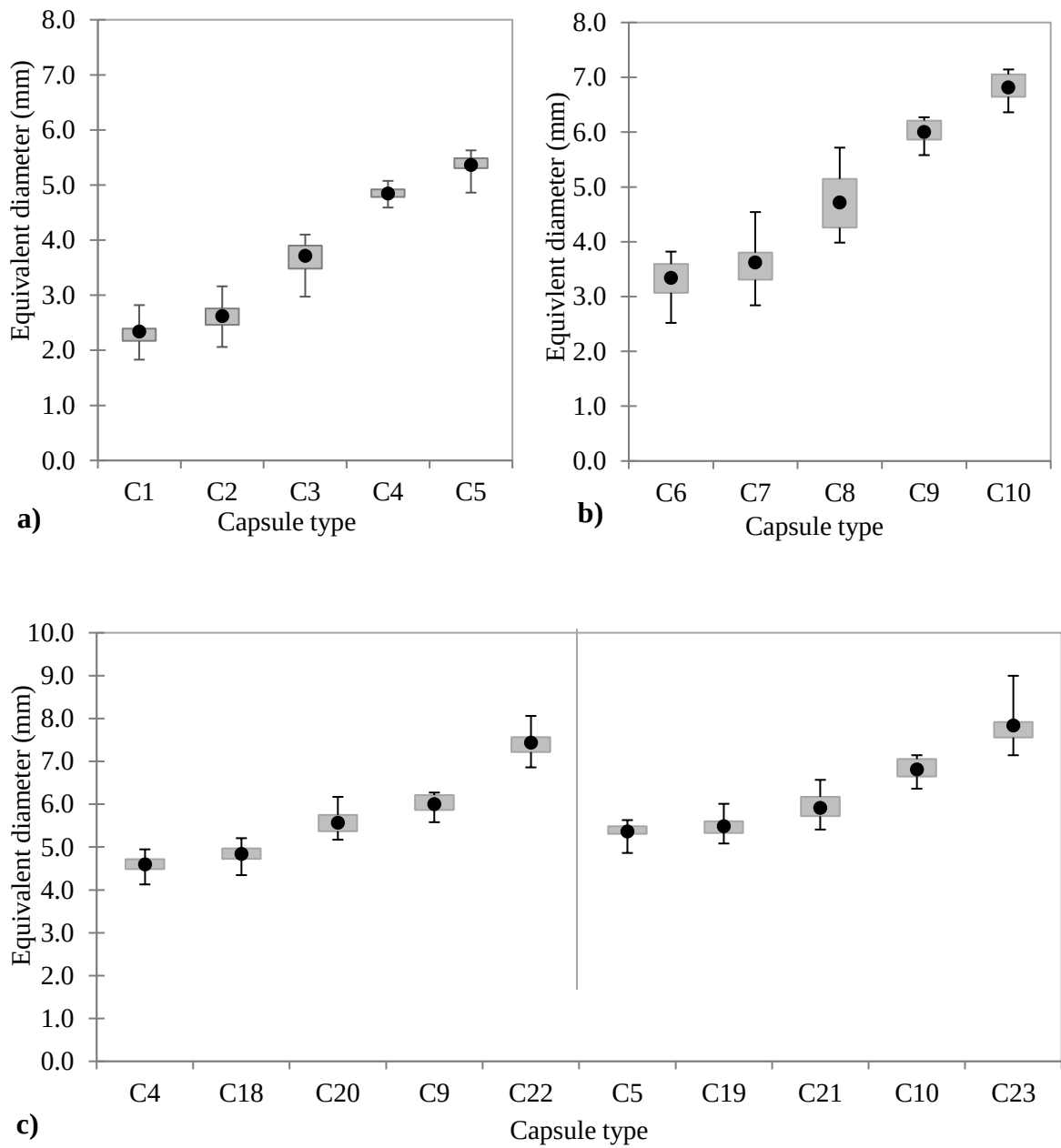
The diameter of the capsules was determined from images taken under a stereoscopic microscope with a Nikon Digital Eclipse DXM1200 camera, and processed with software ImageJ®. The diameters of capsules with different compositions are represented in Figure 4.2. The figure depicts the minimum, maximum, the Q1 and Q3 quartiles and average values for the capsule diameters. Figures 4.2a and 4.2b show a continuous increase of the capsule diameter with the oil to water (*o/w*) ratio for capsules without and with epoxy-cement shell, respectively. The reason for this is that calcium-alginate capsules were noticed to be permeable to water but impermeable to oil. The initial size of capsules (wet capsules) was approximately 9mm, independent of their composition, but during the water evaporation phase, water evaporated from the capsules and they shrank. The *o/w* ratio was the factor that most affected the diameter of the capsules.

In addition, Figure 4.2c shows that the capsule diameter increased with the number of epoxy-cement coatings independent of the *o/w* ratio. Two types of capsules having different *o/w* ratios were tested. On average, each additional coating increased the capsule diameter by about 0.4-0.7mm. Furthermore, it was noticed that the thickness of the epoxy-cement coating was independent of the core diameter.

Moreover, Figure 4.2d shows the effect of chitosan addition on the capsule diameter. From the figure and going back to Table (3.1), it can be noticed that chitosan addition has no effect on capsule size. This could result from the fact that chitosan dissolves in the solution and becomes liquid during preparation.

Finally, Figure 4.2e shows three types of the capsule with constant *o/w* and different alginate content. It can be noticed that the amount of alginate in the oil-to-water emulsion did not affect the final diameter of the capsules. Furthermore, when the amount of alginate was lower than 7.5g, no capsules were formed, as the calcium-alginate structure was not strong enough to hold the oil. Besides, it can be observed that as the *o/w* ratio is constant, the final diameter of capsules is approximately constant and equal to 6mm. Finally, the size distribution of

capsules did not significantly vary with the factors tested, and variations were always less than 1 mm for capsules with similar oil contents.



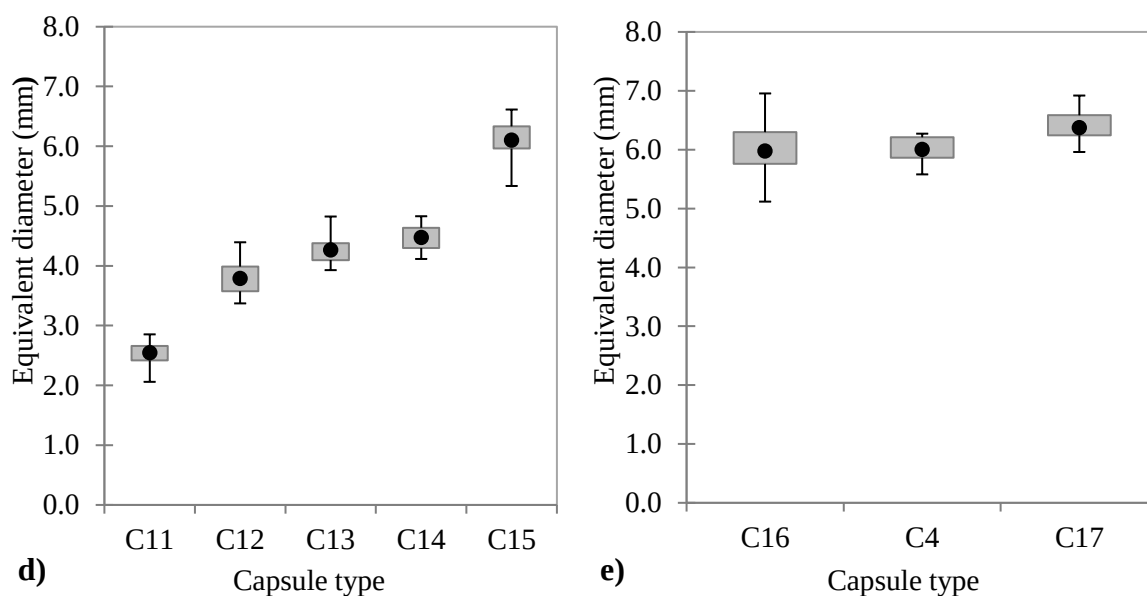


Figure 4.2: Effect of composition of capsules on diameter: a) o/w ratio for capsules without a shell, b) o/w ratio for capsules with shell, c) number of coatings, and d) Chitosan content, and e) amount of alginate.

4.3 Thermogravimetric analysis (TGA)

The composition and thermal resistance of capsules and their individual components were evaluated by means of thermogravimetric analysis (TGA). For this purpose, capsules from experiments C1 to C10 (see Table 3.1), were analysed. Tests were performed on a NETZSCH, TG 449 F3 Jupiter Thermo-Microbalance, using a nitrogen atmosphere and a heating rate of 10°C/min. TGA profiles were recorded over a temperature range of 0-1000°C. Aluminium crucibles were used for the measurements of all samples.

In Figure 4.3a, the TGA analysis of individual components used for the encapsulation process is shown. Calcium-alginate loses about 6% of mass before 200°C and 39% up to 400°C. Afterwards, there is a fast decrease of mass until 1000°C, when only 9.5% of the total mass of calcium-alginate is left. Epoxy resin loses about 3% of mass before 200°C and 79% up to 400°C. At 1000°C, only 5% of the total mass of epoxy is left. Sunflower oil does not lose mass before 200°C and it loses 21% of the mass up to 400°C. At 1000°C, there is no weight left from the oil. Moreover, cement loses 2% of mass before 200°C, and 4% of the mass up to 400°C. At 1000°C, only 14% of the total mass of cement is lost.

Furthermore, TGA test results of capsules from experiments C1 to C5 are shown in Figure 4.3b. The mass change with temperature is dependent on the oil content in the capsule. Capsules with higher oil content show a high resistance to temperature, with just 2% mass lost at 200°C for capsules type C4 and C5. This percentage decreases for other capsule types. However, as temperature increases, capsules with less oil content have a higher mass remaining than those with a higher oil content. This could be related to the mass loss of the oil and the polymer with temperature individually, (see Figure 4.3a). Between 300°C and 490°C there is a fast decrease of mass of oil and, afterwards, only a small mass loss can be observed. The remaining mass of the capsules after 1000°C in the TGA test was 7%, 6.5%, 6.0%, 2.9% and 1.9%, for experiments C1, C2, C3, C4 and C5, respectively.

In Figure 4.3c, results for capsules types C6, C7, C8, C9 and C10 are shown. It can be seen that the mass change with temperature is very similar to the capsules in Figure 4.3b. The mass loss was only 2% at 200°C. Between 320°C and 480°C there is a fast decrease of mass and, afterwards, only a small mass loss. The epoxy-cement shell protected the temperature sensitive components (oil and alginate) up to about 300°C. Above this temperature, epoxy resin was affected by temperature, the external shell decomposed and a major mass loss occurred. The mass of capsules at the end of the test was almost entirely cement. As the capsules with smaller internal core diameter had a higher proportion of epoxy-cement, because the shell thickness was independent of the core diameter, they had higher remaining mass at the end of the test. The remaining mass after TGA analysis at 1000°C was 65%, 59%, 58%, 48% and 46% for experiments C6, C7, C8, C9 and C10, respectively.

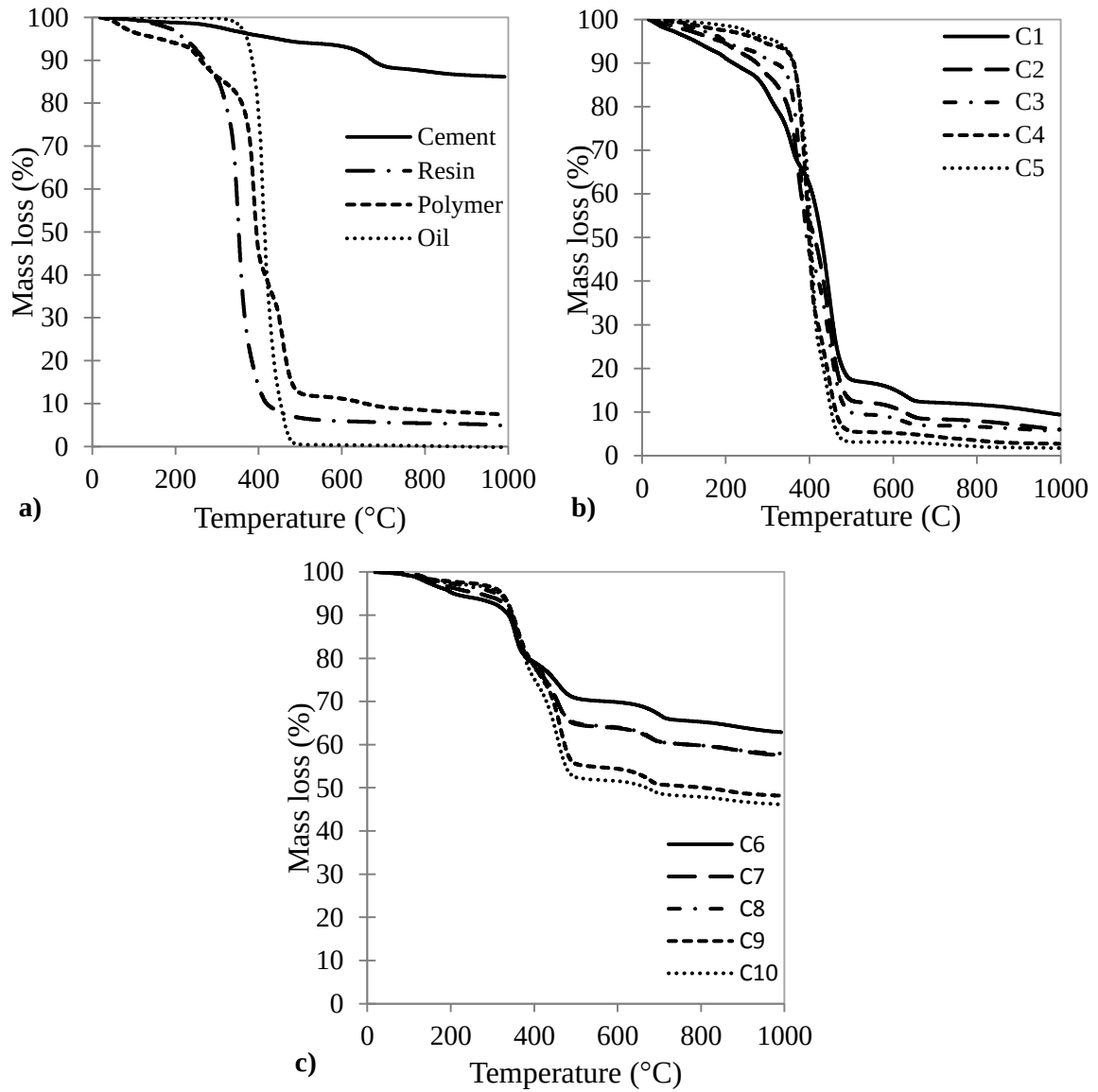


Figure 4.3: Thermogravimetric analysis of a) individual materials of the capsules, b) capsules with different o/w contents without a shell, and c) capsules with different o/w contents with the shell.

4.4 Capsules composition

Generally, the total mass of the capsules used in this study consists of four components: oil, polymer, cement and epoxy. The content of each of these components can be determined from the approximate volumetric proportion of the core and shell in capsules, determined from the SEM images, and from the TGA analysis. A four-equation system with the unknowns being the weight proportions of the four components is built as follows:

$$\left\{ \begin{array}{l} M_o + M_p + M_c + M_e = 1 \\ \rho_{cap} \cdot \left(\frac{M_o}{\rho_o} + \frac{M_p}{\rho_p} \right) = V_{o+p} \\ \rho_{cap} \cdot \left(\frac{M_c}{\rho_c} + \frac{M_e}{\rho_e} \right) = V_{c+e} \\ 0.86 M_c + 0.095 M_p + 0.05 M_e = M_r \end{array} \right. \quad 4-1$$

where, M_o is the mass proportion of oil; M_p is the mass proportion of polymer; M_c is the mass proportion of cement; M_e is the mass proportion of epoxy resin; M_r is the remaining mass proportion of the capsules after heating to 1000°C; ρ_{cap} is the density of the capsules; ρ_o is the density of the oil (g/cm³); ρ_p is the density of the polymer (g/cm³); ρ_c is the density of cement (g/cm³); ρ_e is the density of the epoxy (g/cm³); V_{o+p} is the volume proportion of the core in the capsules; V_{c+e} is the volume proportion of the shell.

The volume and density of the dry capsules were measured by using a Gas Pycnometer AccuPyc II 1340 equipment based on the gas displacement method. The sample weight of the capsules in each test was about 4-9g depending on the capsule type. For all tests, the inert gas used as the displacement medium into the capsules was helium. The capsules tested for their material composition are from C1 to C10.

The imaging analysis of the capsules showed the effect of the *o/w* ratio on the capsules size and core/shell proportion in capsules. The higher the *o/w* ratio used the higher the volume of the capsule occupied by the oil and the lower the volume of the epoxy-cement shell. The core proportions varied from 21% to 58% for the capsules with three coatings (C6 to C10). The remaining masses of all capsules and their individual materials were calculated from the TGA tests at 1000°C (from Section 4.3). Introducing these data into Eq. (4-1), the approximate proportions of the components in capsules can be calculated. Table 4.1 presents the calculated proportions of the capsule materials in terms of weight proportion of the total capsules. These results are only valid for capsules C1 to C10.

The densities that were considered for the capsules and materials are also presented. The amount of rejuvenator presented by these types of capsules is obviously considerably higher than that presented in the literature. For example, the percentage of the rejuvenator was 80% for the capsules type C5, which is 8.5 times greater than the proposed by García et al.

(2010b), which had 9.4% of rejuvenator by mass of capsules. This factor is highly positive for the asphalt rejuvenation ability of these capsules.

Table 4.1: The components of capsules with different amounts of oil with the epoxy-cement shell.

Capsule type	Capsule components			
	Oil (0.922 g/cm ³)	Polymer (1.221 g/cm ³)	Cement (3.141 g/cm ³)	Epoxy (1.217 g/cm ³)
C1	0.27	0.73	-	-
C2	0.48	0.52	-	-
C3	0.58	0.42	-	-
C4	0.71	0.29	-	-
C5	0.80	0.20	-	-
C6	0.18	0.15	0.41	0.09
C7	0.24	0.13	0.34	0.08
C8	0.26	0.12	0.30	0.07
C9	0.37	0.09	0.25	0.04
C10	0.42	0.08	0.23	0.04

It can be observed that the percentage of cement by total weight decreases when the oil content increases; 0.41 for C6 (0.05 o/w) ratio and 0.23 for C10 (1.0 o/w ratio). Furthermore, it is noticed that the amount of epoxy and the amount of polymer, by mass and by volume, of all capsules, are relatively low compared to the content of cement and oil, which indicates that their cost will not be too high. However, these capsules are still expensive because of the amount of cement and epoxy required for making the shell. On the other hand, the capsules without external shell (C1 to C5) are relatively cheap because of the less expensive materials used and reduced production time.

4.5 Mechanical properties of individual capsules

The compressive strength of capsules was measured through uniaxial compression tests on ten capsules of each type. Capsules were loaded until failure at a loading rate of 0.2mm/min. The tests were performed at 20°C and 130°C, using an Instron Model 5969 with a 5kN load cell and an environmental chamber with temperature control.

The two test temperatures represented the cabinet temperature and asphalt mixing temperature. Figure 4.4 shows the average force-displacement curves for selected capsules C1 to C10. Figure 4.4a shows the results of capsules C1 to C5 tested at 20°C, where they showed a limited stiffness and it was affected by the o/w ratio used. The capsules showed a ductile behaviour and the peak load was reached at deformation levels between 0.3mm and 0.6mm. Figure 4.4b shows the results of capsules C6 to C10 tested at 20°C. It can be seen that capsules with a shell showed an initial elastic behaviour, with an average elastic modulus of 525N/mm, independent of the type of capsules studied, and then a sharp decrease when the peak load of the epoxy-cement shell was reached. The peak loads were reached at deformation levels ranging from 0.1mm to 0.2mm, show the brittle behaviour of capsules in the presence of an epoxy-cement shell. As the test continued, the calcium-alginate core was loaded and a second peak could be observed, when the core broke.

Figure 4.4c presents the force-displacement curves, at a temperature of 130°C, for capsules C1 to C5. It is obvious that the higher temperature has a noticeable effect on the capsule strength, as it can be seen that the peak values at 130°C are lower than those at 20°C for the same capsule types. However, the difference is not significant, and the deformation levels are the same for same capsules tested at 20°C.

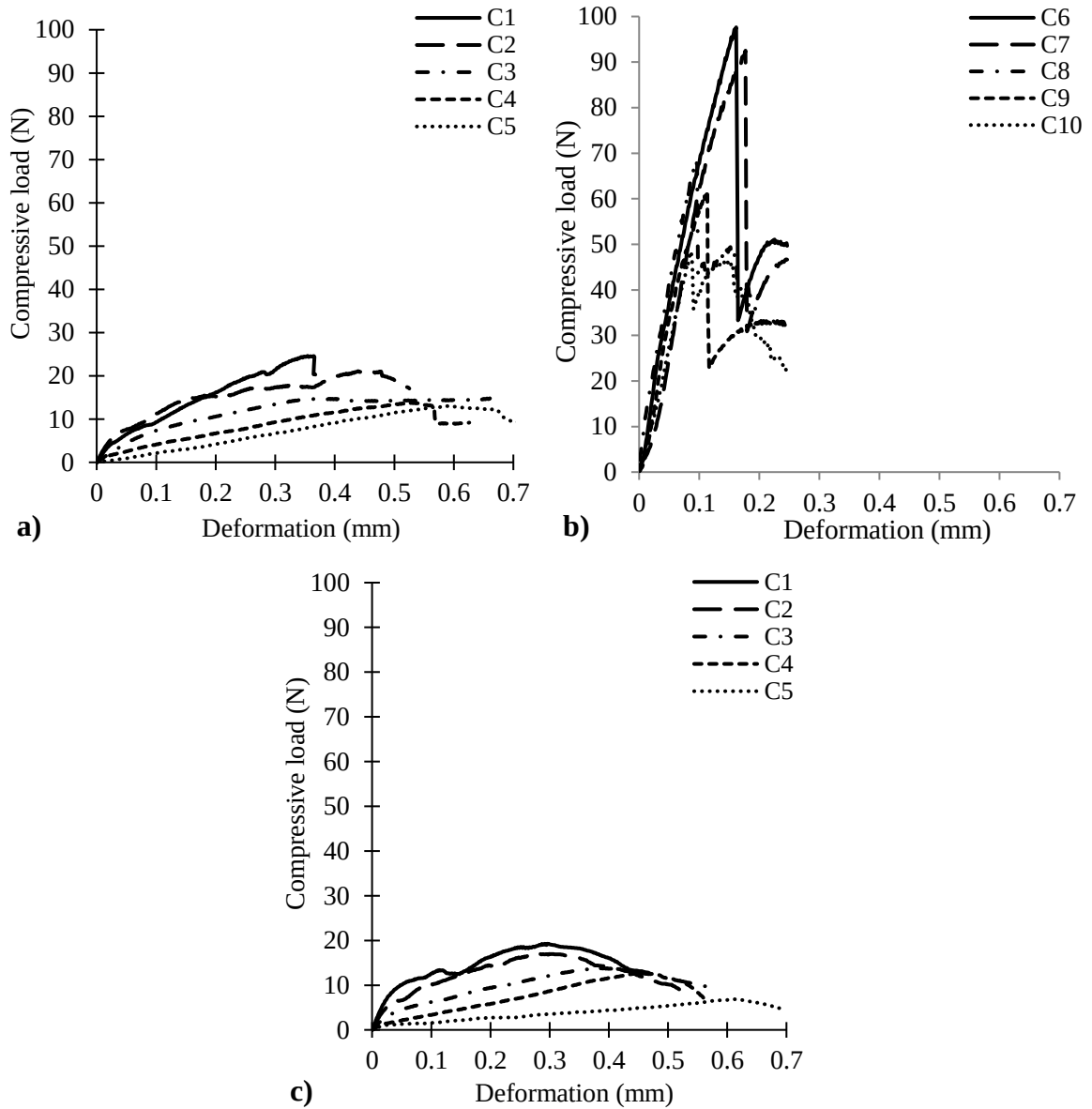


Figure 4.4: Load-deformation evolution in compression tests: a) with external epoxy-cement shell at 20°C, b) without external shell at 20°C, and c) without external shell at 130°C.

Figure 4.5 summarises the results (peak load) of compressive strength of capsules made with different materials and different *o/w* ratios, all tested at 20°C. The results show a large dispersion of peak loads for all types of capsules. In Figures 4.5a and 4.5b, the compressive strength values of capsules from experiments C1 to C10 are presented. These capsules have the same range of *o/w* ratios and differ in the epoxy-cement shell. It can be seen that the compressive strength of the capsules decreases with increasing *o/w* ratio despite the hard shell for the capsules in Figure 4.5b. It is concluded that although the amount of oil leads to

an increase in the size of capsules, this does not necessarily make them stronger. The reason for this is that when there was more oil in the emulsion, the density of the calcium-alginate matrix (see Figures 4.1c and 4.1f) decreased. It can be seen that the average values from Figure 4.5a range from 13N to 26N, depending on the o/w ratio. The average compression values in Figure 4.5b range from 35N to 90N.

Figure 4.5c shows a comparison between the compressive strength of capsules treated with chitosan (C12, C13 and C14) and untreated capsules with similar oil content and external shell (C6, C8 and C10) as detailed in Table 3.1. The chitosan was added as 1% of the total volume of water used in the capsule production. It can be seen that the effect of chitosan on capsule mechanical strength is not clear, showing an increased strength in capsules of 0.2 o/w (C8 and C13) and less strength in capsules of 0.05 and 1.0 o/w (C6, C10, C12 and C14). From these graphics, it can be seen that the compressive strength of capsules treated with cement-epoxy did not show a clear relationship to the o/w ratio, or chitosan treatment. Differences in compressive strength between capsule batches may have occurred due to inconsistencies during the fabrication process, such as the shaking energy, which was done manually.

Furthermore, Figure 4.5d shows the compressive strength of capsules with different epoxy-cement shells (external shell). The external shell has an important effect on production time and cost. It can be seen that the average strength of capsules is significantly affected by the number of external shells. The higher the number of external shell coatings the higher the mechanical strength of the capsules. However, a very high strength is not always a desirable objective, because it may make the capsules far too strong to break under normal traffic loading, which will prevent the capsules from doing what they are designed for.

Figure 4.5e shows the effect of using different amounts of polymer in the core of the capsules (C16, C9 and C17). It was supposed that increasing the amount of polymer increases the density of the alveolar structure in the core, which would lead to stronger capsules. However, the amount used has to be balanced to the point that the capsules survive the mixing process and free the rejuvenator when broken.

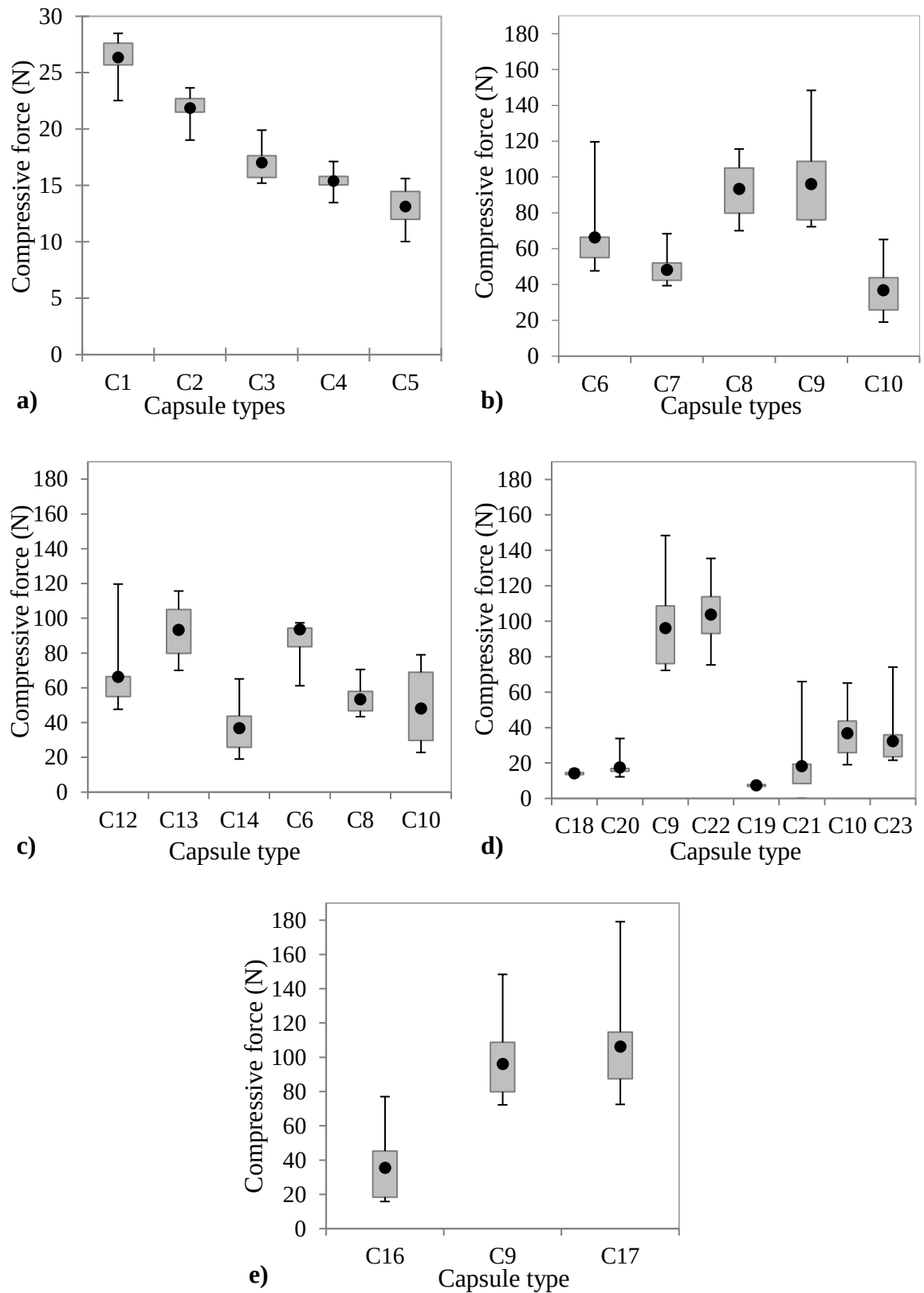


Figure 4.5: Compressive strength of capsules depending on the a) o/w ratio for capsules without a shell, b) o/w ratio for capsules with shell, c) chitosan treatment, d) number of cement-epoxy coatings, and e) mass of alginate. All tested at 20°C.

The results show a large increase in strength from 7.5 to 15g but only a minor effect for higher polymer contents. Also, the variation in peak loads increases with the polymer in the oil/water mixture. It can be seen that once the amount of alginate was higher than 15g, the compressive strength of capsules was constant and approximately 100N, while for less than 15g the strength reduced to 35N. The reason for this is that the calcium-alginate core of capsules type C16 was very oily and soft, which affected the bond between the epoxy-cement layers and the inner core.

Finally, Figure 4.6 presents the compressive strength of capsules from experiments C1 to C5, tested at 130°C. It can be observed that the average force values measured at 130°C reduced by more than half with respect to values measured at 20°C (Figure 4.5a), which proves that the compressive strength of the capsules is highly influenced by the test temperature. Previous research (García et al., 2011a) showed that the minimum strength necessary to resist the mixing and compaction process for capsules of similar size to those in this research was 14N. Hence, based on the results obtained in this study, capsules made with 0.5 and 1.0 o/w ratio (i.e. types C4 and C5) are not recommended to be used inside asphalt mixtures for self-healing purposes.

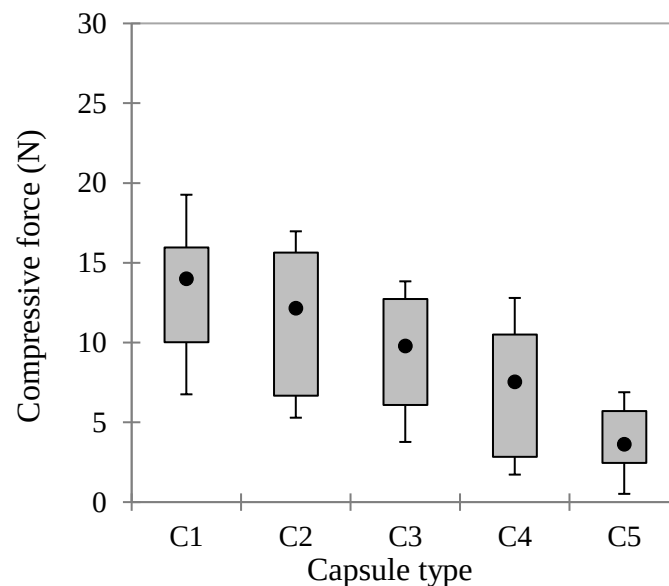


Figure 4.6: Compressive strength of capsules with respect to the o/w ratio tested at 130°C.

4.6 Capsule ability to release oil in bitumen

The ability of the capsules to release the rejuvenator was investigated from the change in the bitumen chemical composition after being exposed to broken capsules. Capsules were inserted in a hot bitumen layer of dimensions 5*5cm and up to a thickness of approximately 5mm. After cooling, capsules were mechanically broken with a hammer. The specimens (binder and capsules) were placed at room temperature for various times (2, 6, 12, 14, 16, 24, 30, 48, 50, 60 and 72) hours. Later, samples were collected and analysed using Fourier Transform Infrared spectroscopy (FTIR). The FTIR spectrum was obtained in the absorption mode with the wave length ranging from 400 to 4000cm⁻¹, with a resolution of 4cm⁻¹. A reference sample of pure bitumen was also analysed for comparison purposes. The effect of the sunflower oil on the bitumen was evaluated from a comparison of the absorption peak at wave lengths of 1700 to 1800cm⁻¹ (as previously explained in Section 3.5.4).

Figure 4.7 shows the concentration of the diffused oil in the bitumen at several rest times. The area method (RILEM method) was used to measure the differences in the oil concentration of samples with respect to their rest time. It is observed that the bitumen was affected by the oil immediately after the capsules were broken. The maximum change is detected between 6h and 12h. This is a clear signal that oil had diffused from the capsules into the bitumen. The reduction in the aromatic index after 12h is likely related to the oil diffusion equilibrium in the test sample because only one capsule was used in each specimen.

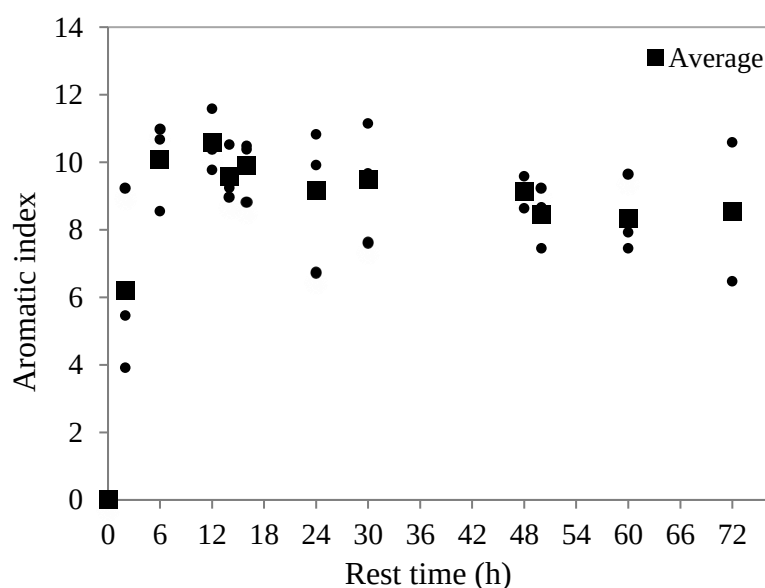


Figure 4.7: The diffusion of oil in bitumen with time.

Chapter 5: Effect of Capsules on Asphalt Mechanical Properties

5.1 Introduction

In this chapter, an experimental study to investigate the ability of the capsules to rejuvenate aged asphalt mixtures and to induce self-healing is presented. The tests analyse the effect of capsules on the mechanical behaviour of aged asphalt specimens subjected to cyclic loading and the influence of rest periods on the self-healing properties of asphalt mixture containing capsules. The capsule's effect is visualised using computer tomography scans (CT scans).

An overview of the effect of capsules on the durability and mechanical performance of asphalt mixture is also presented in this chapter. With this purpose, an extensive experimental programme has been performed on asphalt mixtures containing capsules, based on standardised tests commonly used by industry. Standard testing protocols have been used to evaluate the most important properties, such as water sensitivity, particle loss, stiffness, rutting resistance and fatigue. All tests were performed on samples with and without capsules for comparisons.

5.2 Stiffness and deformation evolution of aged asphalt mixture

The capsules were added to the aged asphalt mixture just 15sec before the end of the remixing process. The mass proportion of capsules type C10 and C20 were 6% of total asphalt, while capsules type C4 were added as 3% of the total asphalt. Fewer capsules from type C4 were used to compensate for the high proportion of oil in these capsules. Cylindrical test specimens with a diameter of 100mm and final height of approximately 50mm were

compacted using a gyratory compactor with a maximum of 250 gyrations. Mixtures of aged and unaged asphalt without capsules were fabricated for comparative purposes.

The stiffness evolution of selected test samples with and without capsules (C4) is shown in Figure 5.1. The stiffness (K) of the test sample without capsules increased steadily, which is a sign that the packing level of aggregates increased during cyclic loading. On the other hand, the stiffness of the test sample with capsules decreased after the first 500 cycles, which shows that capsules broke during testing. After the rest period, the stiffness of the test sample without capsules remained constant, while the stiffness of test sample containing capsules increased, which may be due to self-healing of cracks in the test specimens.

The evolution of vertical accumulated deformation (d) of asphalt containing capsules (C4) is shown in Figure 5.1b. During the initial cycles, there was approximately 1 to 2mm of imposed deformation. Thereafter, the test specimens with and without capsules had different deformation trends. The specimens containing capsules showed higher deformation rate than the test specimens without capsules. The reason for this is that capsules broke during cycling loading and the oil was released in the asphalt mixture. Moreover, the test specimens without capsules showed a similar deformation rate before and after the rest period. However, the deformation rate of test specimens containing capsules was higher after the rest period, which shows that the oil in the capsules reduced the viscosity of the asphalt mixture. The rest period was 48h.

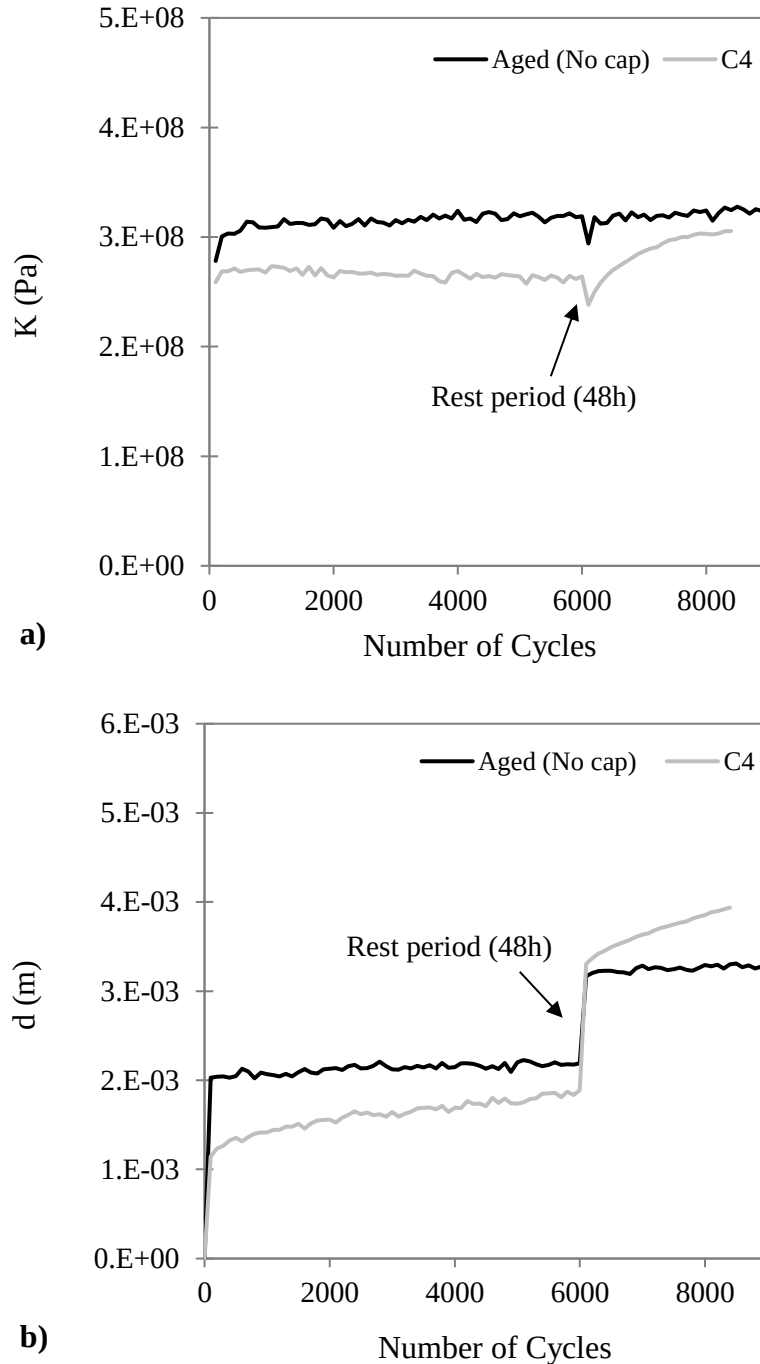


Figure 5.1: Variation of (a) stiffness (K) and (b) permanent deformation (d) with loading cycles in asphalt mixture with and without capsules.

Moreover, Figure 5.2 shows the relationship between the average stiffness before (K^{1st}) and after (K^{2nd}) the rest period. Figure 5.2a shows the relationship between aged and unaged test samples, without capsules, while Figure 5.2b shows the relationship between aged test samples containing capsules types C20, C10 and C4. It can be observed that the stiffness

ratio did not change consistently with rest time for test specimens without capsules and it was higher on average for aged test specimens. The reason for this is that 48h were not enough for bitumen to flow into cracks and repair them inside the asphalt mixture. On the other hand, the stiffness ratio of asphalt mixture containing capsules type C4 increased approximately 15% between 3h and 48h, which is a clear sign that the oil was released and cracks were repaired. Moreover, the stiffness increased progressively with the rest period. Note that the stiffness of asphalt mixture containing capsules type C20, the strongest, did not change significantly. This shows that these capsules were too strong and did not break and release their content. Moreover, changes in test specimens containing capsules type C4, without an epoxy-cement shell, are higher than in test specimens containing capsules type C10, with three layers of cement-epoxy around the calcium-alginate core. This shows that more oil was released from capsules type C4 and that these were more able to change the properties of the asphalt mixture.

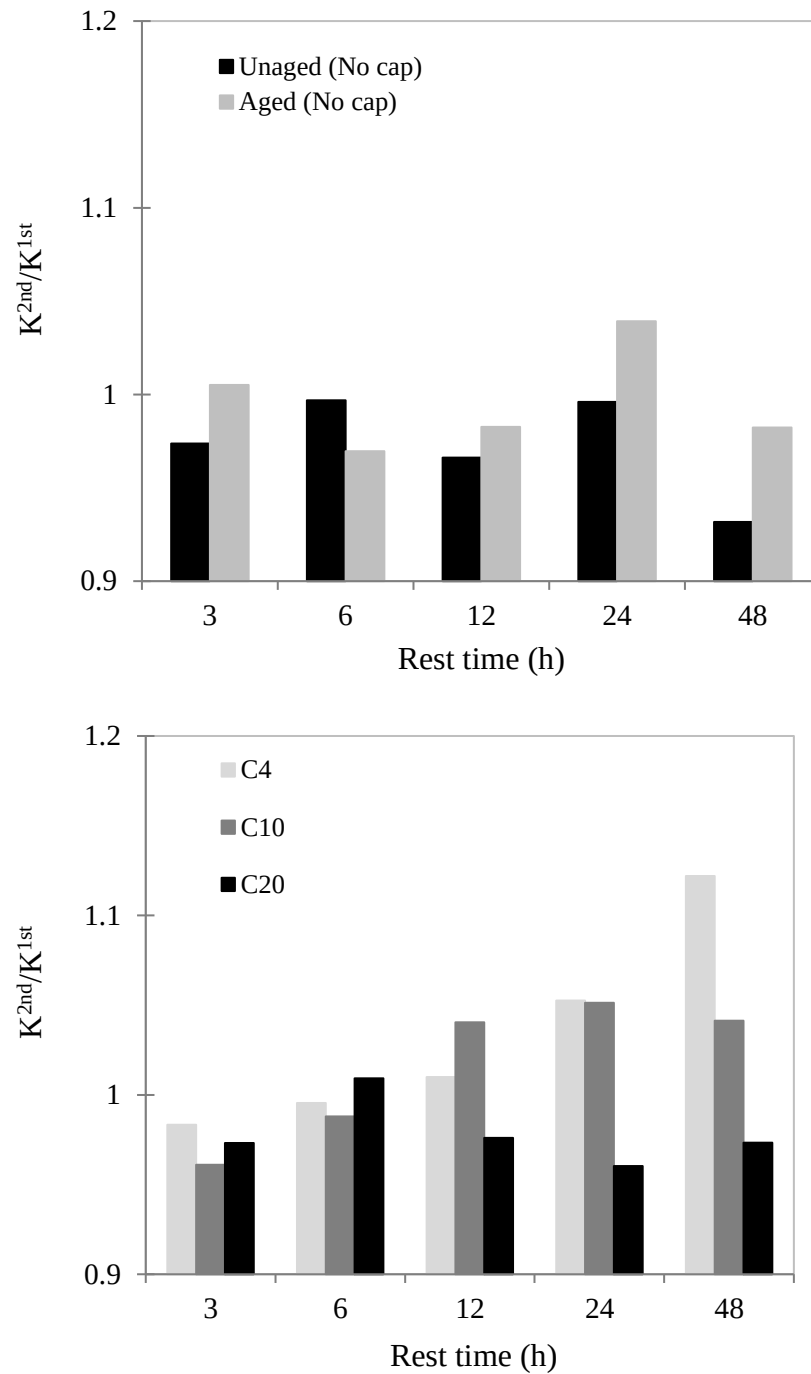


Figure 5.2: Variation of stiffness with rest time for test specimens (a) without capsules and (b) with capsules.

Figure 5.3 shows the relationship between the average deformation of test samples before (DS^{1st}) and after (DS^{2nd}) the rest period. Figure 5.3a shows the relationship between aged and unaged test samples, without capsules, while Figure 5.3b shows the relationship for aged test samples containing capsules type C20, C10 and C4. It can be observed that the

deformation levels of test samples without capsules did not change with the rest period, while in general, they increased with the rest period for test specimens containing capsules type C10 and C4. The reason for this could be that the viscosity of bitumen in the asphalt mixture containing capsules type C10 and C4 was modified by the oil diffusion coming out from the capsules. No effect was noticed for capsules type C20.

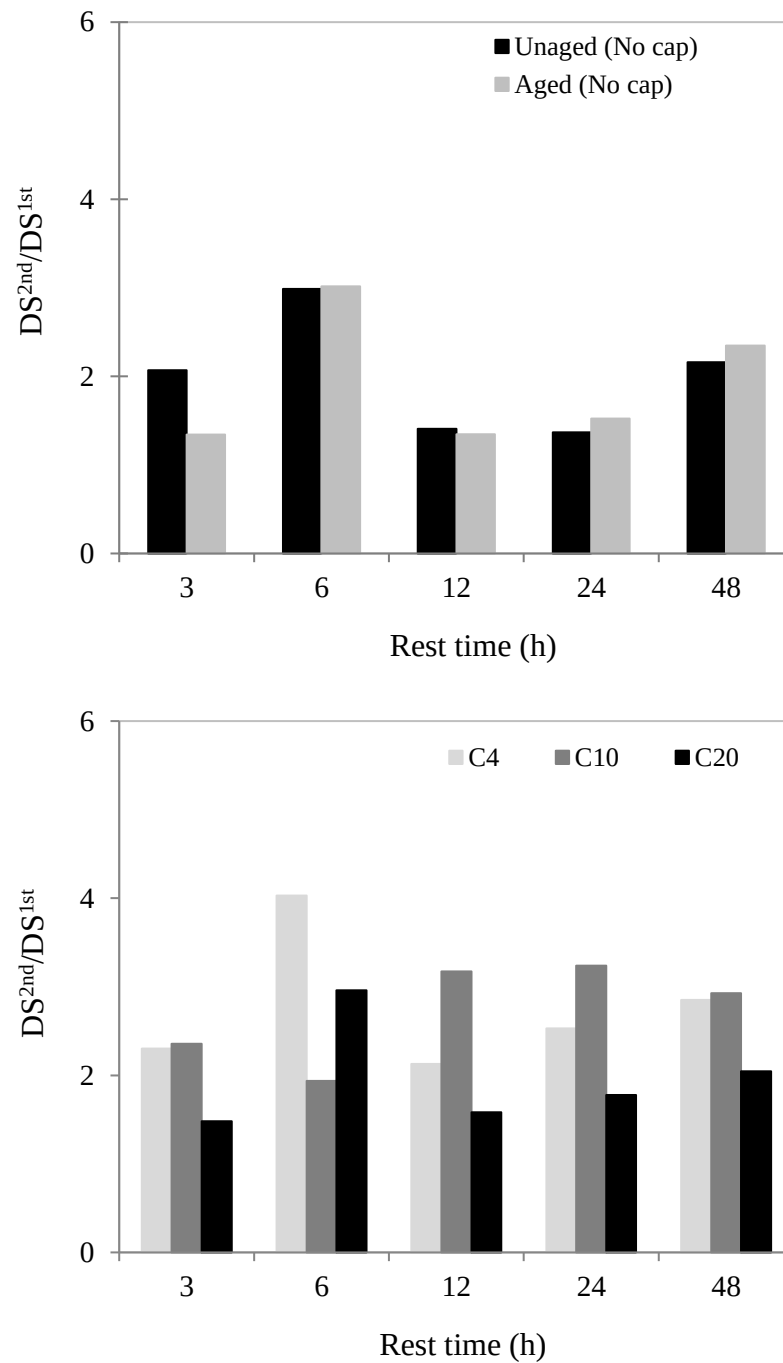


Figure 5.3: Variation of deformation slope with rest time for test specimens (a) without capsules and (b) with capsules.

5.2.1 Assessment of oil release

To assess the amount of oil released from the capsules before and after loading, mastic samples were obtained (section 3.5.4) from the test specimens and tested using FTIR spectrometry. For comparison purposes, oil, aged bitumen extracted from asphalt test samples and aged bitumen mixed with 5% and 10% of oil by mass were also tested using FTIR. These amounts were chosen because they are representative of the amount of oil contained in the capsules. Figure 5.4a shows the normalized absorbance curves of the oil and binders for wavenumbers ranging from 1700 to 1800 cm^{-1} . The binders modified with oil show a peak at $\sim 1746\text{cm}^{-1}$, with the absorbance value being proportional to the oil content.

Furthermore, Figure 5.4b compares the area under the absorbance curve for the different materials studied. Samples were taken from asphalt test specimens containing capsules that (1) had been loaded and let to rest for 48h and (2) had not been loaded. It was found that bitumen from test samples that had not been loaded contained oil because some capsules broke during compaction. Moreover, the peak for capsules type C10 and C4 was higher than the peak for capsules type C20, which shows that less capsules type C10 and C4 resisted mixing and compaction. In addition, the absorbance curves of all the test samples containing capsules show higher area after loading-resting and capsules type C4 released substantially more oil than the other capsules.

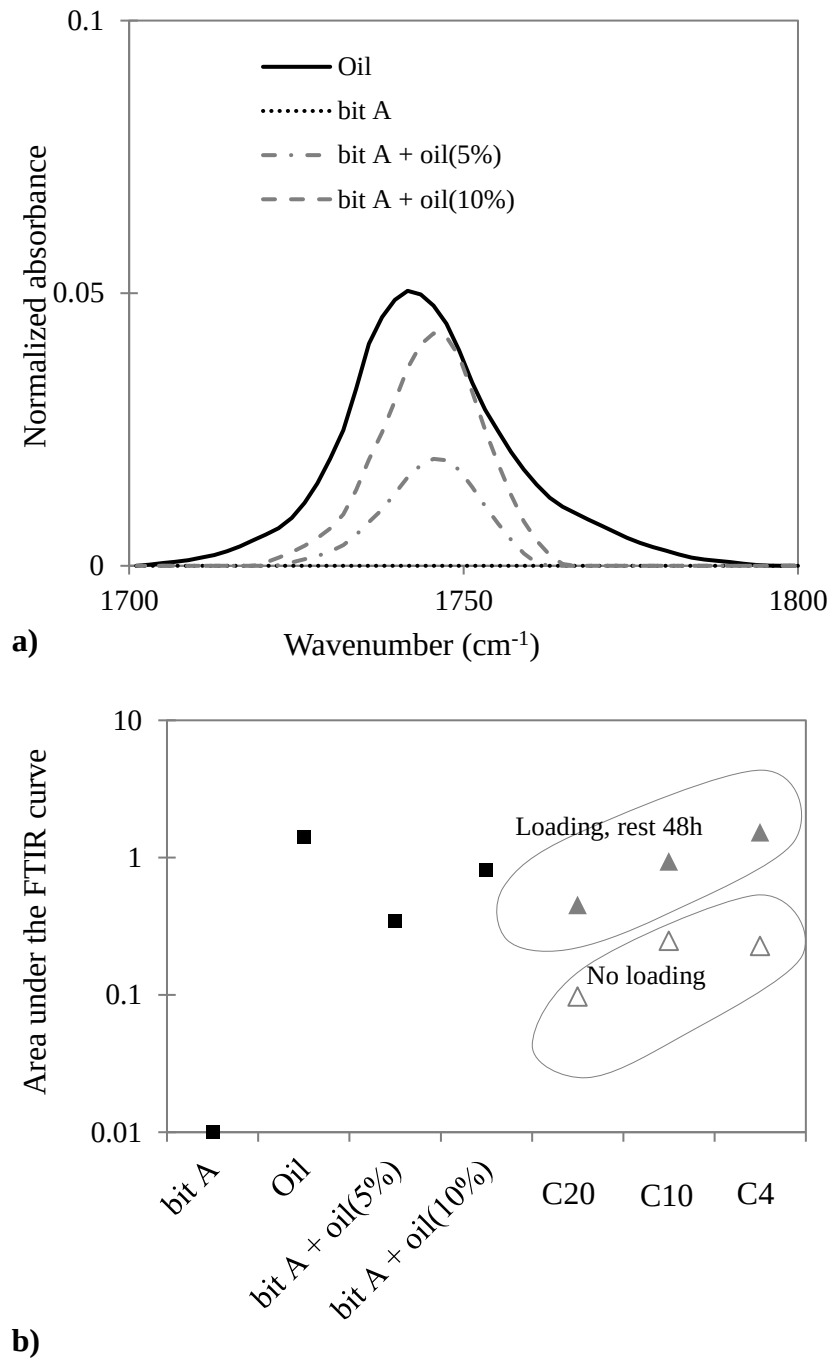


Figure 5.4: Oil release (a) FTIR testing results. (b) Areas of the normalized absorbance curves.

5.2.2 Assessment of aged asphalt rejuvenation

Figure 5.5 shows the percentage of capsules along the vertical axis of a selected test specimen of 40*40*50mm containing capsules type C4. This test specimen was damaged under cyclic loading and cracks with average width 600 μm were created. It can be observed

that the concentration of capsules was higher at the bottom of the test specimen. This may be due to capsules being mixed in the last place and not uniformly distributed in the mixture. Moreover, the change in air voids (dV) was determined during the rest period. The CT-scanned asphalt specimens were divided in a stack of cross sectional images and the relationship between the air voids before and after the rest period was calculated as:

$$dV = \frac{V_x - V_d}{V_d} \quad 5.1$$

where, V_d is the percentage of air voids, including cracks, in the test specimens' cross section after loading and, V_x is the percentage of air voids, including cracks, in the test specimens' cross section after x days resting.

A negative value for dV means that there was a decrease of the air voids during the resting period and this can be interpreted as cracks closing. As can be observed, there was a reduction of air voids all along the test specimen, which occurred mainly during the first 4 days. The greatest reductions in air voids were located approximately 3mm from the bottom of the section containing capsules. This may be due to the oil and bitumen flowing down under the effect of gravity.

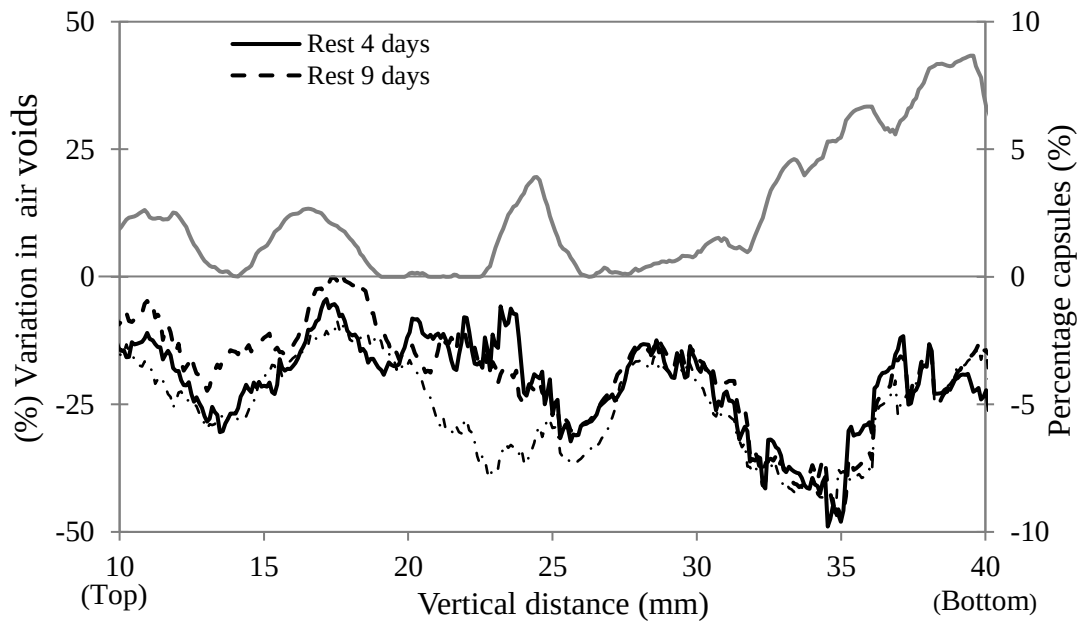


Figure 5.5: Percentage of C4 capsules and variation in air voids vs. vertical distance.

To confirm that changes in the air voids content were due to the reduction of crack size, Figures 5.6 shows cracks without surrounding capsules and Figure 5.7 shows cracks near capsules. Both figures present selected sections of the computed tomography scans of the asphalt mixture, after mechanical testing, and after 4 days resting at 20°C. It can be observed that cracks partially healed in the areas around the capsules, while they did not heal in areas without capsules. The possible reason for crack closure is that the oil coming out of the capsules reduced the viscosity of bitumen, which favoured the drainage of bitumen into the cracks.

Finally, a 3-Dimensional representation of a single crack before and after 4 days resting at 20°C was reconstructed from CT-Scan images, see Figure 5.8. This crack had a total length of about 20mm and a maximum width of 500µm. Moreover, at each end of the crack, there were capsules (coloured yellow). It can be observed that before resting the crack was continuous between the capsules, while after the rest period the crack was partially filled around the capsules. Moreover, a closer look at the planar CT images shows that the crack width was reduced to approximately 60µm at its widest point. These results prove that capsules are able to induce crack healing in asphalt.

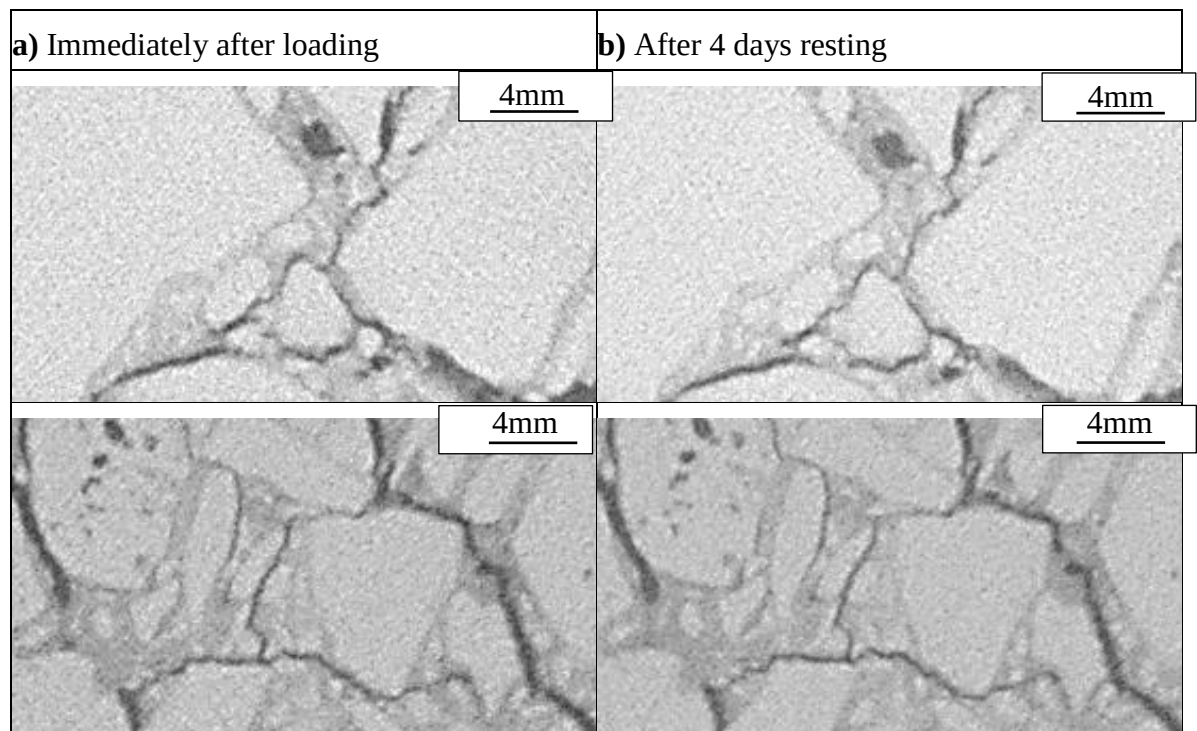


Figure 5.6: Examples of asphalt mixture without capsules, (a) after mechanical testing, (b) after 4 days rest at 20°C.

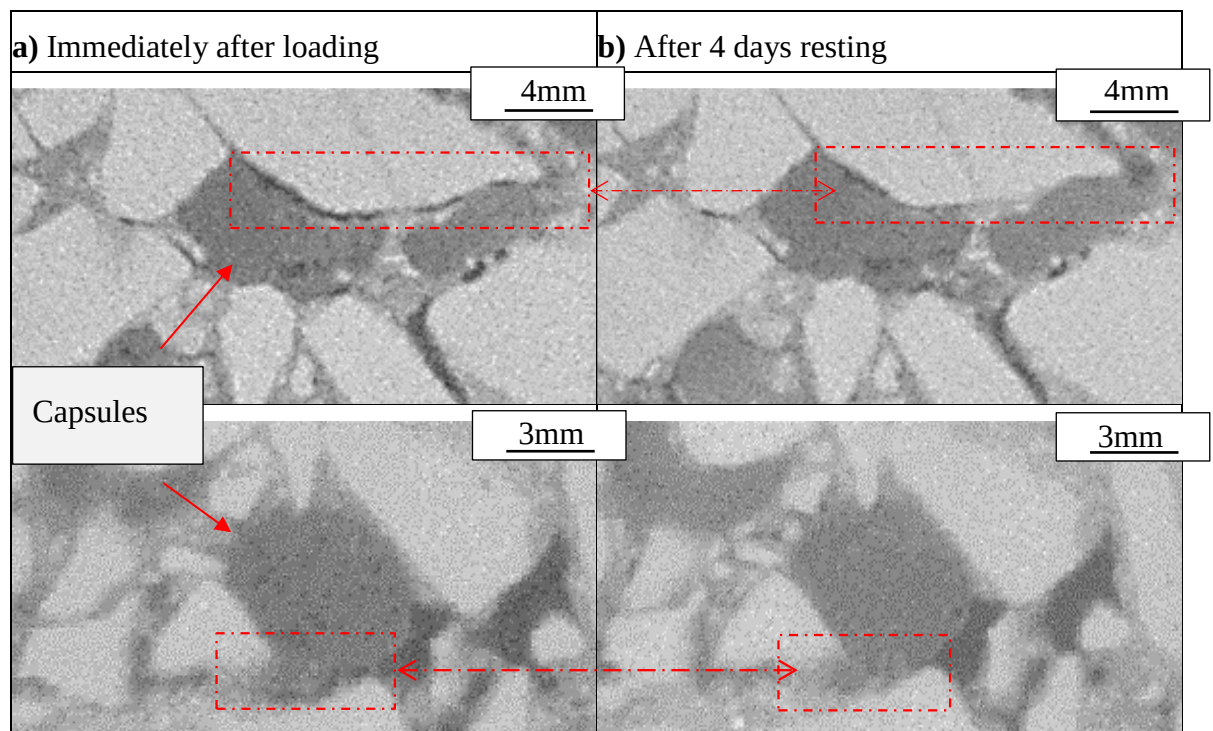


Figure 5.7: Examples of asphalt mixture with capsules, (a) after mechanical testing, (b) after 4 days rest at 20°C.

Note that these cracks were exceptionally wide (approximately 500 μ m) and that in a real road situation capsules will start healing much smaller cracks (shorter and narrower), for which the healing efficiency is expected to be much higher (García, 2012). For this reason, future research should focus on the maximum width of crack that can be healed at a particular temperature by the action of capsules.

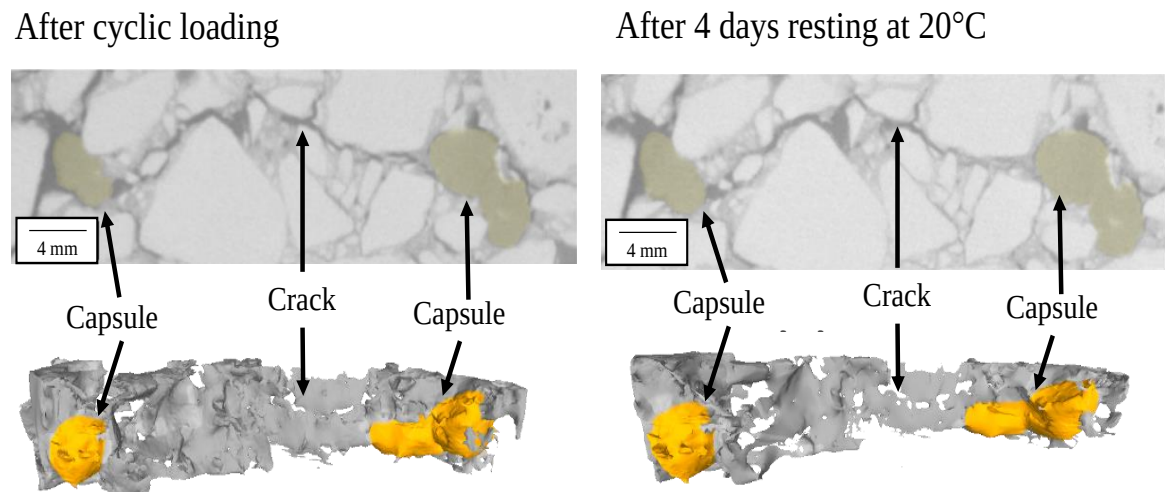


Figure 5.8: A crack healing due to the effect of capsules (a) after cyclic loading, (b) after 4 days resting at 20°C.

5.3 Effect of capsules on mechanical properties of asphalt mixture

The following tests were experimentally performed with real unaged asphalt concrete to measure the effect of capsules (type C2) on asphalt durability and strength. Cylindrical test samples were used in all tests with dimensions of 100mm diameter and approximately 50mm thickness, compacted by a gyratory compactor with a maximum of 250 gyrations. More details of sample manufacturing and properties can be found in Sec. 3.3.2, and the principles of the following tests were presented in Sec. 3.5.2. This experimental program is presented in Figure 5.9.

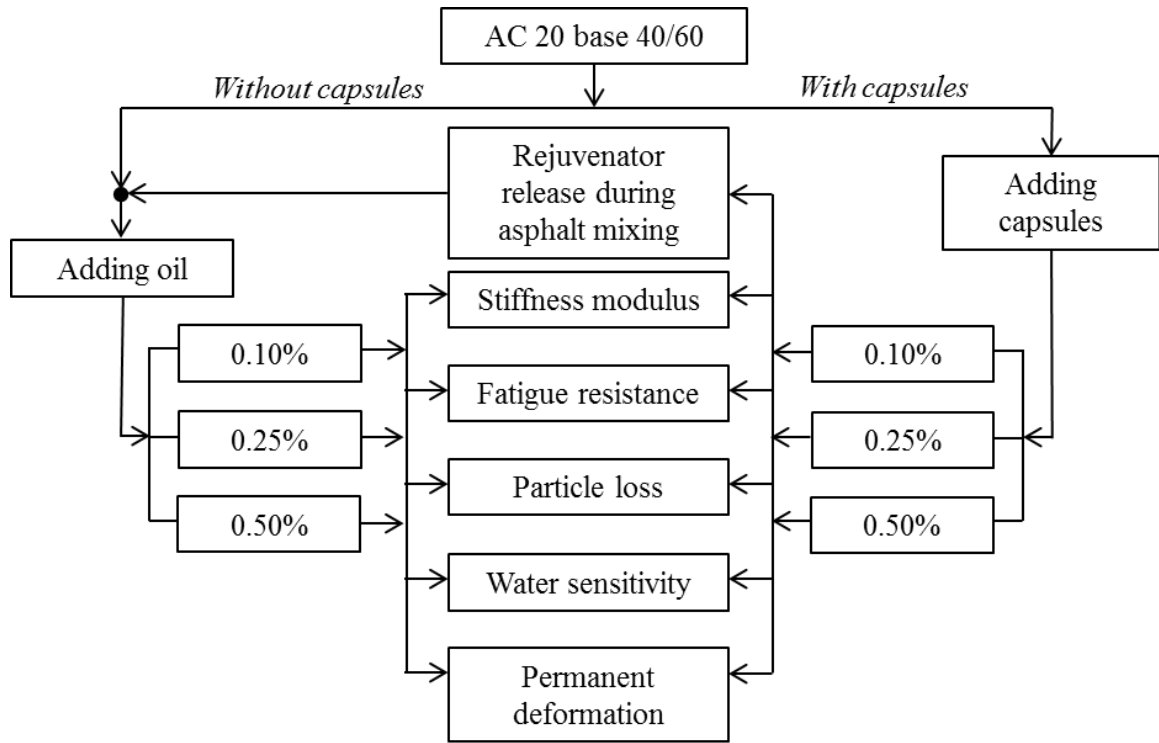


Figure 5.9: Flowchart of experimental programme used to study effect of capsules (C2) on mechanical properties of asphalt mixture.

5.3.1 Oil released by capsules during asphalt mixing and compaction

The average amount of oil release from broken capsules, defined as the ratio of oil released from capsules broken during mixing and compaction to the total oil content of capsules in the mixture, identified in asphalt specimens containing 0.1%, 0.25% and 0.5% of capsules was 1.12%, 1.27% and 1.53%, respectively (see Figure 5.10). It has been assumed that the oil released during mixing and compaction was uniformly dispersed in the asphalt mixture. Note that not all the oil release is due to the capsules broken during mixing and compaction and some may originate from the oil released due to depolymerisation of the outer layers of capsules at high temperature. To compensate any effect that the released oil could have on the self-healing and mechanical properties of asphalt, 0.10g, 0.25g and 0.50g of sunflower oil, corresponding approximately to 0.001%, 0.002% and 0.004% of the total mass of the asphalt mixture, were added to each 14kg batch of asphalt mixture without capsules. These added amounts of oil are similar to those released in the mixture during the mixing and compaction processes.

It is interesting to observe that the air void content was 8% lower on average in asphalt mixtures containing capsules, as presented in Table 5.1. A possible reason for this is that capsules can adapt their shape to the aggregates and their naturally spherical shape makes them flow better during mixing and compaction.

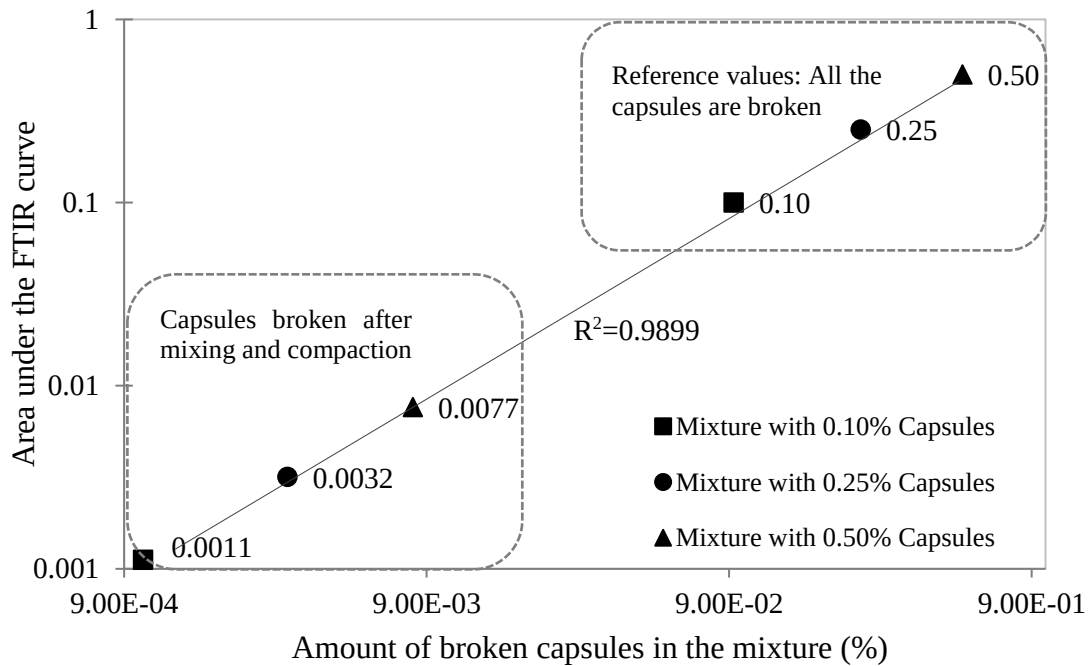


Figure 5.10: Amount of oil release from broken capsules in the mixing and compaction process.

The results in the figure are average for several samples tested. In general, increasing the amount of sunflower oil in asphalt without capsules reduced the air voids content of the mixture from 5.2% to 4.6%. Variation of air voids between nominally identified specimens was low ($\leq 0.5\%$).

5.3.2 Rutting resistance

Figure 5.11 shows an example of the average axial strain and stiffness modulus variations when the test samples were subjected to uniaxial cyclic compression, using the conditions recommended in DD226 (BS DD, 2002), 100kPa, 1800 cycles and 30°C. The average axial strain at the end of testing, see Table 5.1, was 0.84% for asphalt mixtures, both with and without capsules. Oil was added to samples without capsules to simulate the oil released from capsules in samples with capsules. There is no clear difference between test samples

with and without capsules. For that reason, these results show a satisfactory resistance to permanent deformation of asphalt mixture with capsules: they did not have any effect and for this reason, they can be used safely on the road.

Furthermore, the results of the slope of deformation or deformation rate (see Table 5.1) are very similar for the different asphalt mixtures studied. This suggests that cyclic compression loading did not break many capsules, or cause substantial oil release in the specimen. In addition, no rest time was given between loading cycles to allow oil diffusion. This could have led to decreased deformation due to self-healing of asphalt cracks. This will also be an interesting topic for future research.

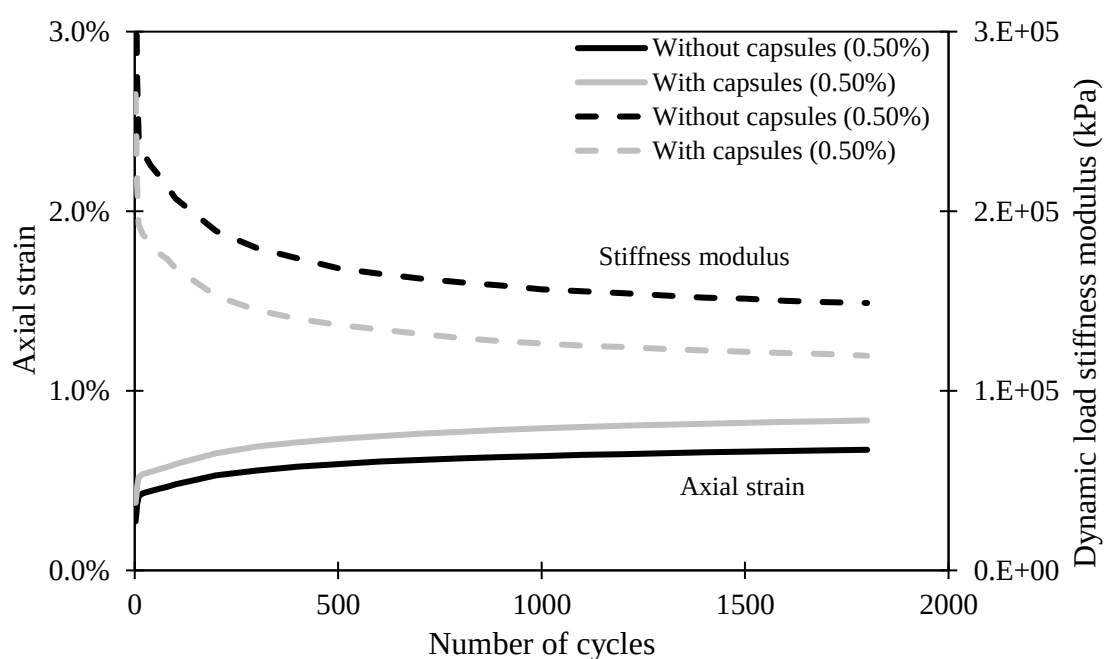


Figure 5.11: Deformation and stiffness evolution under uniaxial cyclic compression of test samples without capsules and containing 0.5% of capsules (C2).

5.3.3 Stiffness modulus and resistance to fatigue

The stiffness moduli for the different asphalt mixtures measured at 20°C are presented in Table 5.2. Asphalt specimens with capsules had a lower stiffness than the equivalent specimens without capsules. The average reduction in modulus values varied from 23%, for 0.10% by mass of capsules, to 38% for 0.25% by mass of capsules. This may have happened

because at 20°C, the stiffness of capsules was approximately 200N/mm lower than that of the aggregate particles and the bitumen used. As a hypothesis, this effect could have been magnified by the size of the capsules because they are forming part of the solid skeleton and virtually acting as soft aggregates. This could be corrected in future research by reducing the capsule diameter.

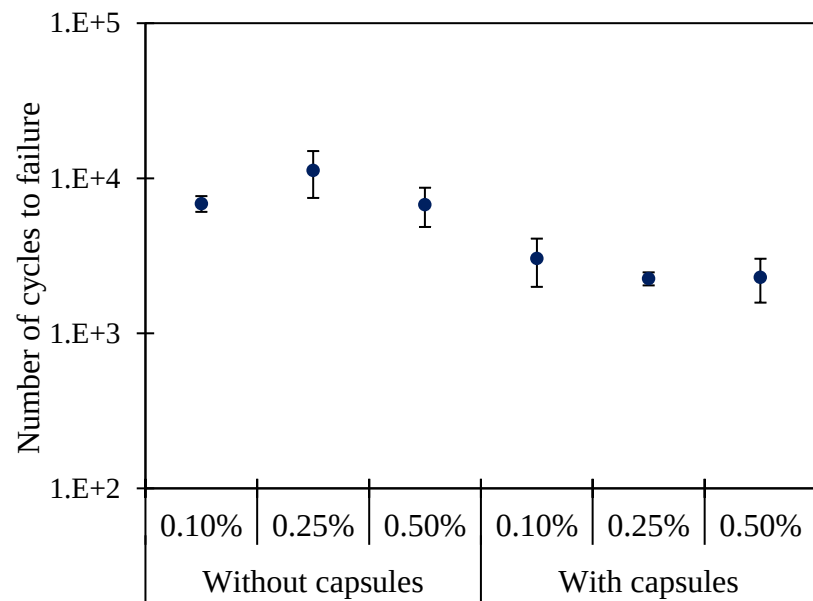
The number of cycles until indirect tensile fatigue failure of the different asphalt mixtures is depicted in Figure 5.12a. The number of cycles to failure was obtained for a single value of maximum tensile stress applied at the centre of the specimen (600kPa). Therefore, no fatigue line could be drawn. Moreover, note that the number of cycles to fatigue failure has to be compared on a logarithmic scale (Callister Jr and Rethwisch, 2012). In this sense, it can be observed that the amount of capsules in asphalt test samples did not have a significant influence on the fatigue life of the test specimens with capsules. On the other hand, the fatigue life of asphalt test specimens containing capsules was approximately 15% lower than specimens without capsules.

It is well-known that in either stress- or strain-controlled fatigue tests, the number of cycles to failure decreases with increasing applied stress or strain level (Matthews et al., 1993). Under diametric loading, by linear elastic analysis, the maximum horizontal tensile strain (ϵ_x^{max}) occurring at the centre of the specimen is:

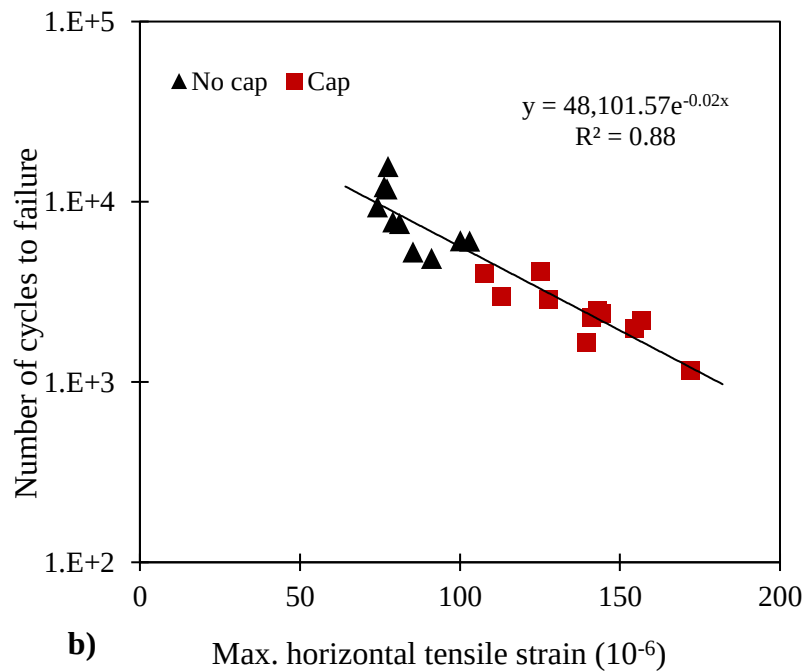
$$\epsilon_x^{max} = \frac{\sigma_x^{max} \cdot (1 - 3\nu)}{S_m}, \quad 5.2$$

where S_m is the stiffness modulus (MPa); σ_x^{max} is the maximum tensile stress at the centre of the specimen; ν is the Poisson's ratio (0.35). Before the initiation of cyclic loading in the fatigue tests, the stiffness modulus was also measured in stress-controlled conditions, with the application of 5 load pulses, at the target loading level (600kPa). In Figure 5.12b the number of cycles to failure is plotted against the initial maximum horizontal tensile strain determined by using Eq. (5.2). The two sets of data, representing asphalt specimens with and without capsules, can be fitted with a single fatigue function. Moreover, the coefficient of determination (R^2) is reasonably good, 0.88. On this basis, the analysis therefore suggests that the capsules do not decrease the fatigue resistance of asphalt mixtures. The most

important factor influencing the lower number of cycles resisted by the specimens with capsules was their lower stiffness modulus when compared to specimens without capsules.



a)



b)

Figure 5.12: Number of cycles to failure vs a) type of asphalt mixture and b) maximum horizontal tensile strain.

5.3.4 Particle loss, indirect tensile strength and water damage susceptibility

Results of particle loss test (see section 3.5.2) are listed in Table 5.1 and Table 5.2, respectively. Mass loss values, in dry conditions, varied between 16.7% and 20.9% for test specimens with and without capsules, respectively. Specimens with capsules had approximately 2.8% less mass loss than specimens without capsules. In addition, particle loss was not systematically affected by the amount of capsules in the mixture. Visual inspection of specimens with capsules showed that capsules could resist the impacts with the drum's walls, see Figure 5.13.

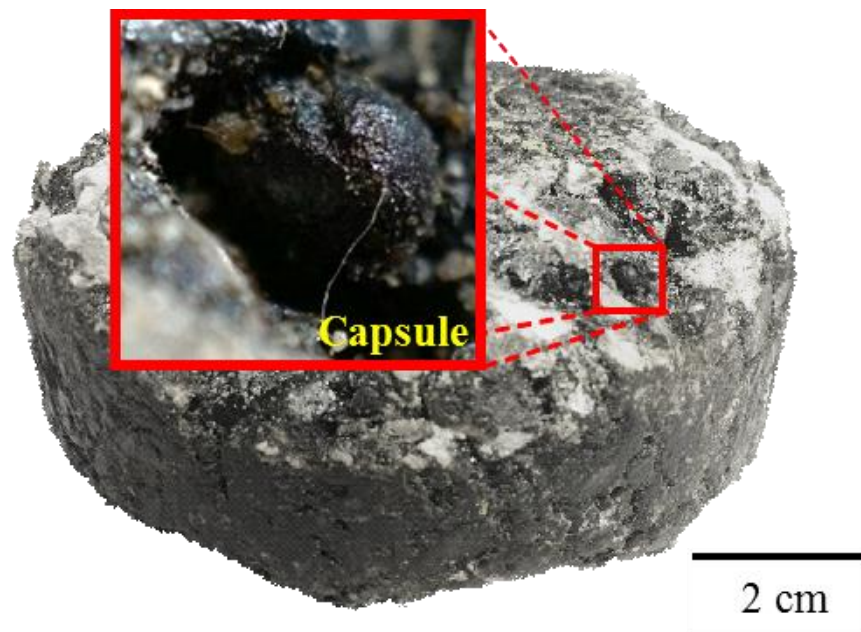


Figure 5.13: Image of a capsule exposed to the air after particle loss testing.

Furthermore, capsules decreased the moisture damage susceptibility of asphalt by 4.4%. The reason for the improvement in particle loss could be that capsules adapted their shape to the surrounding aggregates, reducing the air voids content and creating more homogeneous mixture..

Moreover, Table 5.1 presents the indirect tensile strength (ITS) values of specimens after dry and wet conditioning, and the relationship between the strength of test samples with capsules and without capsules (strength ratio, ITSR). ITSR values were approximately 100% for all tested materials, which means that moisture damage did not influence the ITS results.

In addition, despite some variation in ITS values of asphalt mixtures with capsules, the content of capsules did not affect the tensile strength of specimens.

These results show that capsules were strongly bonded into the asphalt structure due to strong adhesion to bituminous mastic and to the good interlocking with aggregates. In addition, water damage was reduced by the action of capsules as they reduced the air voids and produced more cohesive mixture. This suggests that water was not able to penetrate the mastic layer around the capsules.

Table 5.1: Properties of asphalt mixture with and without capsules.

Property measured		Units	Without capsules			With capsules		
			0.10%	0.25%	0.50%	0.10%	0.25%	0.50%
Air voids content		%	5.2	4.7	4.6	4.5	4.4	4.4
Particle loss	Dry conditioning	%	20.9	19.1	20.7	18.0	16.7	17.7
	Wet conditioning	%	17.9	18.1	17.8	12.8	16.4	11.3
	After crack healing	%	-	-	10.5	-	-	7.2
Water sensitivity	ITS dry conditioning	N	1470	1482	1302	1315	1561	1435
	ITS wet conditioning	N	1483	1461	1420	1412	1583	1418
	ITSR	%	101	99	109	107	101	99
Rutting	Strain	%	0.8	0.97	0.75	0.83	0.78	0.89
	Strain rate	mm/cyc	10.1E-07	8.2E-07	8.2E-07	7.6E-07	7.9E-07	9.6E-07
Stiffness modulus		MPa	9485	10937	9516	7325	6799	6886

Table 5.2: Standard deviation values of the results presented in Table 5.1.

Property measured		Units	Without capsules			With capsules		
			0.10%	0.25%	0.50%	0.10%	0.25%	0.50%
Air voids content		%	0.2	0.5	0.4	0.3	0.1	0.1
Particle loss	Dry conditioning	%	3.0	0.7	2.7	1.0	0.9	2.1
	Wet conditioning	%	1.4	1.5	1.8	0.9	2.9	1.8
	After crack healing	%	-	-	1.2	-	-	0.3
Water sensitivity	ITS dry conditioning	N	37	81	53	76	60	147
	ITS wet conditioning	N	14	23	60	160	120	153
	ITSR	%	-	-	-	-	-	-
Rutting	Strain	%	0.07	0.33	0.14	0.16	0.02	0.23
	Strain rate	mm/cyc	2.0E-07	2.5E-07	3.0E-07	0.6E-07	0.6E-07	3.1E-07
Stiffness modulus		MPa	819	454	1350	851	613	371

Figure 5.14 provides a summary of the effect of manufactured capsules on the mechanical and self-healing properties of the asphalt mixture. These capsules positively affected the compactibility, particle loss and self-healing properties, whereas the stiffness modulus was negatively affected. Susceptibility to water damage and permanent deformation was similar in asphalt with and without capsules. Capsules were strongly bonded to the asphalt mixture and water did not affect the capsule-bitumen interface more than it does the aggregate-bitumen interface. It is hypothesized that with the reduction in the size of capsules, and consequently the number of aggregate-capsule-aggregate bridges, the stiffness modulus of asphalt can be preserved.

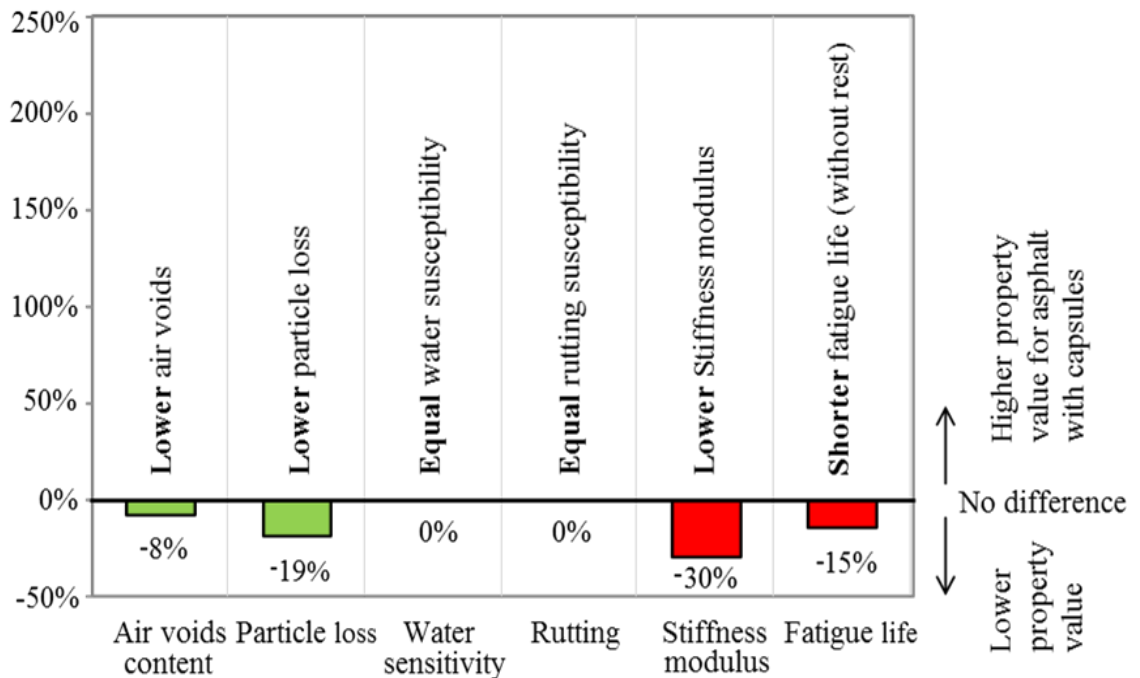


Figure 5.14: Performance comparison of asphalt mixture with and without capsules.

Chapter 6: Investigation of Crack Healing of Asphalt Beams

6.1 Introduction

In this chapter, the capsules' effect on asphalt self-healing is investigated. A new test was designed and applied for this purpose, which is the 3PB test (Sec. 3.5.3). The self-healing test program started by investigating the effect of capsules on the healing of cracks in mastic beams, as they have more bitumen content and only fine aggregate. Five different types of manufactured capsules were used in evaluating the self-healing properties of asphalt mastic at four different temperatures.

The effect of capsules and the healing temperature on the self-healing properties of asphalt mixtures is also investigated in detail. For this purpose, an extensive experimental programme was carried out to measure the crack-healing of real asphalt beams at different temperatures and healing times. Samples were tested with and without capsules. Crack healing was evaluated by the healing level, which is the flexural strength of beams after healing divided by their initial strength, measured by 3PB. It should be known that the average initial flexural strengths of all beams, (mastic and asphalt) are the same with and without capsules. Section 3.5.3 presented the amounts of capsules used for this test for both asphalt mastic and asphalt mixture with the methodology of carrying out the test.

In addition, sunflower oil was added to mixtures without capsules (mastic and asphalt) to exclude the effect of the released oil from self-healing evaluations and keep it restricted to

the oil released from capsules after applying compressive loads to damage the capsules in the mixture.

6.2 Crack healing in asphalt mastic

Asphalt mastic beams were manufactured by hand mixing and compaction, moulded in Teflon moulds as illustrated in Sec. 3.31. The capsules effect on crack self-healing was first investigated on mastic samples. Different types of capsules with different mechanical strength and different oil contents were used in this test. Samples were fractured at low temperature and then subjected to different healing temperatures and different healing times.

6.2.1 Amount of released oil

Fourier Transform Infrared spectroscopy (FTIR) tests were used to assess the modification of bitumen in asphalt mastic when the capsules release their content. Figure 6.1a presents the FTIR curves and their peaks in the wavenumber range 1730cm^{-1} to 1765cm^{-1} for asphalt mastic samples with and without oil. In the figure, the curve of asphalt mastic with oil represents the optimum amount of oil in the mastic beams supposed to be provided by the capsules if they all break and release their oil content. This amount of oil was measured to be 7.2% of the bitumen mass in the mastic mixture. Likewise, the curve of asphalt mastic without oil represents the mastic without capsules, which proves the effect of the capsules on mastic mixture.

Furthermore, Figure 6.1b shows the relationship between the oil content of the mixture as a percentage of the bitumen and the areas under the normalised FTIR curves for the same wavenumber range the asphalt mastic samples healed at 20°C . These areas can be termed the “oil index” of the mastic. In this figure, five different oil percentages 0%, 1.5%, 3.5%, 5.0% and 7.2%, which represents 100% of oil released from the capsules after full capsule breakage, are presented. From this figure, it can be proved that the area under the FTIR curve increases with the percentage of oil in the bitumen following a linear relationship ($R^2 \approx 0.98$). Additionally, the percentage of oil release from broken capsules (defined and measured in section 3.5.4) and their relationship with the areas under FTIR curves are also presented in Figure 6.1b. Finally, Figure 6.2 shows the amount of oil release before and after the compression explained in (Step B, section 3.5.3), as a percentage of the total oil in the asphalt mastic samples containing different capsules (with different oil contents) (Figure 6.2 a) and

one type of capsule tested at different healing temperatures, ranging from 5 to 20°C (Figure 6.2b). These results are discussed in more detail in the Sections 6.2.2 and 6.2.3.

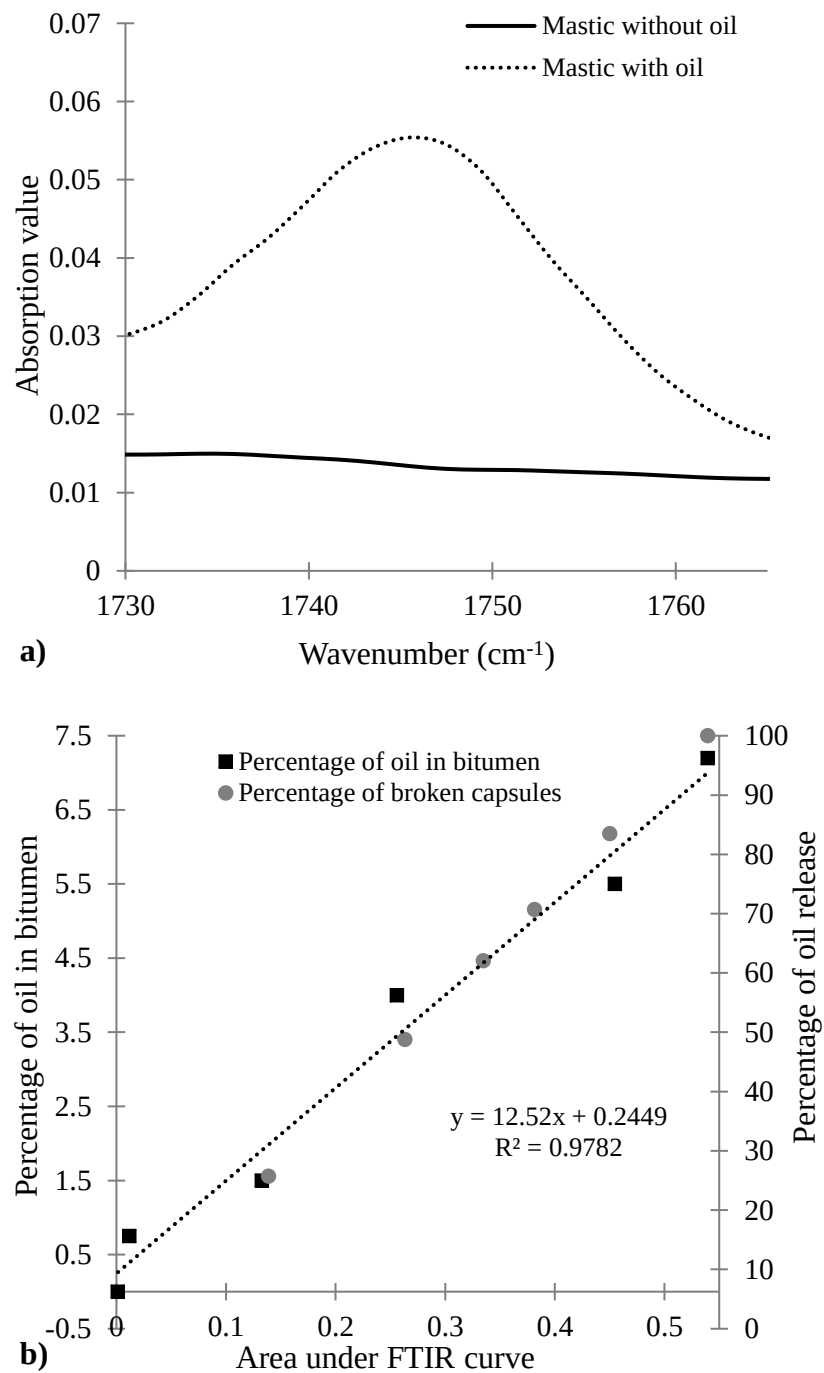


Figure 6.1: a) Example of FTIR curves for mastic samples with and without oil, and b) relationship between areas under FTIR curves and the percentage of oil in bitumen and oil released from broken capsules.

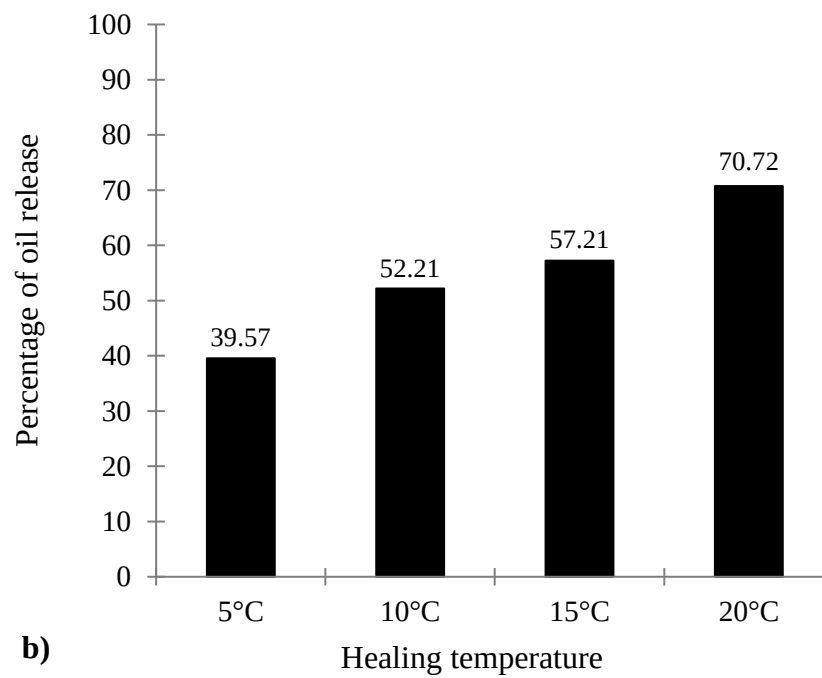
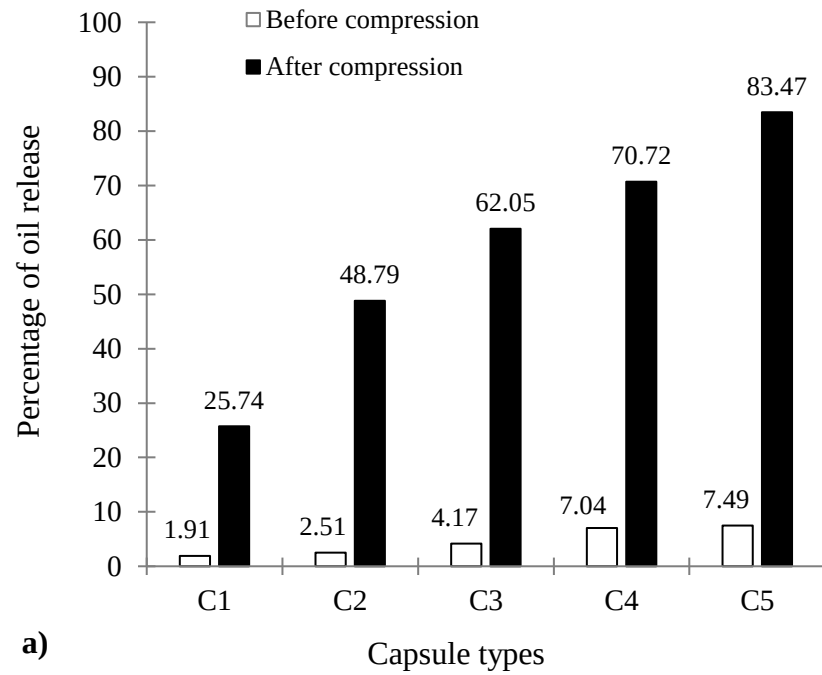


Figure 6.2: Percentage of oil released from broken capsules for mastic samples with different compositions: a) types of capsules before and after compression at 20°C, and b) with capsules type C4 after compression at different healing temperatures.

6.2.2 Effect of capsule oil content on the self-healing properties of asphalt mastic

Figure 6.3a shows the healing level results for all the asphalt mastic samples with and without capsules, tested at a healing temperature of 20°C and in the healing time range from 6 to 216h. From this Figure, it can be observed that: 1) the healing levels in the asphalt samples with capsules were greater than in samples without capsules, and 2) the healing level of asphalt samples with and without capsules increased with healing time until a maximum value, then remained constant until the end of the test. Based on the results, this maximum healing level value was reached, in general, at 96 hours and remained constant until 216 hours. The average healing level obtained from these healing times (from 96h to the end of test) is called the average maximum healing level. Figure 6.3b shows these average maximum healing level values as 54.08%, 66.13%, 77.99%, 83.74% and 94.58% for asphalt mastic samples with capsules C1, C2, C3, C4 and C5, respectively. Likewise, asphalt mastic samples without capsules (WO/C) presented an average maximum healing level of 52.93%. These results prove that: 1) the capsules with higher o/w ratio present higher crack-healing levels in the asphalt mastic, and 2) asphalt is a self-healing material by nature. It is hypothesized that the healing level reached by cracked asphalt mastic samples with capsules, can be directly related to the amount of oil released from the capsules that diffused into the bitumen.

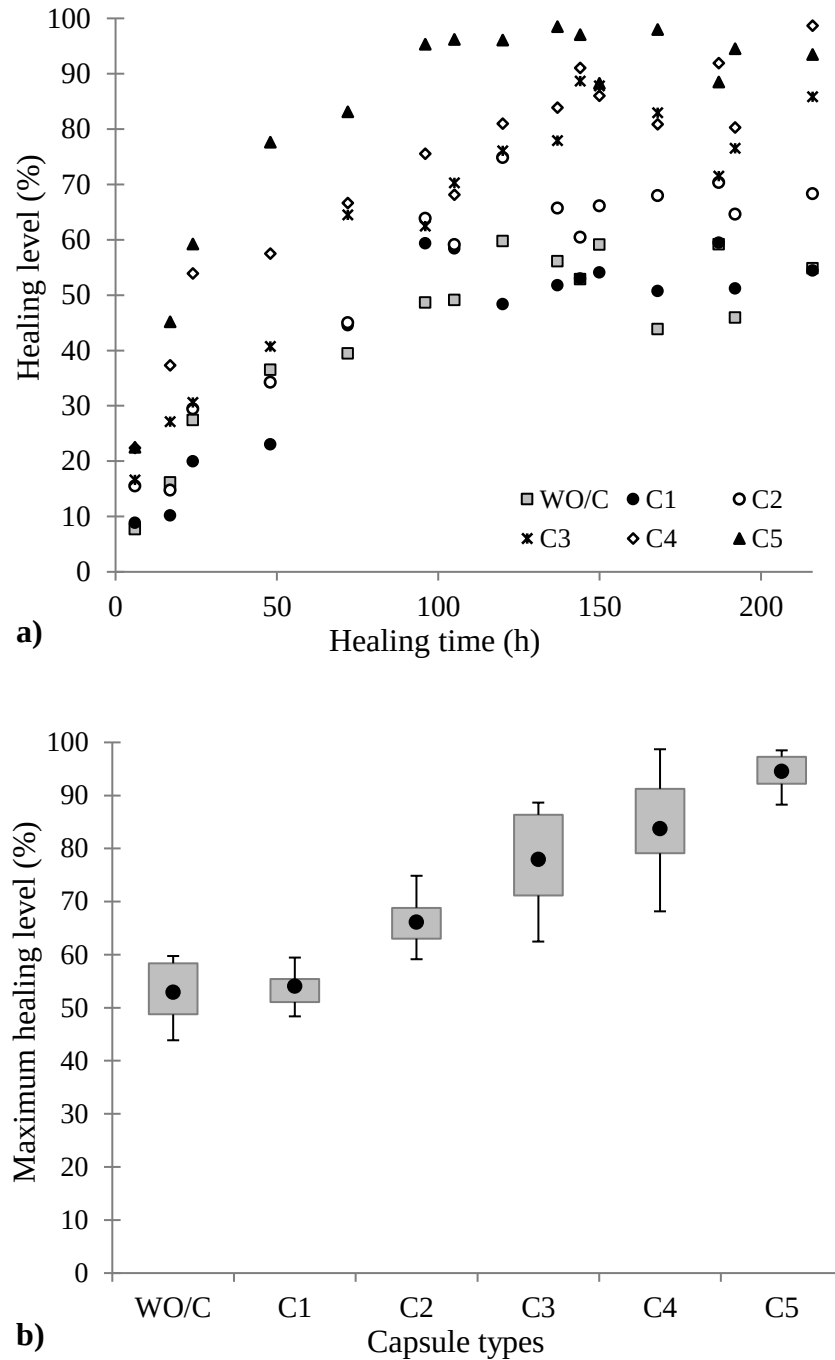


Figure 6.3: a) healing level results for all asphalt mastic beams with and without capsules (WO/C) tested at 20°C, and b) average maximum healing level of the samples with capsules relative to samples without capsules.

To prove this hypothesis, Figure 6.2a shows the results of the amount of oil release from broken capsules as a percentage of the total oil in capsules used for the mastic samples containing capsules with different oil contents and tested at a healing temperature of 20°C. The results of oil release are shown before and after the compression load. From this figure,

it can be observed that all asphalt mastics with capsules released between 1.91% and 7.49% of oil before the application of the compressive load (described in section 3.5.3, Step B). Additionally, the oil release increases with higher oil content. This possibly result from the lower mechanical strength of capsules with higher o/w ratio. In addition, the amount of polymer to oil will be reduced when increasing the oil content, leading to weaker capsules, see Figures 4.5a and 4.6, and Table 4.1, respectively. In this context, TGA test results showed a small mass loss of the calcium-alginate polymer at temperatures below 200°C (see Figure 4.3a), which could have caused some oil leakage from the external oil pockets of the capsules towards the asphalt mastic.

6.2.3 Effect of healing temperature on the self-healing properties of asphalt mastic

Figure 6.4 shows the healing level results for all asphalt mastic beams without (Figure 6.4a) and with (Figure 6.4b) capsules type C4, tested at four different healing temperatures (5, 10, 15 and 20°C) in the healing time range from 6 to 216h. Results show that the healing level of asphalt increased with time until a maximum value at which it remained constant. This maximum healing level value was reached after approximately 96 hours and remained approximately constant until the end of the test. Average maximum healing levels for specimens without capsules ranged from 23.92% to 52.94% for healing temperatures of 5°C and 20°C, respectively. While those for specimens with capsules ranged from 51.57% to 83.74% at same temperatures, 5°C and 20°C, respectively. The difference was due to higher temperatures reducing the mastic viscosity and allowing the bitumen to flow and fill the surrounding micro-cracks. Therefore, the drainage of the bitumen into the crack was easier and faster. This can be observed in Figure 6.2b where a higher percentage of oil release from broken capsules is reached at the highest temperature (20°C), which improves the healing process in the cracked asphalt mastic.

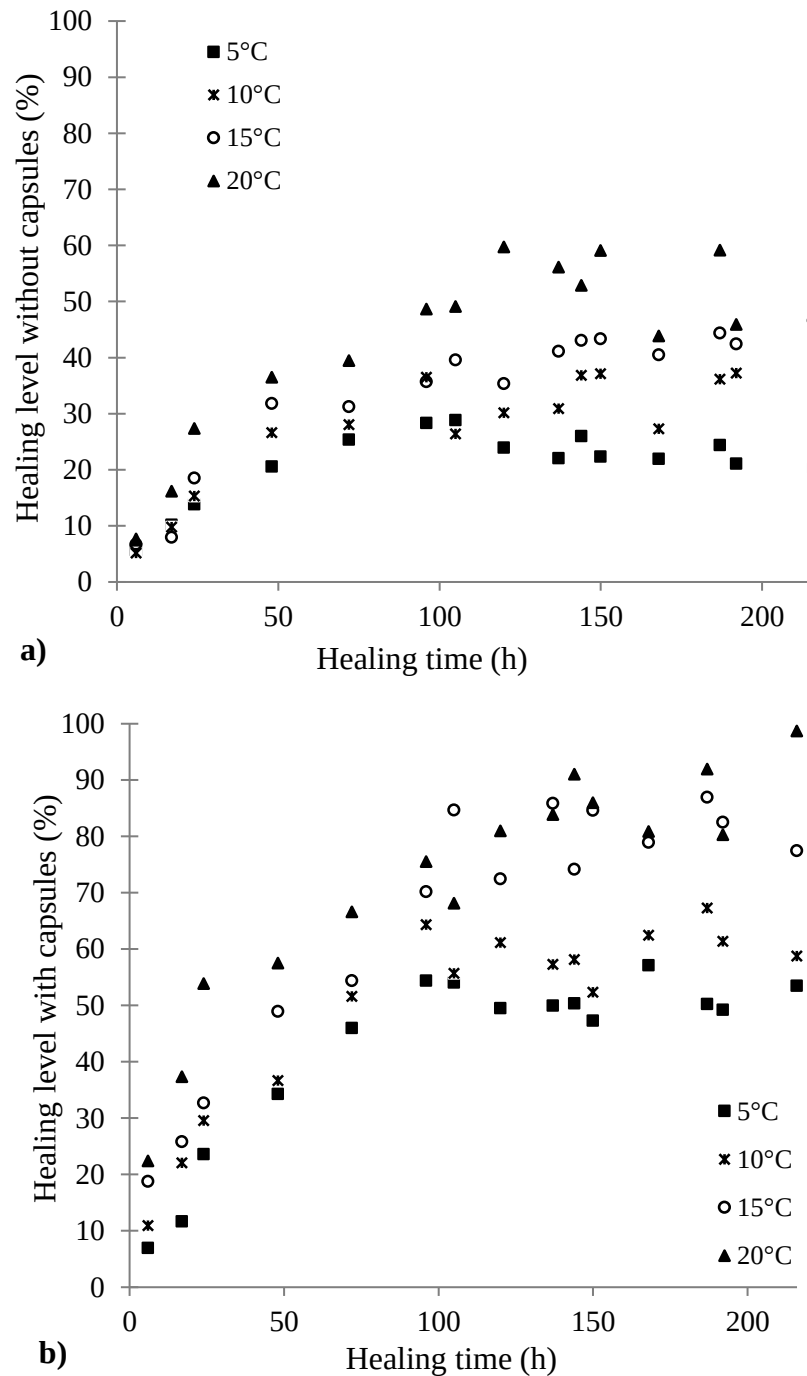


Figure 6.4: Healing level results for all asphalt mastic beams, a) without, and b) with capsules type C4 tested at four different healing temperatures.

In summary, from Figure 6.4 it can be observed that: 1) asphalt mastic samples with and without capsules present a proportional increase in healing level with an increase of temperature, and 2) there is a proportional relationship between the healing level results of asphalt mastic with and without capsules, independent of the temperature and time

evaluated. To prove this, a Healing Level Ratio (HL_R) has been defined in this study as the quotient between the i^{th} healing level value (HL_i) reached by a mortar sample with capsules type C4 ($HL_{(i-with\ capsules)}$), and the healing level value reached for the equivalent mortar sample without capsules ($HL_{(i-without\ capsules)}$), evaluated at a certain temperature and time, as follows:

$$HL_R = \frac{HL_{i-with\ capsules}}{HL_{i-without\ capsules}} \quad 6.1$$

Thus, to demonstrate the hypothesis that there is a proportional relationship between the healing level results of mastic with and without capsules, Figure 6.5a presents a P-P Plot for all HL_R data using the normal distribution function. From this Figure, it can be observed that all the results can be aligned in a 1:1 straight line, which confirms that all data can be considered to be from the same statistical population. In addition, the HL_R average value, approximately 1.9, is the correlation factor between the healing level with and without capsules type C4. If healing levels of asphalt without capsules are multiplied by 1.9, the values for asphalt mastic containing capsules will be obtained, as is observed in Figure 6.5b. It could be imagined that this value will change as a function of the amount or type of capsules in the asphalt but this may exceed the scope of the thesis and will have to be discussed in future research.

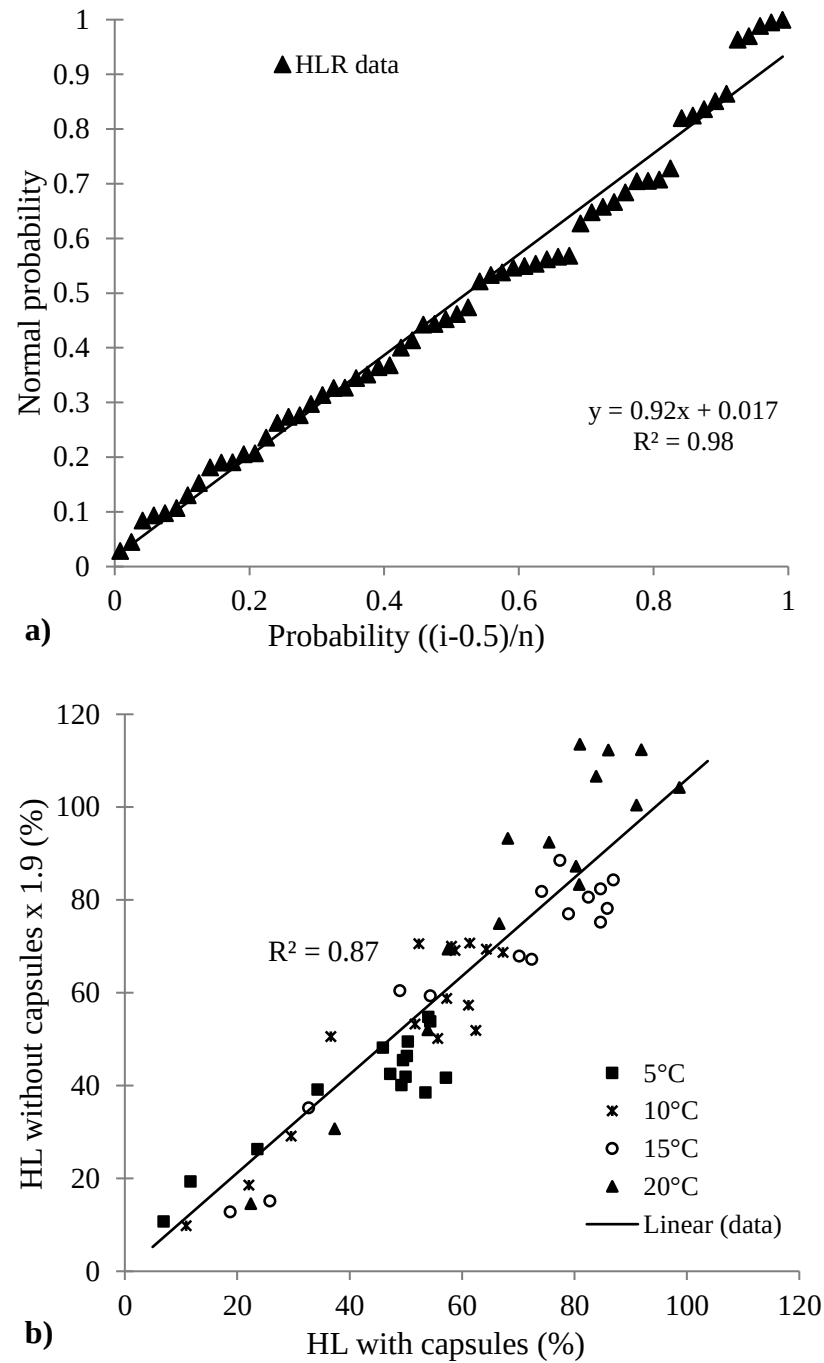


Figure 6.5: a) Normal P-P plot of all Healing Level Ratio data, and b) relationship between the healing levels (HL) of asphalt mastic samples with capsules and without capsules type C4 multiplied by the correlation factor.

6.3 Crack healing in asphalt beams

After proving that capsules can survive mixing and compaction and that they break inside the asphalt mixture due to application of external loads, releasing the encapsulated oil, the

capsule's influence on crack self-healing in real asphalt mixture is investigated. The test procedure is the same as that followed in the mastic samples. The effect of amount of capsules and healing temperature are evaluated at different healing times. Control samples without capsules are also tested.

6.3.1 Theoretical framework

The healing of the asphalt beams in this research is represented by the amount of strength gain after allowing the broken asphalt beam to rest for a specified period of time (t). The relationship between the original flexural strength (F_i) and the strength after that time period (F_t) during a three point bending test (3PB) can be defined as the healing level, as shown in Eq. (3-9).

The rate of healing is assumed to be constant with time and directly dependent on temperature (T) and the amount of capsules used, as in the function below:

$$f(T) = \frac{dh}{dt} \quad 6-1$$

Which means that the healing rate can be constant with a fixed temperature for a specific amount of capsules and changes dependently as these change.

By separating the variables and integrating, it is obtained that:

$$dh = f(T)dt \longrightarrow h(t) = \int_0^t f(T)dt \quad 6-2$$

If the process is happening at a fixed temperature (T_o), with a constant healing rate, then:

$$t = \frac{h(t)}{f(T_o)} \quad 6-3$$

Where t , is the time required for the asphalt containing rejuvenator to reach a specified healing level,

$h(t)$, is the targeted healing level, and

$f(T_o)$, is the healing rate at specified temperature and capsule content, as a combined effect of both.

Seemingly, the healing process occurs when the binder moves in a sort of capillary flow to fill the cracks. When the crack occurs in the asphalt pavement, there will be some contact points and other empty spaces. The presence of oil (rejuvenator) will work on reducing the viscosity of the surrounding binder leading to a pressure difference to take place in the contact points. This pressure difference could be the driving force for a capillary flow of the binder, which will work on filling the cracks and closing them. García (2012), made a modification to the Lucas-Washburn equation (Hamraoui and Nylander, 2002) in which he simulated the cracks as a set of capillary tubes working jointly.

The trigger for this process is the healing agent. The cracks are usually subjected to main forces that affect their healing progress, these are: 1) the surface tension, which depends on the crack width and the contact angle in the wetting point, 2) the viscosity of the liquid, and 3) the effect of gravity, which is the hydrostatic pressure in the area where the binder is flowing into the crack. The equation obtained by balancing all these forces is:

$$2\pi r\gamma \cos(\theta) = 8\pi\eta b(t) \left(\frac{db(t)}{dt} \right) - \rho g(h_p - b(t)) \quad 6-4$$

the part $2\pi r\gamma \cos(\theta)$ is the surface energy, where r is the capillary radius (crack width in this case), θ is the angle of the wetting point and γ is the surface tension of the liquid.

the part $8\pi\eta b(t) \left(\frac{db(t)}{dt} \right)$ is the viscosity of the liquid at capillary movement, where η is the general viscosity of the liquid, $b(t)$ is the height of the liquid within the capillary at a time t . and $\rho g(h_p - b(t))$ is the hydrostatic pressure when the binder is flowing into the crack, where $\rho g h_p$ is the positive hydrostatic pressure being ρ is the density of the binder and h_p is the distance from the beam surface to the bottom of healed zone and $\rho g b(t)$ is the weight of the healed zone. The reference point in this case is h_p , which is variable in time for each healed zone but considered constant and equals to the full height of the beam when the whole beam is considered in healing rather than a crack.

The dissipation parameter β can finally be introduced so as to consider possible sources of energy dissipation during healing. Combining this parameter with equation (6-3) can give:

$$2\pi r(\gamma - \beta \frac{db(t)}{dt}) = 8\pi\eta b(t) \left(\frac{db(t)}{dt} \right) - \rho g(h_p - b(t)) \quad 6-5$$

Since the diameter of the crack in study is relatively small, a possible effect of inertia could happen. However, the inertia term can be neglected for a nonviscous fluid moving inside a porous media (Duarte et al., 1996, Siebold et al., 2000). By considering this, the equation (6-4) can be rewritten as:

$$2\pi r \left(\gamma - \beta \frac{db(t)}{dt} \right) = \rho g(h_p - b(t)) \quad 6-6$$

And the analytical solution would be:

$$b(t) = \left(-\beta \frac{db(t)}{dt} \right) = (h_p + \frac{2\pi r \gamma}{\rho g}) (1 - e^{-\frac{\rho g t}{2\beta \pi r}}) \quad 6-7$$

The last equation indicates that when time extends to infinity, an equilibrium height will take place, which is equal to:

$$b(\infty) = H + \frac{2\pi r \gamma}{\rho g} \quad 6-8$$

and the speed at which this process happens, which is considered to be constant in all directions, is given by:

$$\frac{db(t)}{dt} = \frac{\rho g h_p}{2\beta \pi r} e^{-\frac{\rho g t}{2\beta \pi r}} \quad 6-9$$

The healing level, which represents the resisting area (A) in the broken beam after a healing time (t) is:

$$A(t) = \int_0^h 2\pi b(t) db(t)$$

$$= \frac{\rho g b(t)}{\beta r} \left(h_p + \frac{2\gamma\pi r}{\rho g} \right) \int_0^t (1 - e^{-\frac{\rho g t}{2\beta\pi r}}) e^{\frac{\rho g t}{2\beta\pi r}} dt \quad 6-10$$

By solving this equation and considering that initial healing does not start from zero due to the initial adhesion from contact:

$$A(t) = h_o + C \cdot e^{-C_1 t} (-1 + e^{-C_1 t})^2 \quad 6-11$$

Where,

h_o is the initial healing,

$$C = \frac{h_p \pi (\rho g h_p + 2\gamma\pi r)}{\rho g} \quad 6-12$$

$$\text{and } C_1 = \frac{\rho g}{2\beta\pi r} \quad 6-13$$

As known, the healing agent stimulates the crack healing by reducing the viscosity of the binder surrounding the broken capsules near the crack, which makes the binder flows through contact points between both faces of the crack. This process needs both faces of the crack to be completely in contact. After making the crack by 3PB and applying the static load to break the capsules and to make the optimum contact between faces of the crack, there should be some points in both faces of the crack that are close to each other but not in complete contact. Therefore, the possibility of obtaining a complete crack healing and full strength recovery is highly unlikely due to this reason.

6.3.2 Influence of capsule content on the healing properties of asphalt

Figure 6.6 presents self-healing results of asphalt beams containing different percentages of capsules (0.1%, 0.25% and 0.50% by total weight of the mixture) and tested at a healing temperature of 20°C. Figure 6.6a shows the healing level results reached for all the asphalt

mixture beams, with, and without, capsules, at different healing times ranging from 6 to 192h. In this figure, it can be observed that the healing levels in the asphalt beams with capsules were higher than in beams without capsules and that the healing level of asphalt mixtures with and without capsules increased with healing time until a maximum value, and then remained constant. Based on these results, the maximum healing level was reached, in general, at around 96h and remained fairly constant until 192h, see the box in Figure 6.6a.

The average healing levels reached between 96h and 192h are shown in box plots in Figure 6.6b as follows: 13.75%, 39.44% and 52.72% for asphalt mixtures with capsule contents of 0.10%, 0.25% and 0.50%, respectively. Asphalt mixtures without capsules (WO/C) presented an average maximum healing level of 11.22%. These results prove that a higher capsule content in the mixture resulted in higher healing levels for all the healing times studied. This conclusion is reasonable due to the fact that a higher capsule content increases the probability of breaking more capsules when the mixture is subjected to external damage, which increases the potential released oil content in the mixture. To prove this, Figure 6.7 presents the results of oil release as a percentage of the total oil in capsules used for asphalt mixtures with different capsule content and tested at a healing temperature of 20°C. The results of oil release are shown before, and after, the application of the compressive load. From Figure 6.7 it can be observed that asphalt mixtures with the highest capsule content, 0.50%, present the highest percentage of oil release from broken capsules after the compression loading of 56.31% of the total amount of oil in capsules in the mixture, compared to 49.20% and 31.29% for mixtures with capsule contents of 0.25% and 0.10%, respectively.

Asphalt mixtures without capsules were treated with some oil during the mixing process. The amount of oil added to these mixtures was similar to the amount of oil released from damaged capsules during mixing and compaction process.

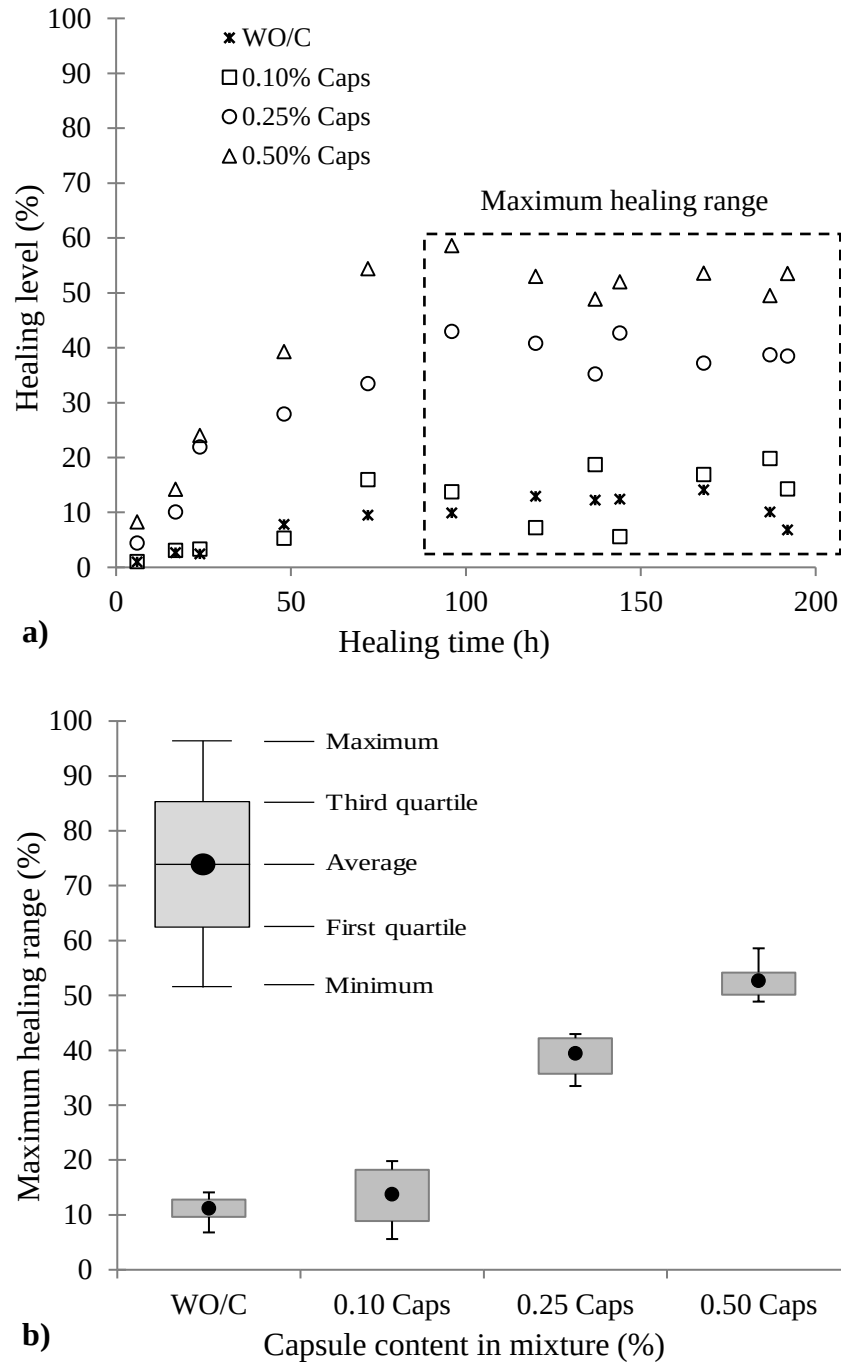


Figure 6.6: Self-healing results for asphalt mixture samples with and without capsules (WO/C) a) healing level depending on healing time, and b) box plots of the average maximum healing (96-196h) with capsule content in the mixture.

Figure 6.7 presents the amount of oil release from capsules before compression, which means during mixing and compaction processes. These amounts were 0.1g, 0.2g and 0.5g, evaluated from the total amount of oil in the capsules (see Table 4.1) for asphalt mixtures with capsule content of 0.1%, 0.25% and 0.50%, respectively. In this way, the amount of oil

added to the mixture without capsules in Figure 6.6b was 0.5g, which was similar to the oil released from asphalt mixtures with 0.50% of capsule content.

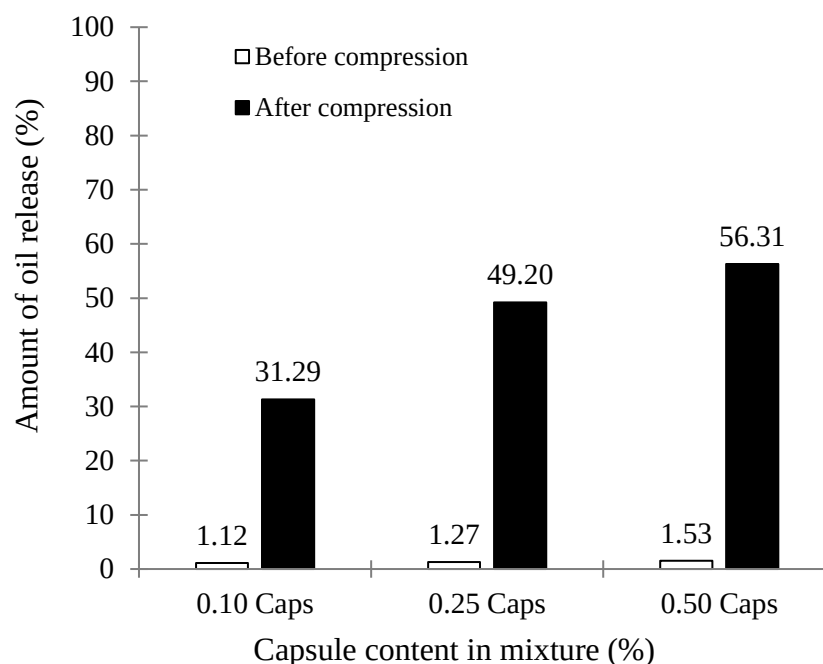


Figure 6.7: Amount of oil release from capsules for asphalt mixtures with different capsule content in the mixture.

6.3.3 Influence of temperature on the healing properties of asphalt

Figure 6.8 shows the results of healing levels for all asphalt mixture beams without capsules (Figure 6.8a) and with capsules (Figure 6.8b), tested at eight different healing temperatures (-5, 5, 10, 15, 20, 30, 40 and 50°C) and healing times ranging from 6 to 192h. The capsules content used was 0.50% of the total weight of the asphalt mixture. Similar to Figure 6.6b, the results from Figure 6.8 show that the healing level of asphalt mixtures increased with time until a maximum value after which it remained constant.

In general, this maximum healing level was reached after approximately 96h and remained approximately constant until the end of the test for both mixtures with, and without, capsules. In addition, healing levels in Figure 6.8 with and without capsules can be fitted with Eq. (6-11). This shows that the combined effect of temperature and capsules will cause lower binder viscosity, lower binder density and higher surface tension, which considerably enhance the self-healing of asphalt. The fitting parameters are presented in Table 6.1.

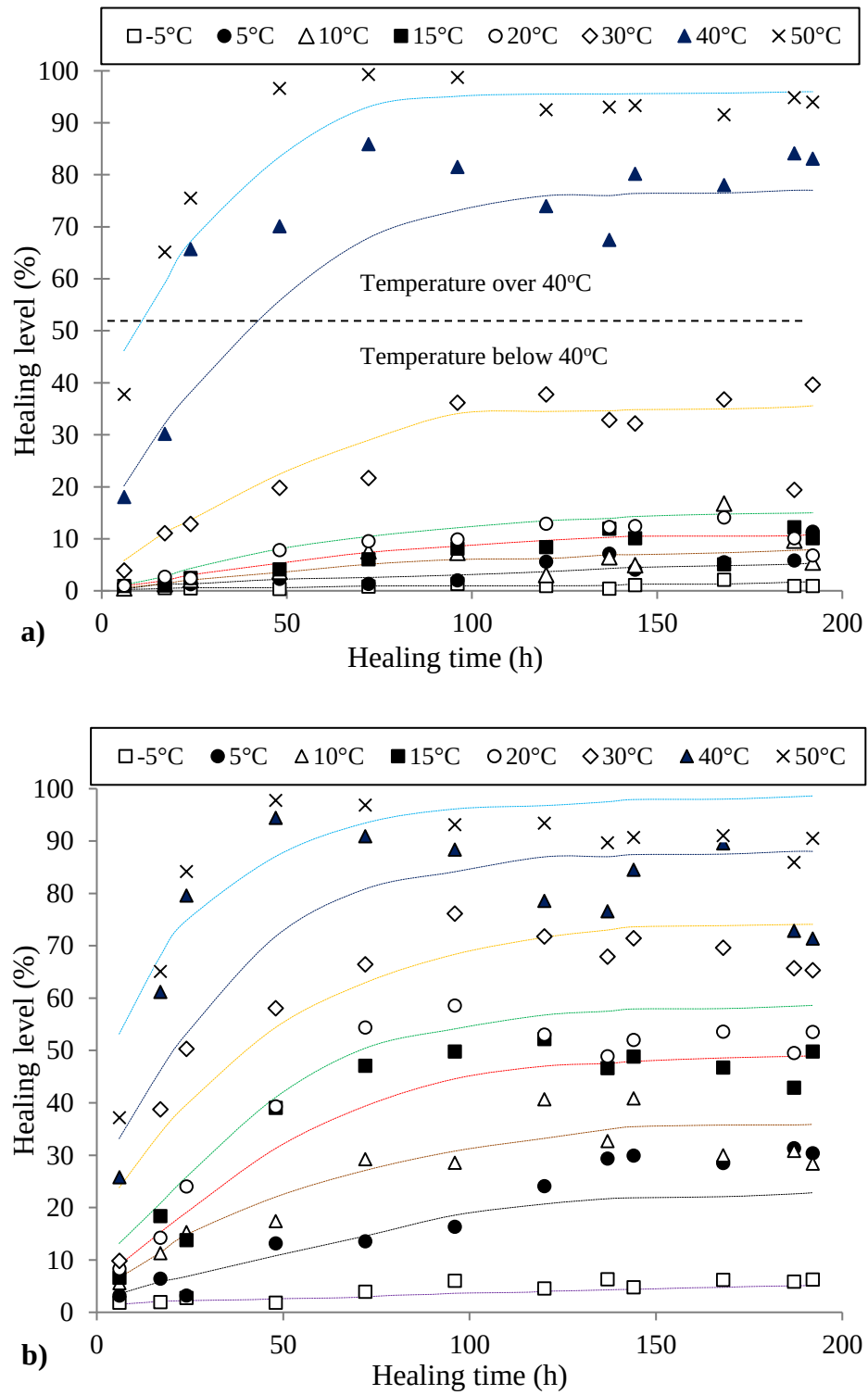


Figure 6.8: Crack-healing results for asphalt samples tested at different temperatures. a) without, and b) with capsules.

Table 6.1: Fitting parameters for obtaining self-healing of asphalt mixture with capsules.

Temperature (°C)	With Capsules		Without Capsules	
	C	C ₁	C	C ₁
-5	0.00448	1.20014	0.00108	0.90345
5	0.00648	1.29944	0.00208	1.07669
10	0.00967	1.32456	0.00457	1.10111
15	0.01998	1.42367	0.01658	1.10022
20	0.20824	1.64837	0.19456	1.22492
30	0.42546	1.95867	0.42206	1.33522
40	0.53568	3.56869	0.45681	2.98524
50	0.89473	5.32576	0.82223	5.80031

Figure 6.9 shows the amount of oil release from capsules broken after compression (section 3.5.3, Step B) at different temperatures. In this figure, it can be observed that the stiffer the asphalt samples the fewer the oil release and that the percentage of oil release increased with temperature as mixtures became less viscous. Therefore, in stiff asphalt samples tested at -5°C the oil release from broken capsules were 10.39% of the total oil in capsules in the mixture, while in asphalt samples tested at 50°C the percentage of oil release reached 60.47%.

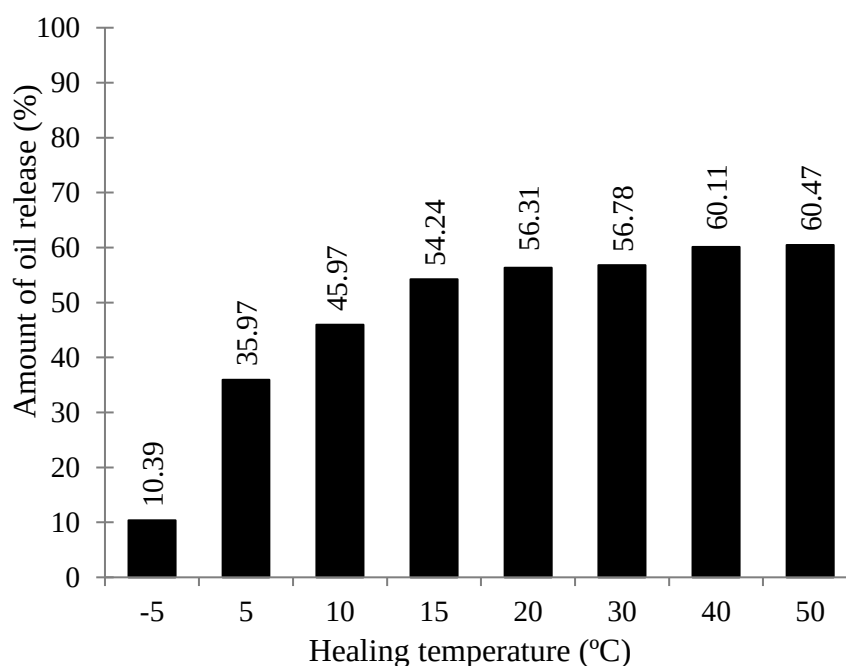


Figure 6.9: Amount of oil release from broken capsules in asphalt mixtures with 0.5% capsule content at different temperatures.

Furthermore, from Figure 6.8 it can be noticed that tests performed at 30°C or below show higher healing levels for asphalt samples with capsules than those without capsules. This is logically due to the reduction of the bitumen viscosity at a given temperature in the presence of the rejuvenator (sunflower oil) as shown in Figure 6.10a. In this figure, it can be observed that the viscosity of bitumen is considerably decreased in the presence of oil, except at +5°C -5°C, when it remains almost the same explaining the lower healing level at this temperature shown in Figure 6.8. This might be due to a physical change of bitumen at low temperatures, increasing its stiffness. Furthermore, by comparing Figures 6.8a and 6.8b, it can be seen that for tests at healing temperatures of 40°C or higher, the healing level of samples without capsules begins to reach similar or higher values to those of the samples with capsules.

To prove this, Figure 6.10b shows the average maximum values of healing level for asphalt samples with, and without, capsules versus the different healing temperatures evaluated. In this figure, it can be seen that the maximum average healing level for samples with capsules changes almost linearly with temperature, while there is a jump in the curve of the healing levels for samples without capsules. The curve for samples without capsules is linear until 20°C then jumps considerably intersecting the curve of asphalt samples with capsules when

it reaches 40°C, see Figure 6.10b. So, the effect of capsule addition on the healing levels of asphalt is more easily appreciable at temperatures lower than 40°C.

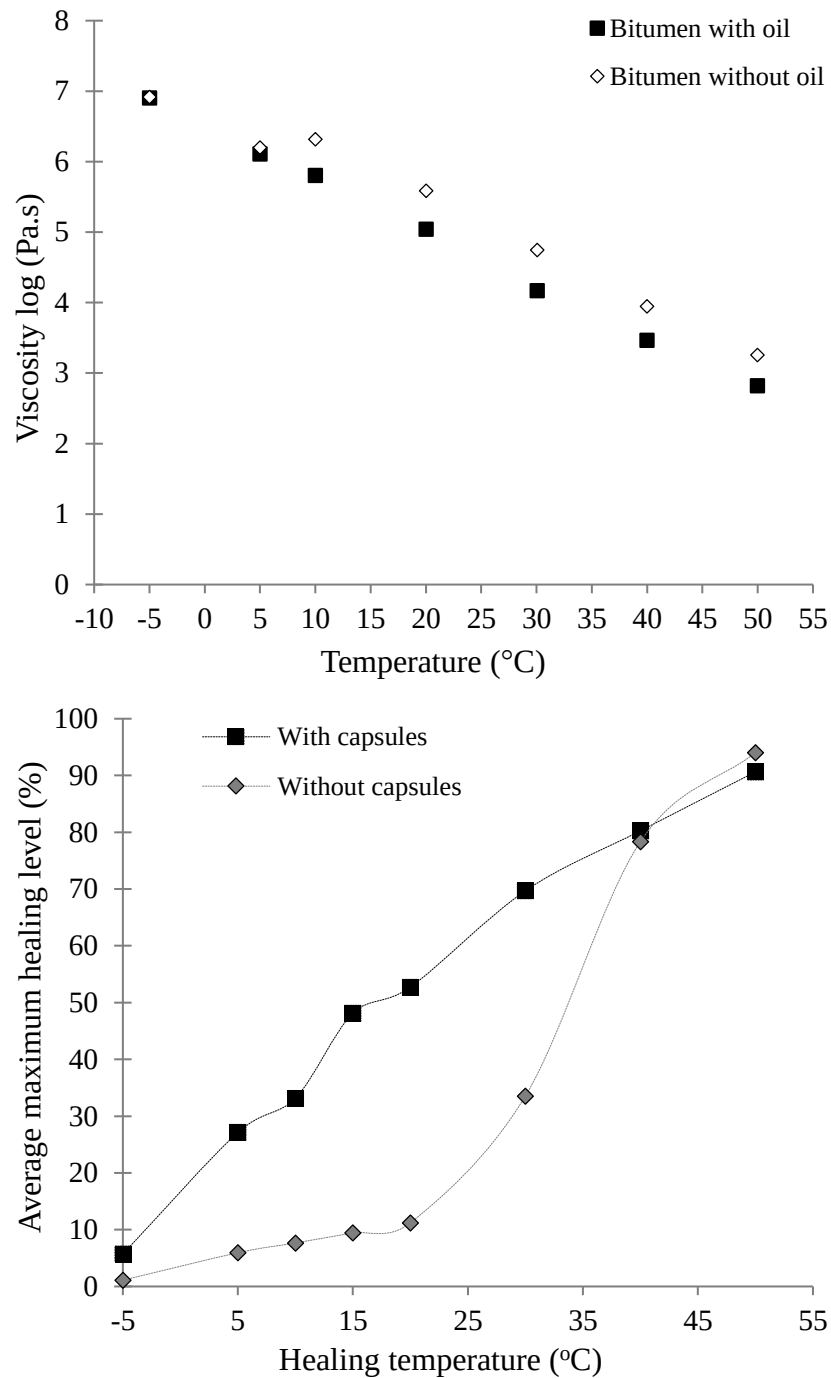


Figure 6.10: a) Oil effect on bitumen and asphalt, and b) Average healing levels achieved for asphalt mixture samples with and without capsules at different temperatures.

This result may be due to the combined effects of decreasing viscosity and thermal expansion with temperature, as presented in Figure 6.11. In this figure, it can be seen that for the temperature range evaluated between 5°C and 50°C, the thermal expansion of asphalt samples without oil, $15.62 \mu\text{m}/(\text{m}.\text{°C})$, was higher than that for asphalt samples with oil $9.202 \mu\text{m}/(\text{m}.\text{°C})$, and it continued until reaching the melting point, which is the temperature at which the thermal expansion stops and the asphalt sample starts to melt. The melting points were 48.05°C and 36.37°C for asphalt samples without and with oil, respectively.

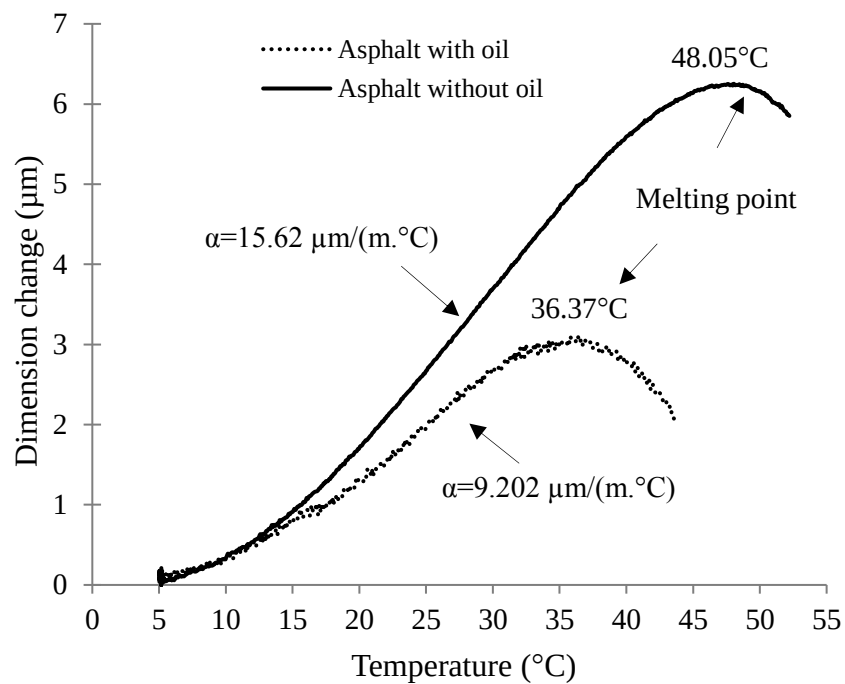


Figure 6.11: Oil effect on the thermal expansion of asphalt samples.

Therefore, from the results in Figure 6.10 and Figure 6.11, it can be concluded that: 1) asphalt samples with, and without, capsules present a proportional increase in healing level when the temperature increases and 2) there is a relationship between the healing level results of asphalt samples with, and without, capsules, which in turn is a function of the variables of viscosity and thermal expansion with temperature.

Chapter 7: Conclusions and Recommendations

7.1 Conclusions

Sunflower oil has been found to reverse the effect of ageing in bitumen used in an asphalt pavement. This starts with reducing the viscosity of the binder by increasing the aromatic fraction in bitumen components, which makes bitumen rejuvenated and workable again. When the capsules break under loading effects, the oil comes out and mixes with the bitumen that surrounds the aggregate in the road to fill the cracks. In this way, small defects in a highway will be prevented from becoming more serious.

The aim of this research was to develop and characterise a self-healing asphalt pavement that can heal and be rejuvenated at ambient temperatures. The work involved a combination of different aspects, such as proposing a new type of capsule containing rejuvenators (sunflower oil). These capsules have more oil and are easier to make than capsules proposed from other research studies. These capsules were then incorporated into asphalt samples and their effect on durability and mechanical properties of the asphalt mixtures was investigated by applying different standard mechanical tests, then comparing the behaviour of these samples with and without capsules. Finally, an asphalt mixture was developed that can heal at room temperature through the use of the encapsulated healing agents inside the capsules. The assessment was based on crack healing in asphalt beams by the actions of capsules. Different temperatures and healing times were applied to evaluate the most effective healing times and temperatures.

In the following sections, a detailed review of the main findings and conclusions are presented after the in-depth investigation and analysis conducted in this study:

7.1.1 Capsule production and characterisation

The new type of capsule to activate and accelerate self-healing of asphalt pavement was produced and characterised. The healing agent (rejuvenator) used was sunflower oil, encapsulated by ionotropic gelation of sodium alginate in the presence of calcium. Some of the capsules were protected with a hard shell made of epoxy-cement composite. Based on the results, the following conclusions have been obtained:

- The encapsulating procedure presented in this study allowed fabrication of capsules with up to 80% by volume of healing agents, which is higher than any other capsules presented in the literature. Later, some capsules were coated with an epoxy-cement composite shell. The calcium-alginate core and the epoxy-cement shell were not bonded. This means when the outer shell breaks the capsule inside might still intact and not releasing the rejuvenator.
- The epoxy-cement shell was found to be unnecessary to resist asphalt mixing and compaction, in fact, the epoxy-cement shell cracked on every occasion. Moreover, capsules without epoxy-cement adapted their shape to the surrounding aggregates.
- Oil was encapsulated inside the capsules in an alveolar microporous structure with the spherical shape made of calcium-alginate. The size of the capsules depended on the oil/water ratio in the sodium-calcium emulsion during the fabrication process.
- The compressive strength of the capsules decreased with the oil/water ratio, and because of that when there was more oil content in the emulsion within the capsules, the density of the polymeric calcium-alginate matrix decreased. This strength decreased with temperature and this did not affect their resistance to mixing and compaction processes during asphalt preparation.
- Thermal stability results proved that the capsules suffered only a minor mass loss in the temperature range used for the production of asphalt mixture, caused by the effect of degradation of polymer and water evaporation. Based on that, all capsule types tested could resist the mixing and compaction process without releasing their content or being deformed. Some minor oil release was noticed but it never exceeded 1.5% of the total encapsulated oil in the mixture.

7.1.2 Capsules effect on Asphalt performance

In the encapsulation-based self-healing asphalt technique, the rejuvenator (sunflower oil) was designed to come out of capsules, under different triggers, and diffuse into bitumen to accelerate self-healing of asphalt under service conditions. This test first investigated the ability of capsules to rejuvenate aged asphalt mixtures, then checked the effect of these capsules on the mechanical performance of the asphalt mixture. There was a risk that capsules containing low viscosity oils would cause loss of adhesion and cohesion strength, and therefore premature failure (permanent deformation, ravelling, bleeding etc.). Therefore, the study investigated the effect of capsules, containing sunflower oil, on the mechanical properties of asphalt mixture and the results showed that capsules can be applied to the road without affecting its durability:

- Capsules broke and released their content during cyclic loading. Capsules without a shell released the largest amount of oil during cyclic loading. Capsules with epoxy-cement shell released a smaller amount of oil.
- Oil diffused into the bitumen at 20°C and modified its chemical properties. Aged asphalt specimens containing capsules showed significant increases in stiffness after being damaged under cyclic loading and then resting. However, the deformation resistance reduced in specimens containing capsules.
- The stiffness and deformation resistance of asphalt mixture after the resting period depending on the type of capsule analysed. For example asphalt mixture containing the strongest capsules, with epoxy-cement shell, had the same stiffness after the resting period. On the other hand, the stiffness of asphalt mixture containing capsules without epoxy-cement shell increased by approximately 15% after resting for 48h.
- Image analysis of cracked aged asphalt mixture showed large reductions in the area of voids and cracks near the capsule locations: oil and/or modified bitumen flowed into and filled the cracks to the bottom of the capsules. In some places, 50% of the air voids disappeared after the resting period.
- Asphalt specimens with capsules produced mixtures with 8% lower air voids content than without capsules. The calcium-alginate polymer softened with temperature and, therefore, capsules adapted their shape and position to the coarse aggregate structure. In addition, it was estimated that 1.1% to 1.5% of the total amount of oil in the capsules was released into the bitumen during mixing and compaction.

- Asphalt specimens with capsules had 19% lower particle loss than asphalt without capsules. Capsules formed a strong bond to the asphalt mixture that remained strong even when the mixture was exposed to moisture for several hours or the oil had softened the bitumen. Furthermore, the indirect tensile strength was the same for test specimens with and without capsules.
- Asphalt containing capsules had the same rutting performance as asphalt without capsules. Moreover, the resistance to permanent deformation was not affected by the capsule content.
- Because capsules were softer than aggregates and bitumen, there was a reduction in the stiffness of asphalt mixture. Consequently, the number of cycles to failure for the same load amplitude decreased with the incorporation of capsules in the asphalt mixture. This may potentially be solved by reducing the size of the capsules.

Overall, the results of the experiments showed an enhanced performance of asphalt mixtures with the use of capsules.

7.1.3 Capsule effect on self-healing

Capsules were added to asphalt mastic and asphalt mixture in order to measure their ability to trigger self-healing of cracks under different healing times and temperatures. A new test to measure the self-healing of asphalt containing capsules has been designed and tested. The test was applied to asphalt mastic first for preliminary self-healing analysis, then applied to real asphalt mixture. The results are very promising for the development of asphalt mixtures with self-healing ability. However further research is necessary before this technology can be applied in roads. The following conclusions were obtained based on the results presented in the study:

- The capsule breaking methodology performed in this research was successful to break the capsules under the effect of external loading, releasing their oil to the bitumen. This method could be followed by other researchers for similar tests.
- Capsules can break inside the asphalt mastic releasing the encapsulated oil into bitumen. The capsules mainly keep their oil content until they break under the effect of external loading. It was found that capsules with higher oil/water ratio release more oil than those with lower oil content.

- Healing levels in the asphalt mastic samples with capsules were greater than in samples without capsules, and the healing level of asphalt samples with and without capsules increased with healing time until a maximum value after which the healing level remained constant.
- Healing levels provided by the capsules inside the cracked asphalt mastic depended on the oil/water content of the capsules and on the temperature at which the healing process occurred.
- It was found that there is a correlation factor of 1.9 between the healing level of asphalt mastic samples with and without capsules, independent of the healing temperature and healing time evaluated. However, this value could be different for different amounts or types of capsule incorporated inside the asphalt mastic.
- Capsules can break inside asphalt mixture beams, under the effect of external loading, releasing oil into the bitumen. The capsules mainly keep their oil content until they break under the effect of loading.
- Broken asphalt beams with 0.50% of capsules recovered more than half of their initial flexural strength after resting for 72h at 20°C. Under the same testing protocol, asphalt beams without capsules or with 0.10% of capsules recovered less than 15%.
- Healing level in asphalt samples with capsules were 40% greater than that in samples without capsules at healing temperatures equal to or less than 30°C. The healing level of asphalt samples with, and without, capsules increased with healing time until a maximum value after which the healing level remained constant. Maximum healing times range from 96h to the end of test, depending on healing temperature and the capsule content in the mixture.
- Healing levels of asphalt samples without capsules started to increase considerably at temperatures higher than 30°C, exceeding those of samples with capsules at 50°C. This resulted from the combined effect of decreasing viscosity and higher thermal expansion of asphalt samples.
- The healing levels for asphalt samples with and without capsules were almost similar at healing temperatures over 40°C. This indicates that these capsules are not useful for asphalt self-healing at hot climate.

7.2 Recommendations for Future Research

This section presents a list of recommendations and suggestions for work that was not included in the current research due to the lack of time and resources. These

recommendations are important to better understanding the incorporation of the capsules for asphalt self-healing in order to accurately predict their performance.

- The average size of the capsules produced in this research ranges from 2-5mm, which could be reduced and optimised for maximum oil content. It is recommended to manufacture smaller size capsules in order to obtain a likely improved capsule distribution in the asphalt mixture and better effect on asphalt performance.
- Capsules are required to be designed to avoid any oil release during mixing and compaction of the asphalt. This requires using different materials in the capsules production such as fibres, lime and/or silica fume. These materials might be used instead of calcium-alginate polymer or can be mixed with it at different percentages. The purpose of that is to keep the mechanical strength of the capsules at its optimum values so that capsules can survive mixing and compaction and break under external damage.
- It is very important to evaluate the capsule's ability to be stored at ambient temperature in large quantities and for longer periods. This is what they are expected to undergo in asphalt plants. Therefore, it is recommended to investigate the effect of bacteria, fungi when left exposed to ambient conditions for long periods. In addition, it is recommended to investigate ageing on capsules and its individual materials, such as oil and calcium-alginate polymers. Then, these aged capsules could be added to the asphalt mixture to investigate their effect on crack healing and mechanical properties of the asphalt mixture.
- Results show that when capsules break, they do not release the full oil content and this is possibly useful to be triggered again by external action, such as applying a heat-induction technique as a multi-time healing process for more extending the pavement life.
- The effect of mixing order of capsules with asphalt materials and their effect on self-healing and mechanical properties of asphalt mixture is recommended to be further investigated. This means adding capsules with asphalt materials before mixing and mixing them together. In addition to applying different temperatures to capsules before mixing, such as 130°C and 160°C and noticing their oil release before compaction.
- A future objective might be to investigate the maximum width of a crack in asphalt pavement that could be healed by the action of capsules. This can be investigated by

measuring different crack widths by CT scans and evaluating the healing levels for these cracks, which could be highly affected by the oil diffusion and wetting between the two faces of the crack. This is important to investigate the increase of strength with crack closure and how this mechanism is affected by capsules and crack characteristics.

- For future work using calcium-alginate capsules with oil, it is recommend that asphalt self-healing tests be performed at healing temperatures below 40°C, in order to obtain a significant influence of the capsules on self-healing. For asphalt pavements in hot climates, it is recommended to study the possibility of providing enough rest period on asphalt roads, similar to the rest period when healing started to be constant. Then measuring the self-healing without using capsules, which might be more economic.
- The aim of this research was to produce a self-healing asphalt pavement by using the capsules and this objective has almost been accomplished within this study. However, further economic investigation is highly recommended for future studies to ensure the feasibility of capsules as a significant replacement for normal pavement maintenance. The economic study can include the life cycle assessment and fatigue life of asphalt pavement with and without capsules.

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